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SOLUTION PHOTOCHEMISTRY OF THE URANYL ION

A thesis submitted for the degree of
Doctor of Philosophy

by

RICHARD JOHN HILL

to the University of Warwick in April 1974

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ABSTRACT

ABSTRACT

Various physical techniques have been applied to the study of the primary processes involved in the photoreaction of uranyl ions with a variety of organic molecules.

Electron spin resonance spectroscopy has been used to identify the primary radical products in many solid matrices at temperatures of down to 77 K and in the liquid state at 200 - 300 K in a slow flow system. In general, primary alcohols, RCH_2OH , yield $R\dot{C}HOH$ in the solid state whilst secondary and tertiary alcohols at 77 K undergo C - C cleavage to give alkyl radicals. Upon softening the matrices by warming, the radicals derived from tertiary alcohols attack parent molecules. Carboxylic acids undergo both abstraction of an α -hydrogen atom and C - C fission, the former process predominating with simple monocarboxylic acids and their esters and some dicarboxylic acids. The H-abstraction mechanism is also important with aldehydes, ketones and amides, the latter preferring to lose a hydrogen atom from N-alkyl substituents where applicable. Phosphorus-centred radicals exhibiting considerable g- and a- tensor anisotropy have been produced in the solid state. The radicals derived from primary alcohols and carboxylic acids in the flow apparatus are essentially the same as those observed at 77 K. n-Butyl lactate is shown to yield two conformational isomers of the radical $CH_3\dot{C}(OH)CO_2C_4H_9$ and mixtures of radicals were obtained from the ethers 1,2-dimethoxyethane and 2-methoxyethanol. The mechanism of photochemical reaction of U(VI) with organic molecules is discussed.

The final section of this work concerns the identification of the (excited state) absorption spectrum of the photoreactive state of the uranyl ion by (spectrographic) microsecond and (kinetic spectroscopic) nanosecond flash photolysis. By monitoring the decay of this absorption at ~590 nm, absolute values for second-order rate constants for the photoreaction with alcohol molecules have been determined and these are compared with the results of luminescence intensity and lifetime quenching by these molecules (the latter by the single-photon counting technique). The appreciable deuterium kinetic isotope effects on the rate constants are discussed in terms of the nature of the primary photochemical step.

ABBREVIATIONS AND CONSTANTS

e.s.r.	electron spin resonance
p.t.f.e.	polytetrafluoroethylene
u.v.	ultraviolet
nm	nanometre
pm	picometre
mT	millitesla
μ s	microsecond
ns	nanosecond
a (with subscript)	nuclear hyperfine coupling constant
g_E	g-factor for the electron
g_N	g-factor for the nucleus
h	Planck's constant
\hbar	$h/2\pi$
k (with subscript)	rate constant
\vec{p}	spin angular momentum vector
H	applied magnetic field (in mT)
I	nuclear spin quantum number
I_f	intensity of luminescence
K_{eq}	equilibrium constant
K_q	Stern-Volmer quenching constant
M_S	total electron magnetic quantum number
M_I	nuclear magnetic quantum number
Q (with subscript)	$\sigma - \pi$ interaction parameter
S	total electron spin quantum number
β_E	Bohr magneton for the electron
β_N	Bohr magneton for the nucleus
γ_E	gyromagnetic ratio for the electron

ρ_c	electronic spin density on a carbon atom
$\vec{\mu}_E$	magnetic moment vector due to electron spin
ψ	electron orbital wavefunction
ϕ (with subscript)	quantum yield - negative sign preceding subscript denotes disappearance
τ_o	lifetime of excited state in the absence of added quencher
* (superscript)	excited state
\ddagger (used in text)	transition state

CHAPTER 1

SPECTROSCOPY OF URANYL COMPOUNDS

1. SPECTROSCOPY OF URANYL COMPOUNDS

1.1 The Nature of U(VI) Species in Solution

The absorption and luminescence spectra of most uranyl salts are due to the stable UO_2^{2+} ion which may be considered as a hydrolysed form of U^{6+} , and consequently the highly characteristic, structured spectra of a wide range of solid and dissolved salts are basically similar, exhibiting slight variations due to the effect of surrounding or coordinated molecules. Additional absorptions corresponding to transfer of electrons from these associated molecules or anions to the central uranyl ion (denoted a charge-transfer-to-metal or CTTM process) are also observable in some cases of inorganic¹ and organic (v.l.) ligands, but in general these occur at higher energies than the u.v.-visible transitions within the uranyl ion itself.

As a result of X-ray,² infrared³ and Raman⁴ data and studies of solvent effects on dissolved uranyl salts,⁵ the UO_2^{2+} ion is now, after earlier controversy,^{6,7} regarded as linear, although the U - O bond length is strongly dependent on the coordinating ligand, figures of between 160 pm and 208 pm having been reported.⁸

In contrast to the case of solid uranyl salts, the nature of the uranium-containing complexes in solution is, in many cases, not well defined. Even in aqueous solution and at low concentration of coordinating ligands, several hydrolytic species, including polyuranyl complexes with hydroxy or oxo bridges, have been identified^{6,9-15} which exhibit differences in spectral band intensities and half-widths.¹⁶ The appearance of additional bands in the luminescence spectrum of uranyl nitrate, perchlorate and chloride upon dissolving in aqueous alkaline solution¹⁷⁻¹⁹ and in frozen aqueous solution²⁰ has been attributed to hydrolysis of UO_2^{2+} , and variations in the luminescence spectrum of solid uranyl acetate with the method of preparation are also believed to be due to the presence of different levels of hydrolysis.²¹

The situation is further complicated upon introduction of coordinating molecules. Early work in this area^{22a} is of limited value due to the absence of pH control and the consequent effect of hydrolysis on the absorption spectrum. Subsequent spectroscopic work has demonstrated the existence, in aqueous

solution, of several complex species containing inorganic ions such as sulphate,^{23, 24} nitrate,^{19, 23} carbonate,²⁵ chloride²⁶ and thiocyanate.¹²

An important property of the perchlorate ion (ClO_4^-) is its relative inability to complex with the UO_2^{2+} ion in aqueous solution;^{9, 27} thus the spectroscopic properties of a solution of uranyl perchlorate in dilute perchloric acid are those of the free, hydrated (but unhydrolysed) UO_2^{2+} ion.²⁸

Little work has been performed on the effects of inorganic ion complexation on the uranyl luminescence spectrum, but emission bands characteristic of $\text{UO}_2(\text{NO}_3)_2$ ¹⁹ and both UO_2NO_3^+ and $\text{UO}_2(\text{NO}_3)_3^-$ ²⁹ have been reported for solutions of uranyl nitrate in nitric acid.

Evidence, mainly spectroscopic and potentiometric, of complex formation between the uranyl ion and the anions of organic acids is much stronger than in the case of mineral acids and reliable and systematic studies have been carried out on systems involving formate,^{30, 31} acetate,^{11, 30, 32} propionate,^{30, 31} glycollate,³³ oxalate,^{30, 34} succinate,^{30, 31, 35} malonate,^{31, 35} lactate,^{30, 36} fumarate,³¹ maleate,³¹ crotonate,³¹ pyruvate,³¹ and anions of some aromatic acids.^{37, 38} Stability constants have been established in all cases and are in the range 10^2 to $10^4 \text{ dm}^3 \text{ mol}^{-1}$ for monodentate aliphatic and aromatic ligands, and $\sim 10^5 \text{ dm}^3 \text{ mol}^{-1}$ for bidentate ligands.

Spectral changes upon dissolving uranyl salts in organic solvents are generally small and indistinct. Kaplan³⁹ has carried out an extensive study of uranyl nitrate solutions in many organic compounds including acetone, cyclohexanone, methyl isobutyl ketone, dioxane, pyridine, chloroform, ethanol, propanol and ethyl acetate and has analysed the results mainly in terms of complexes involving UO_2^{2+} and NO_3^- ions and in only one case (pyridine) did he obtain an absorption that could reasonably be assigned to a charge-transfer process between solvent and metal, although minor effects arising from solvation were noted.

Another report on the absorption spectra of uranyl nitrate in organic solvents⁴⁰ including acetone, methyl ethyl ketone, methyl isobutyl ketone, dioxane, formamide, tributyl phosphate and acetonitrile indicates the existence of a charge-transfer absorption only in the case of formamide (a nitrogen-containing molecule, like pyridine). The inability to correlate solvent dielectric constant with visible and u.v. absorption parameters^{22d} is indicative of the

difficulty in separating the effects of direct coordination from general solvent effects.

The luminescent properties of uranyl compounds in liquid organic media have received very little attention due to the extreme weakness of the emission in most organic solvents, but a study of the luminescence of uranyl acetate and nitrate in glycerol, ethanol and acetone between 93K and 253K⁴¹ reveals this to be of a complex nature. Reports have appeared, mainly in the Russian literature, of studies on frozen organic solutions of uranyl salts,^{42 - 44} and frozen uranyl salt solutions in ethanol have also been studied by Nichols and Merritt⁴⁵ and Howes⁴⁶ who observed luminescence attributed to ethanolated uranyl ions.

1.2 The Electronic Structure of the Uranyl Ion

The absorption and emission spectra of the hydrated uranyl ion in solution are shown in figure 1.

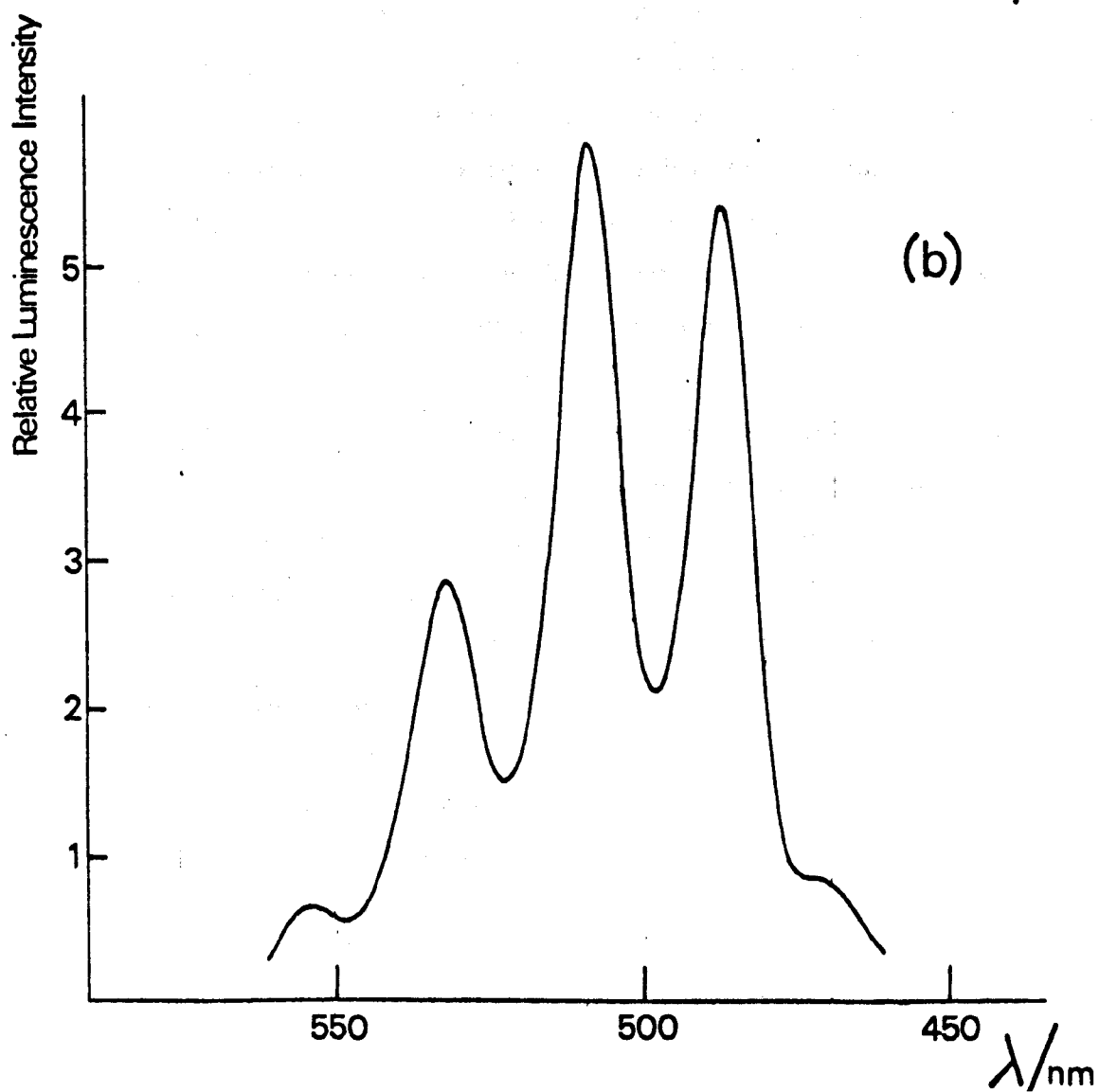
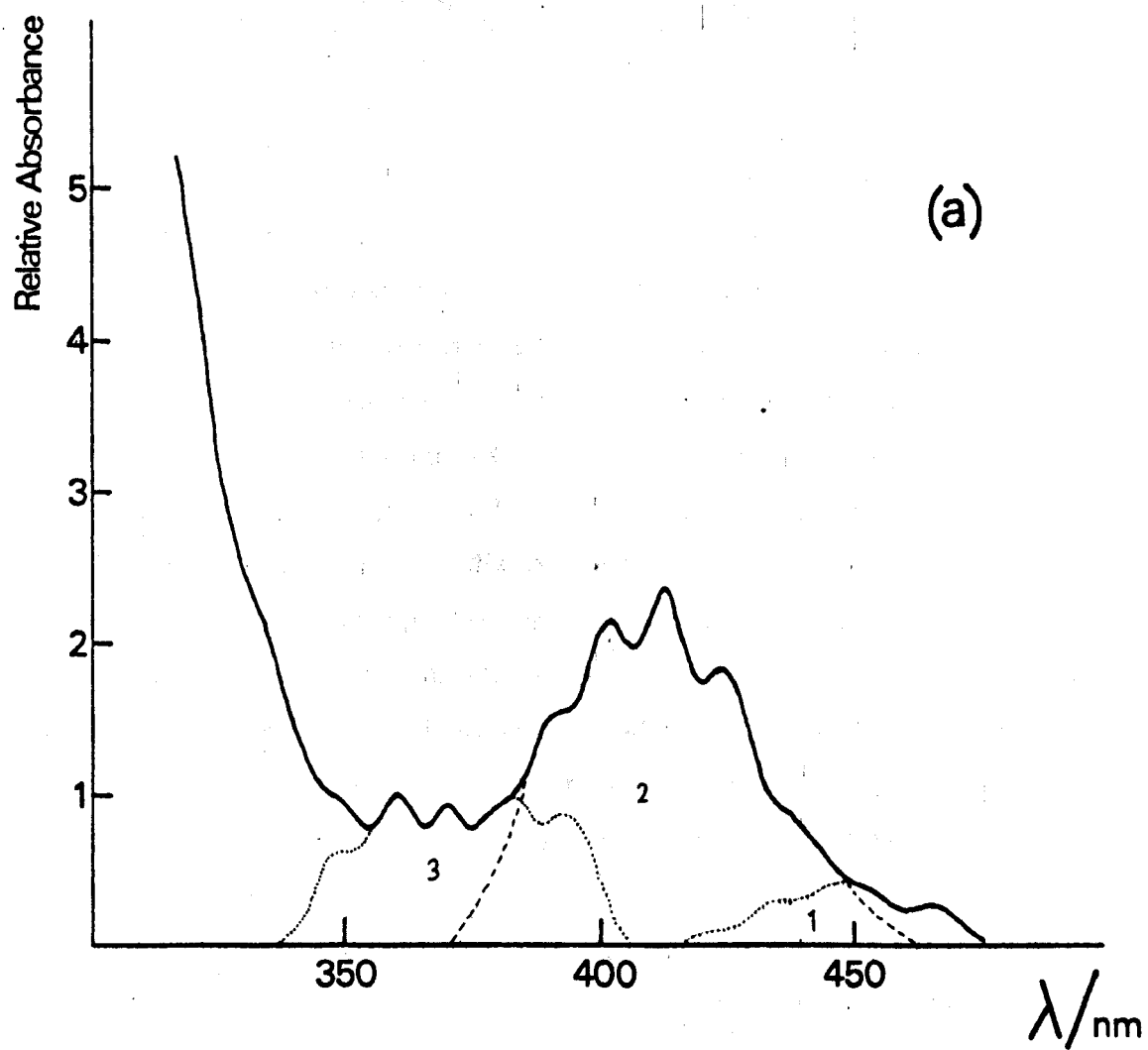
Although the spectroscopic properties of uranyl salts have been studied since 1852, relatively little work on the interpretation of the spectra, with the exception of work by Nichols and Howes during the period 1915 to 1919,^{22b} had been performed until Dieke and Duncan published an extensive study of the absorption and emission spectra of solid uranyl salts in 1949,⁷ to be followed in 1961 by an important paper by McGlynn and Smith⁴⁷ on the interpretation of the solution spectrum of UO_2^{2+} .

Dieke and Duncan studied a large variety of crystalline uranyl salts and double salts at temperatures of between 20K and 273K and, in an extension of the work by Nichols, Howes and coworkers, were able to relate the fine structure in the absorption and emission spectra to the symmetric and asymmetric stretching and the bending modes of the UO_2^{2+} entity. A recent paper suggests that vibrations of groups coordinated to the uranyl ion may also be manifest in the luminescence spectrum.⁴⁸

Using a molecular orbital approach, McGlynn and Smith established symmetry groups for the ground and excited state UO_2^{2+} ion and showed that the U - O bond is formally of third order (one σ and two π linkages) and that the ground state is totally symmetric, confirming the conclusions of contemporary Russian workers,⁴⁹ although they found the low value of the symmetric U - O stretching frequency difficult to explain. The absorption

FIGURE 1

- (a) Absorption spectrum of aqueous uranyl perchlorate (0.1 mol dm^{-3}).
- (b) Luminescence spectrum of aqueous uranyl perchlorate (0.1 mol dm^{-3}) with excitation at 420 nm.



spectrum was explained in terms of vibronic transitions to the three components of a triplet excited state occurring in the visible region (areas 1, 2 and 3 in figure 1,) and transitions to two singlet states in the ultraviolet region. The luminescence spectrum was considered to consist of five bands of symmetrical character and the mirror image of area 1 and was therefore assigned to a transition to the ground singlet state from the lowest excited state, the triplet character of which is supported by experimental evidence.^{50, 51}

Later workers are divided in their interpretations of the visible absorption spectrum, some preferring a singlet-singlet transition^{52 - 55} while others agree with McGlynn and Smith in assigning the transition from the ground singlet state to the three components of an excited triplet state,^{5, 28, 56} although one report, based on an elaborate computer analysis of the visible spectrum, favours a different assignment of the observed vibrational bands between the three electronic absorptions.²⁸

Various interpretations of the ultraviolet absorptions have been offered, but several workers agree that the observations of McGlynn and Smith are in error due to the formation of $\text{UO}_2^{2+}/\text{NO}_3^-$ complexes or of hydrolytic species. Bell and Biggers,⁵⁷ using a computer resolution of the u.v. bands, have reported five singlet-singlet transitions with no vibrational structure, together with a second singlet-triplet absorption which had been proposed on theoretical grounds⁴⁷ but never observed, and Israeli⁵⁶ observes four singlet-singlet transitions. There appears to be no doubt that all transitions represent, in gross terms, transfer of an electron from an axial oxygen atom to the central metal atom.

In addition to studying the absorption spectrum, Bell and Biggers applied their computer resolution techniques to the emission spectrum of the uranyl ion²⁸ and propose this to consist of six bands with no symmetrical character (c.f. five symmetrically distributed bands suggested by McGlynn and Smith⁴⁷). These were interpreted as due to transitions from two vibrational levels of the lowest excited triplet state to five vibrational levels of the ground state, although only 4.66% of the emitted energy is from the higher of the two vibrational levels. (Emission mainly from the lowest vibrational level is to be expected as the period of a molecular vibration at room temperature [10^{-13} to 10^{-12} s] is short compared to the intrinsic lifetime of the excited state [$\sim 10^{-3}$ s] and hence a thermal

equilibrium distribution of excited molecules over their vibrational levels will be achieved before emission becomes observable). This is also consistent with the observation that the form of the emission spectrum (although not the intensity) is independent of the exciting wavelength.^{58, 59}

The designation of the uranyl emission as either fluorescence or phosphorescence has provoked much discussion, extra confusion being introduced by early suggestions that two emissions of different durations are observable,^{60, 61} although it is now accepted that only one pathway is operative. The long lifetime of the emission caused several authors to use the term 'phosphorescence',^{58, 62 - 65} and an apparent dark interval between cessation of illumination and beginning of emission was thought to confirm this,⁶⁵ but this observation was later proved wrong.⁵⁹ Perrin and Delorme^{66, 67} and Rabinowitch and Belford²² favour the term 'fluorescence', pointing out that, because of the low intensity of the visible absorption bands, excited uranyl ions must, of necessity, have an unusually long natural lifetime, and the absence of Zeeman splitting of the luminescence spectrum^{7a} has also been advanced as evidence for the singlet nature of the excited state.⁶⁸ In fact, the long observed lifetimes of certain compounds at 4K ($\sim 2.4 \times 10^{-3}$ s),⁶⁹ which are in good agreement with the natural lifetime of 2.7×10^{-3} s calculated from the extinction of the visible absorption bands according to the Strickler-Berg equation,⁷⁰ merely indicate that absorptions in the visible region directly populate that electronic level from which emission occurs.

Suggestions as to the multiplicity of this level are based only on the theoretical calculations described earlier and on rather weak experimental evidence. Molecular orbital calculations and the low extinction of the visible absorption spectrum indicate that the transitions are either spin-forbidden and Laporte-allowed⁴⁷ or spin-allowed and Laporte-forbidden.⁵⁵ The author inclines to the view that the single electronic state to which absorption excites the uranyl ion, and from which emission occurs, is a triplet state and the emission is a true phosphorescence for the following reason :

The high emission quantum yield (which approaches unity under favourable conditions^{22c, 69, 71}) is more compatible with emission from a (triplet) state directly populated as a result of spin-orbit coupling by the heavy U atom than with that from a singlet state which would be strongly

depopulated by inter-system crossing (also by spin-orbit coupling).

1.3 Emission Lifetimes of U(VI) Species

The first-order nature of the decay of the luminescence from uranyl salts following excitation was first noted by Vavilov and Levshin⁶⁵ using the incorrectly analysed data of Nichols and Howes.⁵⁸ Emission lifetimes in the range 0.3×10^{-4} to 6.7×10^{-4} s were estimated for a selection of compounds in the solid state and values obtained subsequently by other workers fall in this region.^{66, 67, 69, 72, 73}

The lifetimes increase upon cooling^{66, 67, 69, 73} and approach the theoretical value for certain compounds at 4K (section 1.2). This suggests that at low temperatures virtually all of the absorbed light is re-emitted, but that increasing the temperature causes a proportion of the excited state energy to be dissipated by non-radiative mechanisms of which the most important must be a loss of energy to lattice vibrations. The rôle of H₂O molecular vibrations in this process is indicated by the increase in the lifetime of excited UO₂SO₄ · 3H₂O upon substitution by D₂O.⁷⁴ Deactivation processes are less efficient for solutions of uranyl salts in borate and silicate glasses as evinced by the increased emission lifetimes in these media (3.2×10^{-4} to 1.1×10^{-3} s at room temperature⁷⁵), and weakening of the bonds between the uranyl ions and the bulk of the glass by the introduction of fluorinating agents can further increase the observed lifetime by a factor of 16.⁷⁶

Another possibility for energy dissipation is intermolecular transfer of the excitation energy to other UO₂²⁺ ions, but it has been shown, at least in the case of silicate glasses, that this "self-quenching" mechanism is unimportant,⁷⁷ although radiationless transfer in glasses from excited uranyl ions to Ho³⁺⁷⁸ and Er³⁺⁷⁹ and in frozen aqueous solution to U(IV)⁸⁰ does take place. This probably occurs via a resonance mechanism.

Dissolution of uranyl compounds invariably causes a reduction in both the luminescence lifetime and, as a consequence, the intensity. An example is provided by uranyl nitrate which has an emission lifetime of $\sim 5.6 \times 10^{-4}$ s in the crystalline state⁷³ and $\sim 2.6 \times 10^{-6}$ s in dilute aqueous solution (section 6.2).

Three mechanisms have been postulated to explain quenching effects in solution :

- (i) Association of the uranyl ion and the quenching molecule prior to excitation (quenching by complex formation); in this case efficient energy dissipation by the quencher in the excited complex can cause the complex to appear non-luminescent.
- (ii) Proximity of the excited and quenching molecule, which may include a second UO_2^{2+} ion (quenching by resonance transfer).
- (iii) Encounter between the excited molecule and the quencher (quenching by kinetic encounter); this process may involve formation of a complex between the excited uranyl ion and the quenching molecule⁸¹ (known as an "exciplex").

In all of these cases quenching may be either "physical", whereby the excitation energy originally destined for a radiative process is dissipated as vibrational energy, or "chemical", whereby the excess energy is utilised in chemical reaction.

Perrin and Delorme⁶⁶ and Vavilov and Levshin^{63,65} measured the emission lifetimes of solutions of uranyl sulphate in concentrated sulphuric acid and found them to decrease with both increasing temperature and increasing uranyl concentration and to decrease upon addition of water. The latter workers undertook an exhaustive study of the dependence on concentration and temperature and found that these arose from, respectively, a self-quenching mechanism (i.e. $\text{UO}_2^{2+*} + \text{UO}_2^{2+} \rightarrow 2\text{UO}_2^{2+} + \text{heat}$) and the effect of temperature on the viscosity of the medium.

In aqueous solution, the luminescence is quenched to a much greater extent than in sulphuric acid. Evidently this is not purely a result of the lower viscosity of water as this is about one-twentieth of that of sulphuric acid whilst the luminescence quantum yield is reduced by a factor of 330 from 0.25^{63} to $\sim 7.5 \times 10^{-4}$ ⁸² and the lifetime from $\sim 2.0 \times 10^{-4}$ s⁶⁶ to 2.6×10^{-6} s, a factor of 77. In addition, substitution of D_2O for H_2O as solvent increases the lifetime by a factor of 2.⁸³ This suggests that water deactivates the excited uranyl ion by a mechanism similar to that for the quenching of the fluorescence of Sm^{3+} ,⁸⁴ Eu^{3+} ,⁸⁴⁻⁸⁷ Tb^{3+} ,^{84,85} Dy^{3+} ,⁸⁴ and Gd^{3+} ^{88,89} which involves excitation of an O-H stretching mode to a high vibrational level, i.e.

this is a physical process and decomposition of the water does not occur.⁹⁰

Prior to the work described in this thesis, direct measurement of the emission lifetime of UO_2^{2+} in an aqueous medium had not been achieved; indirect measurements suggest values of $1.5 \times 10^{-6} \text{ s}$ ⁸³ and 3.7×10^{-8} to $1.1 \times 10^{-6} \text{ s}$.⁸² The deactivation of excited uranyl ions by water molecules in an aqueous environment is of such greater efficiency than the self-quenching process that luminescence quantum yields in reasonably dilute solutions ($5 \times 10^{-3} \text{ dm}^{-3} \text{ mol}$ to at least $3.5 \times 10^{-2} \text{ dm}^{-3} \text{ mol}$) are independent of solute concentration.⁸²

Many inorganic and organic species, both ions and neutral molecules, have long been known to quench UO_2^{2+} emission. Volmar and Mathis⁹¹ were able to classify a range of inorganic ions according to their quenching ability. Several anions and all cations studied, except Ag^+ , were found to be inactive. It has also been shown that Eu^{3+} acts as a quencher in aqueous solution, becoming electronically excited in the process.⁸³ Virtually all organic molecules act as quenchers. Matsushima and Sakuraba have shown that aromatic species deactivate by a physical process^{81,92} as evidenced by the apparent absence of photochemical products and the identical quenching efficiencies of C_6H_6 and C_6D_6 . This process is thought to involve exciplex formation. In contrast, aliphatic molecules invariably undergo a photochemical decomposition during the quenching process and this is discussed at length in the next chapter.

CHAPTER 2

PHOTOCHEMISTRY OF URANYL COMPOUNDS

2. PHOTOCHEMISTRY OF URANYL COMPOUNDS

2.1 Introduction

The uranyl ion occupies a unique position among metal ions in that it is, in solution, both luminescent and capable of photo-redox reactions and consequently no ready comparison may be drawn between this species and other photoreactive metal ions, e.g. Ce(IV), Pb(IV) and Fe(III).

Thermal oxidations by U(VI) are restricted in number owing to the low value (0.063 V) of the oxidation potential for the U(VI)/U(V) couple,⁹³ but the photochemical reactions between uranyl compounds and a wide range of inorganic and organic molecules and ions are well known and have been studied for over a century, being the subject of an exhaustive review by Rabinowitch and Belford²² and a shorter, but more recent treatment by Balzani and Carassiti.⁹⁴

The uranyl ion undergoes three types of photochemical reaction :

- (i) Oxidation of inorganic and organic substrates, accompanied by reduction of U(VI).
- (ii) Sensitization of oxidation reactions by other oxidants, particularly molecular oxygen ("autooxidation").
- (iii) Catalysis of the photochemical decomposition of organic molecules (in particular the decarboxylation of organic acids).

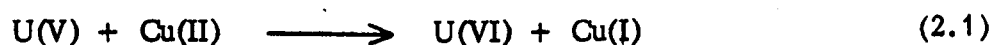
Reactions of types (ii) and (iii) involve no net reduction of U(VI). During any of the reactions (i) - (iii) electronic energy normally destined for phosphorescent emission is diverted to chemical reaction with consequent quenching of the emission intensity and reduction of the radiative lifetime. Reactions (i) - (iii) may, therefore, be regarded as subdivisions of the "chemical" type of luminescence quenching processes detailed on page 7.

Photo-oxidation and sensitization reactions are closely related; both involve reduction of U(VI) as a primary step, but in the latter process the reduced uranium species is reoxidized by the "co-oxidant," normally O₂. Photochemical decarboxylation of organic acids, on the other hand, may be

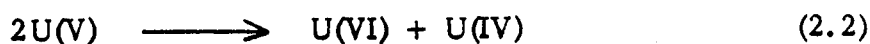
viewed as the oxidation of one part of the acid molecule by U(VI) and the reduction of the other part by the reduced uranium.^{22e} Both decarboxylation and photo-oxidation processes are evident simultaneously in reactions between uranyl compounds and certain carboxylic acids and they may be differentiated by the formation (or lack) of U(IV) as product (providing O₂ is excluded from the reaction) and by the type of organic end product. In general, RCO₂H will yield RH plus CO₂ by a decarboxylation route and R₂ plus CO₂ by an oxidative process.

Many attempts have been made to correlate the nature of the primary step in U(VI)-carboxylic acid photoreaction with the overall chemical reaction induced, viz. decarboxylation or oxidation, but this discussion remains confused and no relationships are apparent, even in the case of the U(VI)-oxalic acid system which has been most rigorously examined.

Whilst U(IV) is the reduced form of uranium normally reported as a product of photolysis, there is evidence to suggest that U(V) is the primary photochemical product and that this subsequently disproportionates to U(IV) and U(VI). Cupric ion has been shown to interfere with the formation of U(IV) during photoreduction of U(VI) by ethanol,⁹⁵ via the reaction :



In addition, a "dark reaction" involving the build-up of the concentration of U(IV) has been observed following illumination of aqueous solutions of uranyl ions containing carbohydrates,⁹⁶ methanol⁹⁷ and ethanol.^{98,99} Assuming a simple second-order reaction, viz.



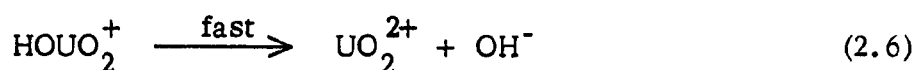
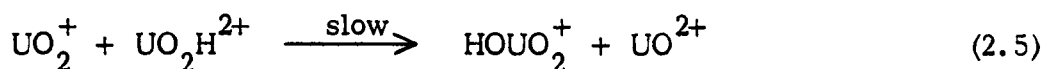
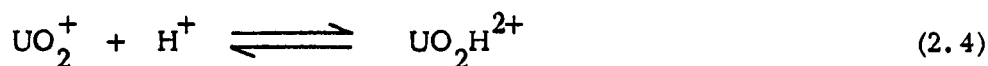
Heidt determined the rate constants at 298 K with sucrose and methanol to be 150 dm³ mol⁻¹ s⁻¹⁹⁶ and 135 dm³ mol⁻¹ s⁻¹⁹⁷ respectively, while a French group⁹⁹ calculated the third-order rate constant corresponding to the equation :

$$-d[\text{U(V)}]/dt = k[\text{H}^+][\text{U(V)}]^2 \quad (2.3)$$

as 2.3 x 10⁵ dm⁶ mol⁻² s⁻¹ during the reaction between U(VI) and ethanol in aqueous sulphuric acid at 298K; this corresponds to a pseudo second-order constant of 2.14 x 10⁴ dm³ mol⁻¹ s⁻¹ at pH 1.03 (the value utilised in the experiments of Heidt on methanol). Evidently the rate of disproportionation

is sensitive to the type of ion in solution. It has been established that the disproportionation reaction can be accelerated by the addition of organic⁹⁹⁻¹⁰² and inorganic¹⁰³ acid anions as well as by decreasing the pH.^{99, 101-104}

It has been proposed that the disproportionation occurs as follows :



The photoreduction of UO_2^{2+} in liquid media has been studied exclusively either by analysis of reaction products or by steady-state techniques, such as quantum yield determination and fluorimetry, as set out below. Detailed studies on organic compounds exist only in the cases of carboxylic acids, alcohols and aldehydes.

2.2 Carboxylic Acids

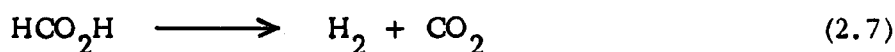
2.2.1 Monobasic Carboxylic Acids

Formic Acid

This substrate undergoes efficient photoreaction with uranyl ions exclusively by a redox process to yield mainly CO_2 , H_2O and U(IV) ^{35, 105-110} together with minor amounts of CO ,^{35, 106, 109} with $\phi\text{-HCO}_2\text{H}$ variously reported as 0.4,¹¹⁰ 0.7¹¹¹ and 0.97.¹⁰⁸

Evidence for the existence of formatouranyl complexes^{30, 31} and the attainment of maximum photoreduction rate at a formate concentration of $\sim 2 \text{ mol dm}^{-3}$ ¹⁰⁸ (whereas a substrate concentration of $\sim 10^{-3} \text{ mol dm}^{-3}$ should be sufficient for an excited molecule with a lifetime of 10^{-4} s to encounter a formate molecule during this time) suggest a photo-oxidation mechanism involving complex formation, although the nature of the complexes responsible has not been fully resolved.^{22f}

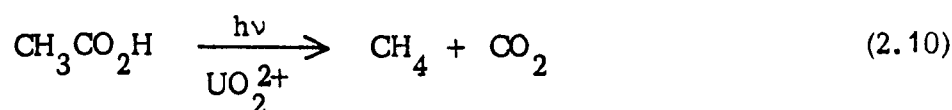
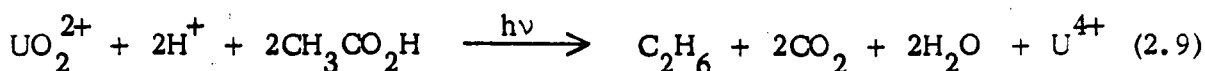
An explanation for the absence of products (particularly H_2) arising from a sensitized decarboxylation process, in contrast to the cases of higher aliphatic acids, is provided by considering the energy requirements in the following reactions :^{22g}



A C - C bond is ~84 kJ weaker than a C - H bond which is, in turn, ~21 kJ weaker than an H - H bond; decarboxylation of formic acid would therefore require 63 kJ more energy than the same reaction with its homologues.

Acetic Acid

The gaseous products of the photochemical reaction of U(VI) with this compound are reported as CO_2 with either CH_4 ,^{35,109} C_2H_6 ¹¹² or a mixture of both,^{113,114} depending on reaction conditions, and two stoichiometries are evident :



The proportion of C_2H_6 increases with increase in the ratio

$$[\text{CH}_3\text{CO}_2\text{H} + \text{CH}_3\text{CO}_2^-]/[\text{U(VI)}]$$

and this has been interpreted as indicating that complex formation (at high acetate concentration) leads to photo-oxidation of the organic molecule (reaction 2.9) whilst free uranyl ions sensitize the decarboxylation of the acid (reaction 2.10).^{22h}

Propionic Acid

Only CO_2 and C_2H_6 , in approximately equal proportions, have been detected in the photochemical decomposition of uranyl propionate^{106,109} and mixtures of uranyl salts and propionic acid,^{35,115} indicating an exclusive sensitized decarboxylation process.

Higher Monobasic Carboxylic Acids

Few detailed studies have been made of product distribution in these cases. Photolysis of solutions of uranyl butyrate, iso-butyrate, valerate and iso-valerate in water has been reported as producing CO_2 and a mixture of saturated hydrocarbons;^{106,109} more specifically, aqueous solutions of uranyl nitrate with both butyric^{115,116} and iso-butyric¹¹⁵ acids yield CO_2 and C_3H_8 in approximately equal quantities when photolysed. Similarly, valeric acid reacts

photochemically with aqueous uranyl chloride to produce CO_2 and $n\text{-C}_4\text{H}_8$,³⁵ the oxidative nature of the reaction being supported by the production of U(IV) valerate upon photolysis of a solution of uranyl valerate.²²ⁱ

It is noteworthy that the importance of the decarboxylation reaction for substrates $\text{C}_n\text{H}_{2n+1}\text{CO}_2\text{H}$ increases sharply with n , being negligible for $n = 0$ and predominant for $n > 2$, and that the decomposition rates of solutions of uranyl propionate, iso-butyrate, valerate and iso-valerate increase with the molecular weight of the acid.^{106,109} A possible explanation for the absence of decarboxylation of formic acid was presented earlier, but there appears to be no reason why propionic acid should react solely by this process whilst acetic acid undergoes photo-oxidation to a considerable extent. The stability constants of uranyl formate ($77.6 \text{ dm}^3 \text{ mol}^{-1}$), acetate ($252 \text{ dm}^3 \text{ mol}^{-1}$) and propionate ($340 \text{ dm}^3 \text{ mol}^{-1}$) are comparable³⁰ and it is unlikely that differences in the extent of complexation in these three cases is important in governing the reaction route, especially as, in the case of acetic acid, complex formation is thought to promote a photo-oxidation process.

2.2.2 Dibasic Carboxylic Acids

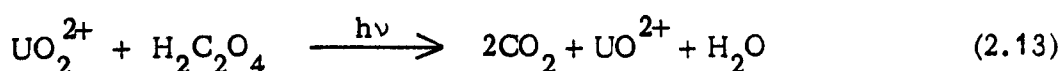
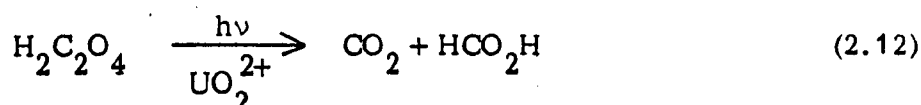
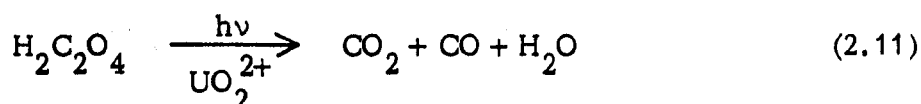
Oxalic Acid

The aqueous uranyl-oxalate system has afforded the most extensively studied photochemical reaction of U(VI), mainly because of its application as a chemical actinometer for which its virtually constant quantum yield under varying conditions (0.49 to 0.58)^{94a} makes it particularly suitable.

The production of CO_2 and CO by illumination of an aqueous solution of uranyl oxalate was first noticed in 1842¹¹⁷ and this has been confirmed by subsequent investigators for solutions of both uranyl oxalate¹¹⁵ and uranyl salts with added oxalic acid.^{35, 118 - 125} The production of U(IV),^{117, 118, 122 - 124, 126 - 130} and HCO_2H ^{115, 118, 119, 121, 124, 125, 131} has also been established, the latter up to an extent of 29% of the total reaction,¹³² whilst the yield of U(IV) is always low ($< 10\%$)^{111, 123, 133} in solutions containing excess oxalic acid but is higher for photolysis of solutions containing uranyl oxalate only¹¹¹ and rises dramatically when $[\text{H}_2\text{C}_2\text{O}_4] < [\text{U(VI)}]$.¹²⁸ This is evidence for a mechanism producing U(IV) by kinetic encounter (v.i.). The ratio of CO_2 to CO was found to reach a maximum (1.2:1) under conditions of excess oxalic acid.¹³¹

Numerous attempts have been made to establish the mechanisms whereby the various observed products are formed, much effort having been directed towards an elucidation of the rôles of the various complex species in solution, but it is indicative of the great complexity of this subject that all conceivable combinations of reaction type and reaction mechanism have been advanced; several authors suggest the existence of solely a complex formation mechanism,^{34,111,123,124,134} others an encounter mechanism¹²² whilst yet others attribute photo-oxidation to the former¹²⁸ and sensitization to the latter¹²⁹ and other groups believe the reverse situation to hold.^{123,125}

In the most recent paper Volman and Seed¹²⁵ favour the following stoichiometry :



The sensitized reactions (2.11 and 2.12) operate exclusively at high oxalic acid concentration and proceed via complex formation whilst reaction 2.13 occurs by encounter between excited uranyl ions and free substrate molecules. This scheme had previously been proposed by Rabinowitch and Belford.^{22j}

Higher Dibasic Acids

The photochemical decarboxylation of malonic acid to CO_2 and $\text{CH}_3\text{CO}_2\text{H}$ is strongly accelerated by uranyl salts,^{35,134,135} the rate becoming maximal (for an acid concentration of 0.05 mol dm^{-3}) at a U(VI) concentration of $\sim 2.5 \times 10^{-3} \text{ mol dm}^{-3}$ ¹³⁴ with $\phi_{-\text{CH}_2(\text{CO}_2\text{H})_2} = 0.27$.¹³⁵ This was interpreted as representing complete light absorption (by UO_2^{2+} ions or a U(VI)-acid complex), the uranyl concentration still being of a magnitude to ensure a high level of complexation (86.7%).¹³⁴ The complex formation mechanism has also been proposed as a result of a micro-manometric study of the gaseous reaction products,³⁵ whereby it was found that the decomposition rate of the acid is directly related to the concentration of the dianion $\text{CH}_3(\text{CO}_2^-)_2$ which forms a 1:1 complex with UO_2^{2+} with a stability constant of $4.0 \times 10^5 \text{ dm}^3 \text{ mol}^{-1}$.

Succinic acid undergoes photoreaction with uranyl salts in an analogous manner to malonic acid, producing CO_2 and $\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$,^{35,136,137} although one report mentions that inclusion of methylene blue in the photolyte results in bleaching of the latter (presumably by reduction) and formation of "oxidation products."¹³⁸ There is possibly competition between the methylene blue and an organic fragment for re-oxidation of U(V). A suggestion was made that the reaction involves an encounter mechanism but this was based on unjustifiable assumptions^{22k} and a later study showed that reaction occurs via a 1:2 complex between UO_2^{2+} ions and the monoionized acid.³⁵

Photolysis of an aqueous solution of uranyl chloride and glutaric acid continues the trend for photo-decarboxylation observed in its lower homologues and produces CO_2 and $\text{CH}_3(\text{CH}_2)_2\text{CO}_2\text{H}$ via a complex involving the monoionized acid.³⁵

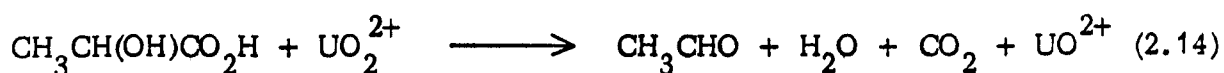
2.2.3 Substituted Carboxylic Acids

Lactic Acid

Photochemical reactions with this compound have received considerable attention and are of particular interest in view of the contemporary studies of Sakuraba and Matsushima (v.i.).

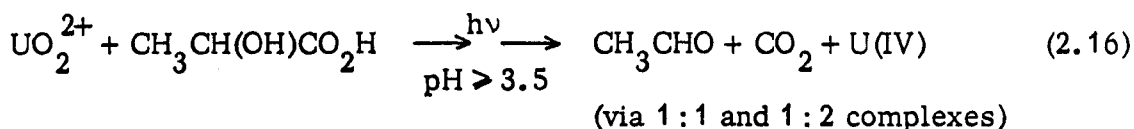
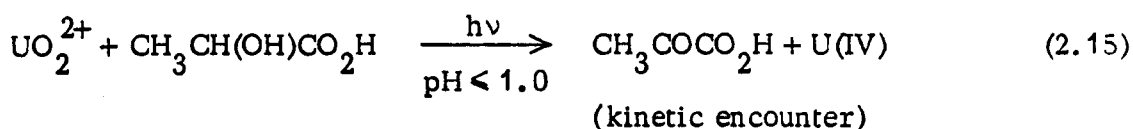
CO_2 and CH_3CHO are the major organic products^{106,109,119,136,139-142} and production of U(IV) has been reported in many cases.^{106,109,139,141-143}

The stoichiometry of the (oxidation) reaction was originally thought to be exclusively as follows:^{139,141}



Sakuraba and Matsushima found, however, that whereas this is the case at $\text{pH} > 3.5$, the major products at $\text{pH} < 1$ are $\text{CH}_3\text{COCO}_2\text{H}$ and U(IV).¹⁴²

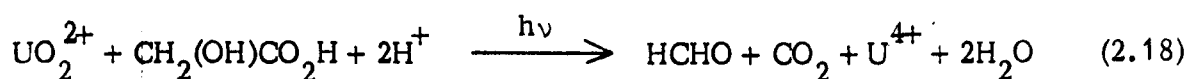
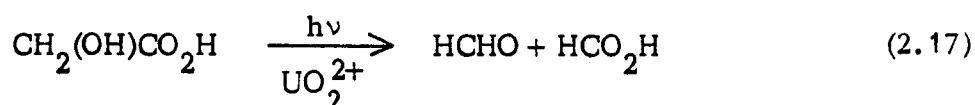
These workers demonstrated that at $\text{pH} 3.5$ 1:1 and 1:2 complexes exist between UO_2^{2+} and the lactate anion, whereas no complexation is evident at $\text{pH} 1.0$. Additionally, a Stern-Volmer plot of I_f/I_{f_0} against [lactic acid] (where I_f and I_{f_0} are the intensities of the uranyl luminescence in the presence and absence, respectively, of lactic acid) at $\text{pH} 1.5$ and of $\phi_{\text{U(IV)}}^{-1}$ against [lactic acid]⁻¹ at $\text{pH} 1.0$ are both linear, whereas this is not the case for the corresponding plots at $\text{pH} 3.5$. The following reactions, both of which are photo-oxidations, were therefore proposed:



The value of K_{eq} for the 1:1 complex determined from the photochemical kinetics for reaction (2.16) was in good agreement with a direct spectroscopic determination.³⁶

Other Substituted Acids

Glycolic acid photodecomposes in solutions containing UO_2^{2+} ions to produce HCHO ,^{109,144} CO_2 ,¹⁰⁹ HCO_2H ¹⁰⁹ and U(IV) ^{109,144} and two reaction schemes have been proposed:²²¹



Rabinowitch and Belford²²¹ draw attention to the fact that no simple sensitized decarboxylation of the substrate, producing CH_3OH and CO_2 , appears to occur, in contrast to the cases of acetic, oxalic and other acids. It is possible that this reaction does, in fact, proceed in the present case as it is most likely that UO_2^{2+} ions further photo-oxidize methanol to formaldehyde (section 2.3.2).

Other substituted acids have been examined and the results are included in Table 1 which summarises the data on U(VI) photo-oxidation of carboxylic acids.

2.3 Alcohols and Aldehydes

2.3.1 Kinetic Studies

In direct contrast to the situation with carboxylic acids, reports on the composition of photochemical products of reactions involving alcohols and aldehydes are scarce, whereas several kinetic studies on these systems have been performed.

Heidt and Moon,⁹⁶ during their work on the photo-oxidation of sugars by U(VI), studied the dependence of $\phi_{\text{U(IV)}}$ on the initial concentration of substrate

TABLE 1

Distribution of Products in U(VI)
Photoreactions with Carboxylic Acids

Substrate	PRODUCTS (excluding H ₂ O)		References
	Decarboxylation Mechanism	Photo-oxidation Mechanism	
HCO ₂ H		CO ₂ + CO + U(IV)	35, 105 - 110
CH ₃ CO ₂ H	CH ₄ + CO ₂		35, 109, 113, 114
		C ₂ H ₆ + CO ₂ + U(IV)	112 - 114
CH ₃ CH ₂ CO ₂ H	C ₂ H ₆ + CO ₂		35, 106, 109, 115
CH ₃ (CH ₂) ₂ CO ₂ H	C ₃ H ₈ + CO ₂		115, 116
(CH ₃) ₂ CHCO ₂ H	C ₃ H ₈ + CO ₂		115
CH ₃ (CH ₂) ₃ CO ₂ H	C ₄ H ₈ + CO ₂		35
		U(IV) + ?	22i
(CO ₂ H) ₂	CO ₂ + CO		35, 118 - 125
	CO ₂ + HCO ₂ H		115, 118, 119, 121, 124, 125, 131

continued

TABLE 1 (continued)

Substrate	PRODUCTS (excluding H ₂ O)		References
	Decarboxylation Mechanism	Photo-oxidation Mechanism	
		CO ₂ + U(IV)	117, 118, 122 - 124, 126 - 130
HO ₂ CCH ₂ CO ₂ H	CH ₃ CO ₂ H + CO ₂		35, 134, 135
HO ₂ C(CH ₂) ₂ CO ₂ H	CH ₃ CH ₂ CO ₂ H + CO ₂		35, 136, 137
HO ₂ C(CH ₂) ₃ CO ₂ H	CH ₃ (CH ₂) ₂ CO ₂ H + CO ₂		35
CH ₃ CH(OH)CO ₂ H		CH ₃ CHO + CO ₂ + U(IV) [*]	106, 109, 119, 136, 139 - 143
		CH ₃ COCO ₂ H + U(IV) ^{**}	142
HOCH ₂ CO ₂ H	HCHO + HCO ₂ H		109
		HCHO + CO ₂ + U(IV)	109, 144
CH(O)CO ₂ H		CO ₂ + "Reduced U"	161
(CH ₃) ₂ C(OH)CO ₂ H		(CH ₃) ₂ CO + U(IV) + CO ₂	162

continued

TABLE 1 (continued)

Substrate	PRODUCTS (excluding H ₂ O)		References
	Decarboxylation Mechanism	Photo-oxidation Mechanism	
C ₆ H ₅ CH(OH)CO ₂ H		C ₆ H ₅ CHO + C ₆ H ₅ CO ₂ H + U(IV) [†]	163
HO ₂ CCH ₂ CH(OH)CO ₂ H	CH ₃ CHO + CO ₂ ^{‡‡}		119
HO ₂ CCH ₂ C(OH)(CO ₂ H)CH ₂ CO ₂ H	(CH ₃) ₂ CO + CO ₂		164
HO ₂ CCH(OH)CH(OH)CO ₂ H	CH ₂ (OH)CH(OH)CO ₂ H + CO ₂ ^{††}		35
	CH ₃ COCO ₂ H + CO ₂		119
		U(IV) + ?	110, 165

* pH > 3.5 ** pH ≤ 1 † C₆H₅CO₂H possibly arises from photo-oxidation of C₆H₅CHO †† not positively identified

‡‡ CH₃CHO is derived from the lactic acid produced by decarboxylation of the malic acid

(C_o) for several sugars and found a linear relationship between $\phi_{U(IV)}^{-1}$ and C_o^{-1} , but admitted that either encounters between the excited uranyl ions and adventitiously neighbouring substrate molecules or complex formation may be inferred from this, and used the phrase "photosensitive cluster" to describe the pair of reacting molecules.

Bhattacharyya and Gulvady^{141,145,146} assumed a complex formation (corresponding to a particularly intimate "photosensitive cluster") between ethanol molecules and the uranyl species but, upon plotting $\{d[U(IV)]/dt\}^{-1}$ against $[ethanol]^{-1}$ they found that the graphs, although linear, gave different values for the (assumed) complex formation constant depending on the wavelength of irradiation. This was taken as evidence against the complex formation mechanism.

A complex mechanism was also assumed by Venkatarao and Santappa¹⁴⁷ to operate for the photoreaction between aqueous uranyl perchlorate and isopropanol and the results from monitoring U(IV) formation were apparently found to fit their surmise. At a later date, however, the same workers assumed a collisional mechanism for their studies on the uranyl-methanol and uranyl-isopropanol systems.⁸² The reaction scheme predicted linear relationships between $\phi_{U(IV)}^{-1}$ and $[alcohol]^{-1}$ and between $\phi_{lumin.}^{-1}$ and $[alcohol]$, both of which were realised. The Stern-Volmer plot is strong evidence for a bimolecular (collisional) deactivation of excited uranyl ions but it is doubtful whether a plot of $\phi_{U(IV)}^{-1}$ against $[alcohol]^{-1}$ can differentiate between the two possible mechanisms,^{95,96} although the slopes of the graphs are a measure of the relative photoreactivities of the substrates.

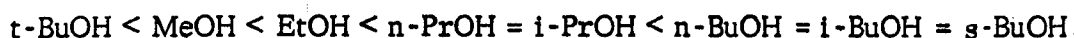
Recently, Sakuraba and Matsushima have published a notable paper on the correlation between luminescence quenching and U(IV) production during the photoreaction of various alcohols with uranyl ions in aqueous solution.⁹⁵ Linear graphs were obtained for the following plots :

- | | |
|--|--|
| (i) $\phi_{U(IV)}^{-1}$ against $[S]^{-1}$; | $S \equiv EtOH, i-PrOH$ |
| (ii) I_{f_o} / I_f against $[S]$; | $S \equiv EtOH, i-PrOH$ |
| (iii) $\phi_{U(IV)}^{-1}$ against K_q^{-1} ; | alcohols studied were MeOH, EtOH, n-PrOH, i-PrOH, n-BuOH, s-BuOH, i-BuOH |
| (iv) $\phi_{U(IV)}$ against temperature ; | alcohols studied were MeOH, EtOH, n-PrOH |

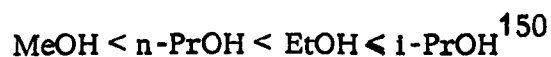
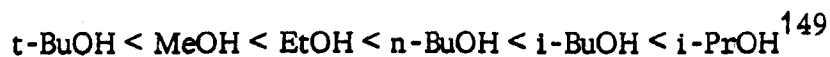
I_f and I_{f_0} are luminescence intensities with and without added alcohols; K_q , the Stern-Volmer quenching constant, is the slope of the graphs obtained in (ii) and a measure of the quenching efficiency of the alcohol.

The first plot was unable to furnish evidence about the reaction mechanism, being applicable to both collisional and complex processes. However, the second plot, which is comparable to the results of Venkatarao and Santappa with methanol and iso-propanol (v. s.) is powerful evidence for the collisional nature of the luminescence quenching and, together with the next plot which indicates a close correlation between quenching efficiency and chemical reactivity, suggests that chemical quenching is more important than the physical process in the radiationless deactivation of excited uranyl ions by alcohol molecules. The fourth plot provides additional support for a kinetic encounter mechanism and affords an apparent activation energy, ΔE^\ddagger , of $\sim 36 \text{ kJ mol}^{-1}$.

Sakuraba and Matsushima extended their studies on uranyl-alcohol systems,¹⁴⁸ which disclosed the following trend in photoreactivity towards the UO_2^{2+} ion :



Similar series had been reported previously, viz :



The observed parallel relationship between photoreactivity and quenching efficiency indicates that the rate-determining steps in both the photo-redox and quenching reactions are the same. The authors conclude, from the following evidence, that this step involves abstraction of a hydrogen atom in a position α to the OH group :

- (i) The rate constant for U(IV) production during the photo-oxidation of *t*-butanol (which has no α H atoms) is only one-tenth of those for reactions involving the other three butanol isomers.⁹⁵

- (ii) The efficiency of *t*-butanol in quenching uranyl luminescence is low ($K_q = 5 \text{ dm}^3 \text{ mol}^{-1}$) in comparison to the other isomers ($K_q = 130 \text{ to } 174 \text{ dm}^3 \text{ mol}^{-1}$).

- (iii) A primary kinetic isotope effect of 2.33 is observable on the rate of U(IV) formation with $\text{CH}_3\text{CH}_2\text{OH}$ and $\text{CD}_3\text{CD}_2\text{OD}$, whereas $\text{CH}_3\text{CH}_2\text{OH}$ and $\text{CH}_3\text{CH}_2\text{OD}$ exhibit a value of only 1.03.^{95,148} In addition, deuterium isotope effects on $\phi_{\text{U(IV)}}$ of 2.21 and 1.94 respectively are displayed by ethanol and iso-propanol and their per-deutero analogues in aqueous solution.¹⁴⁸
- (iv) Isotope effects on the luminescence quenching constants for the same substrates as in (iii) are 2.15 and 2.76 respectively.⁸¹
- (v) The slope, ρ^* , of the Hammett plot of $\log \phi_{\text{U(IV)}}$ against $\Sigma\sigma^*$ (the sum of the Taft σ^* values and a measure of the polarity of the alcohol) has a value -1.1 which falls in the range reported for radical reactions.¹⁴⁸

It was later shown that at $\text{pH} < 1$ another, pH sensitive, α hydrogen abstraction reaction is operative.¹⁵¹

All the experiments of Sakuraba and Matsushima were performed in water-alcohol mixtures. It is interesting that the primary process in the photo-oxidation of neat methanol by uranyl nitrate is abstraction of the hydroxylic H atom, the methoxy radical having been "spin-trapped" during such a reaction,^{152,153} whereas 2/1 v/v water-methanol yields only the hydroxymethyl radical.¹⁵³

In his latest paper⁸¹ Matsushima advances a theory that alcohol molecules combine with light-excited uranyl ions to form an exciplex and that the rate-determining step involves the breakdown of this complex into redox products. Evidence for exciplex formation is, however, not as convincing as in the case of aromatic quenchers (which yield no net chemical reaction). It appears to be impossible to confirm the existence of an exciplex process by kinetic studies on reactants or products (section 6.2, page 73).

Some Russian workers¹⁵⁰ have calculated rate constants corresponding to the expression :

$$-d[\text{UO}_2^{2+}]/dt = k[\text{UO}_2^{2+}][\text{alcohol}] \quad (2.19)$$

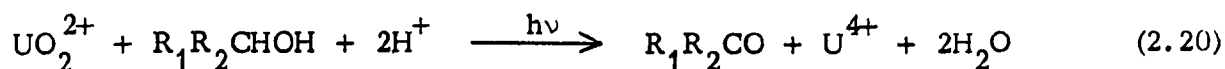
It is highly improbable that the reaction is strictly first-order with respect to UO_2^{2+} , but it may appear so at low concentrations where light absorption is far from complete.

Photo-oxidation of formaldehyde and acetaldehyde by uranyl ions has been examined by Venkatarao and Santappa in a similar way to their study of methanol and iso-propanol. As in the case of the alcohols a linear plot of $\{d[U(IV)]/dt\}^{-1}$ against $[aldehyde]^{-1}$ was originally thought to confirm photoreaction via uranyl-aldehyde complexes^{154,155} but this theory was rejected in favour of an encounter mechanism in a later paper when a plot of $\phi_{lumin.}^{-1}$ against $[aldehyde]$ was found to be linear.⁸² A collisional mechanism had previously been proposed by a second group for the photo-oxidation of formaldehyde.¹⁵⁶

Haas and Gayer¹⁵⁷ established $\phi_{U(IV)}$ for photo-oxidation of propionaldehyde as >0.72 but stated that their experiments, which involved monitoring $[U(IV)]$, were unable to distinguish between the two possible mechanisms. $\phi_{U(IV)}$ has been measured as 0.69 to 0.73 and 0.49 to 0.57 for photo-oxidation of formaldehyde and propionaldehyde respectively,⁸² and has been shown, in the case of formaldehyde, to be strongly dependent on the uranyl salt used.¹⁵⁸

2.3.2 Product Studies

Ethanol is known to give $U(IV)$ and CH_3CHO upon photo-oxidation by $U(VI)$ ^{95,98,141,159,160} with a ratio $[U(IV)]/[acetaldehyde]$ of 1^{95,160} and the assumption has been made that methanol produces $HCHO$ in an analogous manner;^{22m} iso-propanol is similarly oxidised to $(CH_3)_2CO$ ¹⁴⁷ and it appears that the predominant reaction of alcohols is :



In general, aldehydes are photo-oxidized to the corresponding acid, formic and acetic acids having been detected in reactions involving formaldehyde and acetaldehyde respectively,¹⁵⁵ and propionic acid having been proposed as the product from propionaldehyde.¹⁵⁷

CHAPTER 3
EXPERIMENTAL TECHNIQUES
THEORETICAL BACKGROUND

3. EXPERIMENTAL TECHNIQUES THEORETICAL BACKGROUND

3.1 Theory of Electron Spin Resonance

There are several accounts of the e.s.r. method¹⁶⁶⁻¹⁶⁹ and only a brief review is given here.

3.1.1 The Basic Resonance Condition

A system containing n electrons possesses an angular momentum vector, \vec{p} , due to the non-classical intrinsic angular momentum spin, of magnitude $\sqrt{S(S+1)}\hbar$, where S is the total spin quantum number, and can take values $n/2, n/2 - 1, n/2 - 2, \dots, 1/2$ or 0 ; $\hbar = h/2\pi$. Quantum mechanics restricts the number of spin states (for each value of S) to $(2S+1)$, each one characterised by the quantum number M_S which takes values $S, S-1, \dots, -S$, and consequently by the orientation of \vec{p} with respect to an arbitrary (z) direction, the component in this direction having magnitude $\hbar M_S$. The maximum observable value of the spin angular momentum is, therefore, $\hbar S$.

The spin vector gives rise to a magnetic moment, $\vec{\mu}_E$, with proportionality constant γ_E , where

$$\gamma_E = g_E \beta_E / \hbar \quad (3.1)$$

g_E is a dimensionless number whose value for the free electron is 2.0023. Most organic radicals, lacking spin-orbit coupling, have g values in the same region. Thus

$$\vec{\mu}_E = -\gamma_E \vec{p} \quad (3.2)$$

and the component along the z axis assumes values given by

$$\mu_E^z = -\gamma_E \hbar M_S = -g_E \beta_E M_S \quad (3.3)$$

(μ_E^z and M_S differ in sign due to the negative charge of the electron¹⁷⁰).

For a single, unpaired electron, $S = \frac{1}{2}$, $M_S = \pm \frac{1}{2}$, and therefore

$$\mu_E^z = \pm \frac{1}{2} g_E \beta_E \quad (3.4)$$

Application of an external magnetic field, H , along the z direction removes the degeneracy of these two spin states (Zeeman effect) and the interaction between H and μ_E^z may be represented by the Hamiltonian :

$$\mathcal{H}_E = -\mu_E^z H = g_E \beta_E H M_S \quad (3.5)$$

which gives rise to two energy levels differing in energy by $g_E \beta_E H$. Radiation of energy $h\nu_0 = g_E \beta_E H$ induces transitions between the two levels and as, under normal conditions, the population of the lower spin state ($M_S = -\frac{1}{2}$) is slightly greater than that of the upper state ($\sim 0.07\%$ at room temperature), the net result is absorption of energy.

In the absence of relaxation processes whereby excess spin energy may be lost by non-radiative mechanisms, equal population of both spin states would be rapidly achieved and absorption would cease. The most important of these processes is spin-lattice relaxation whereby excess energy is lost to vibrations and rotations of the surrounding molecules. In the solid state this process is highly efficient, leading to short lifetimes for the excited spin state and, as a consequence of the Heisenberg uncertainty principle, broadening of the absorption lines, making analysis of the spectra of radicals with small nuclear splittings (section 3.1.2) almost impossible. Conversely, radicals in solution, where relaxation processes are inefficient, often exhibit very sharp lines (as narrow as 0.008 mT).

3.1.2 Nuclear Hyperfine Coupling

A nearby nuclear spin vector, with quantum numbers I, M_I , analogous to S, M_S may couple with the electron spin vector and this can occur in two ways :

- (i) Fermi contact interaction¹⁷¹ - this is an isotropic coupling represented by

$$\mathcal{H}_F = (8\pi/3) g_E \beta_E g_N \beta_N \delta(\vec{r}) M_I M_S = ha M_I M_S \quad (3.6)$$

Restrictions on the function $\delta(\vec{r})$ cause the coupling constant, a , to be zero unless there is a finite spin density at the nucleus, in which case a is proportional to the spin density.

- (ii) Dipolar interaction - this is a classical interaction between electronic and nuclear magnetic moments and is therefore anisotropic in nature. For a spherically symmetrical molecule or for one tumbling rapidly in solution, the interaction averages to zero¹⁷² and may then be neglected, and for randomly orientated organic radicals in a solid matrix the anisotropic

coupling, which is often much smaller in magnitude than the isotropic component, usually only causes line broadening, although anisotropic couplings and g values have been measured in some cases (e.g. for the radical CH_2OH , page 37).

Coupling between the nuclear spin vector and the external magnetic field, H , may be described in a similar way to that for the electronic spin :

$$\mathcal{H}_N = -g_N \beta_N H M_I \quad (3.7)$$

and the complete "spin" Hamiltonian for a rapidly tumbling molecule is, therefore :

$$\mathcal{H}_S = \mathcal{H}_E + \mathcal{H}_N + \mathcal{H}_F = g_E \beta_E H M_S - g_N \beta_N H M_I + ha M_I M_S \quad (3.8)$$

giving rise, in the "high field" limit (above a few tens of millitesla) where electronic and nuclear spin are quantised independently, to energy levels :

$$E = (g_E \beta_E M_S - g_N \beta_N M_I) H + ha M_I M_S \quad (3.9)$$

and transitions between the levels are governed by the selection rules

$$\Delta M_S = \pm 1, \Delta M_I = 0$$

It is evident from equation (3.9) that coupling with a nucleus of spin I will cause a single absorption (one unpaired electron) to be split into $2I + 1$ lines (corresponding to $2I + 1$ values of M_I), and since observations are generally made with a constant microwave frequency, ν_0 , and variable magnetic field, H , it follows that the lines will occur at field strengths $H_0 + ha M_I / g_E \beta_E$ where $H_0 = h\nu_0 / g_E \beta_E$; a is in units of energy and is independent of ν_0 and H_0 , but, as all the radicals studied in this work have similar g factors (~ 2), it is permissible to quote a in terms of magnetic field strength, i.e. millitesla (mT).

By far the most common nuclear interaction in organic radicals is that due to a hydrogen nucleus ($I = \frac{1}{2}$), where n inequivalent nuclei give rise to 2^n hyperfine lines and n equivalent nuclei (possessing closely similar values of a) produce $2n + 1$ lines of binomial intensity distribution.

An exchange coupling mechanism (suggested simultaneously by several authors¹⁷³⁻¹⁷⁶ and discussed at length by McConnell for coupling with aromatic protons^{173,177-180}) is invoked to explain interaction of electrons in $p\pi$ orbitals with nuclei lying in the nodal plane of zero spin density, when the value of a in equation (3.6) is non-zero only for a finite electron density at the nucleus.

Figure 2a shows the two possible spin arrangements for a C - H section of either an aromatic radical or an aliphatic π -radical, e.g. $\dot{\text{C}}\text{H}_3$. Arrangement I, which represents the triplet state of the carbon atom, occurs more frequently than arrangement II, as a consequence of Hund's rule, and the result is a small negative spin density at the proton (the unpaired electron is, by convention, allocated a positive spin density, i.e. $M_S = +\frac{1}{2}$). The proton hyperfine coupling constant, a_H , and the unpaired spin density on carbon, ρ_C , are linearly related by the formula^{177,179}

$$a_H = Q_{\text{CH}} \rho_C \quad (3.10)$$

Q_{CH} is the $\sigma - \pi$ interaction parameter and has values between - 2.0 and - 3.0 mT depending on the substitution pattern and charge on the trigonal carbon atom.

In addition to coupling between unpaired π electrons and protons in the α position as described above, hyperfine splitting from β protons is also common; an example is given by the ethyl radical where $a_{\text{H}(\text{CH}_3)} = +2.69$ mT and $a_{\text{H}(\text{CH}_2)} = -2.24$ mT. In this case it is possible for the methyl hydrogen orbitals to overlap directly with the 2p orbital bearing the unpaired electron (figure 2b) and, assuming that the latter couples slightly with one electron in the C - H σ bond, the remaining electron is left with a small positive spin density giving rise to an isotropic coupling of positive sign. This process is termed "hyperconjugation."

It is to be expected that the magnitude of the β coupling will be dependent on the dihedral angle, θ , between the 2p axis and the C - H bond associated with the interacting proton (figure 2c) as the p orbital wavefunction, Ψ , indicates a relationship of the form

$$\Psi_{\theta}^2 = \Psi_0^2 \cos^2 \theta \quad (3.11)$$

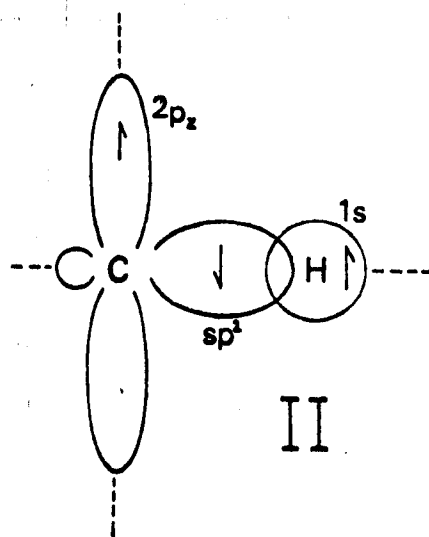
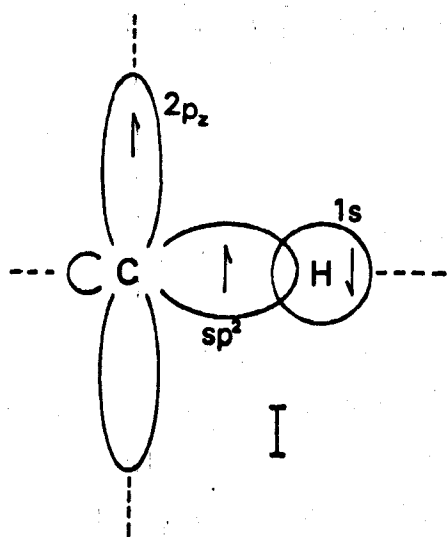
where Ψ_{θ}^2 and Ψ_0^2 are spin densities corresponding to angles θ and zero. The relationship

$$a_{\text{H}(\beta)} = A + B \cos^2 \theta \quad (3.12)$$

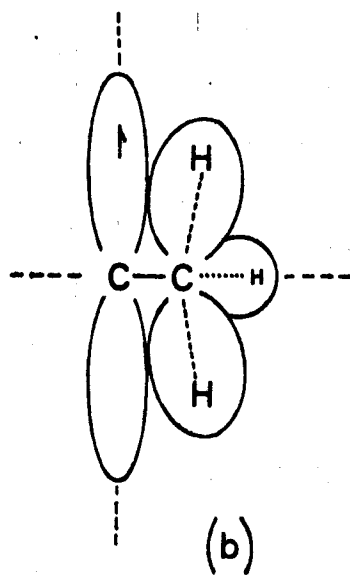
originally suggested by Heller and McConnell,¹⁸¹ is applicable in most cases and various values for A and B have been calculated.¹⁸²⁻¹⁸⁴ A is always small and may often be neglected, leaving the equation :

FIGURE 2

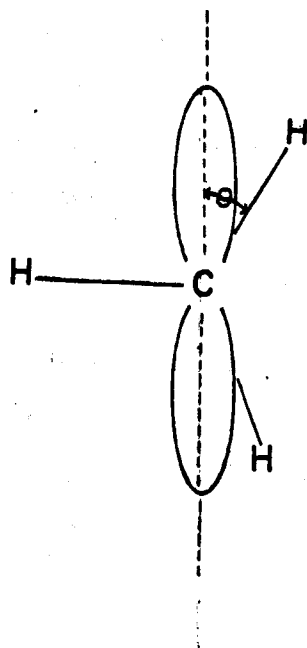
- (a) Possible spin polarization in a C - H section of an aromatic or aliphatic π -radical.
- (b) Overlap of electronic orbitals in a C - CH₃ fragment.
- (c) The dihedral angle θ between the C - H bonds and the 2p orbital in a C - CH₃ fragment.



(a)



(b)



(c)

$$a_H(\beta) = Q_{CCH} \rho_C \cos^2 \theta \quad (3.13)$$

For β protons in a rapidly rotating group, for example the CH_3 group in the ethyl radical,

$$a_H(\beta) = Q_{CCH} \rho_C (1/2\pi) \int_0^{2\pi} \cos^2 \theta \, d\theta = \frac{1}{2} Q_{CCH} \rho_C \quad (3.14)$$

A value for Q_{CCH} of +5.0 mT is generally accepted for the case of the methyl group.

Dipolar interaction between β protons and the unpaired electron is negligible and the corresponding coupling constants, in contrast to those from α protons, do not exhibit anisotropy in orientated radicals. Couplings from γ protons are very small ($< 0.1 \text{ mT}^{185}$) and are rarely resolved.

3.2 Flash Photolysis

Two problems arise in connection with the direct investigation of a very fast reaction. Firstly, the reaction must be initiated in a time which is short in comparison with the overall reaction time and secondly, a significant parameter of the reacting system must be monitored after initiation.

Flash photolysis is a method whereby a non-equilibrium situation is created in a reaction system in a short interval of time by an intense burst of visible or ultraviolet radiation following which products or intermediate species are monitored, usually by absorption spectroscopy. As well as providing a faster initiation (and consequently the ability to follow faster reactions) than such methods as rapid mixing, temperature jump and pressure or electric field pulses, the flash photolysis technique possesses the advantages that large concentrations of reactive species may be built up and that, by choice of a suitable excitation wavelength, specific reactions may often be induced.

Conventional (microsecond) flash photolysis apparatuses originally developed by Porter,¹⁸⁶ Davidson¹⁸⁷ and Herzberg¹⁸⁸ almost invariably utilise the discharge of a capacitor through a quartz tube filled with a rare gas at moderate pressure to produce the initial excitation in the form of a burst of u.v.-visible radiation. A typical flash has an energy of 1 kJ and a duration of 25 μs . Two principal techniques are used for the detection and estimation of the transient intermediates produced by this flash:

- (i) Flash spectroscopy - whereby a second flash, of short duration, timed to fire at any required interval after the photolysis flash, is used to record the absorption spectra of reactive intermediates photographically via a spectrograph.
- (ii) Kinetic spectrophotometry - in this case a collimated beam of light from a conventional lamp (e.g. quartz - iodine) is passed through the reaction vessel thence via a monochromator to a detector (usually a photomultiplier) which is connected to a recorder (usually an oscilloscope).

E.s.r. techniques have also been used to identify radicals produced by flash methods. ^{189 - 191}

Microsecond flash photolysis has been used extensively to study free radicals and excited triplet states of a wide range of organic molecules in gas and liquid phases. The radical $(C_6H_5)_2\dot{C}OH$ has been detected in this way during photoreaction of benzilic acid with uranyl perchlorate. ¹⁹²

Whereas gas discharge lamps are ideal for studying reactions with lifetimes greater than about 1 μs , problems are encountered in trying to reduce the duration of the flash in order to study faster reactions; normally a ten-fold reduction in duration requires a hundred-fold reduction in energy. The development of pulsed lasers (particularly those based on ruby and neodymium) has provided sources of excitation not subject to these energy-duration characteristics and which exhibit the following advantages :

- (i) Their peak powers can be enormous (up to 10^{12} W).
- (ii) The emitted light is coherent, monochromatic and can be focused to very small areas.
- (iii) The pulse is not accompanied by a long afterglow.

The ruby laser is currently the most common in use for flash photolysis purposes, producing a typical flash of 1 J, 20 ns when used together with a 'Q-switch' which suppresses stimulated emission from the excited Cr(III) content of the ruby until the excess population of the excited state (produced by a gas-discharge lamp) is sufficient to produce the short, powerful pulse required. The fundamental frequency of ruby (694.3 nm) is of little use for the excitation of many

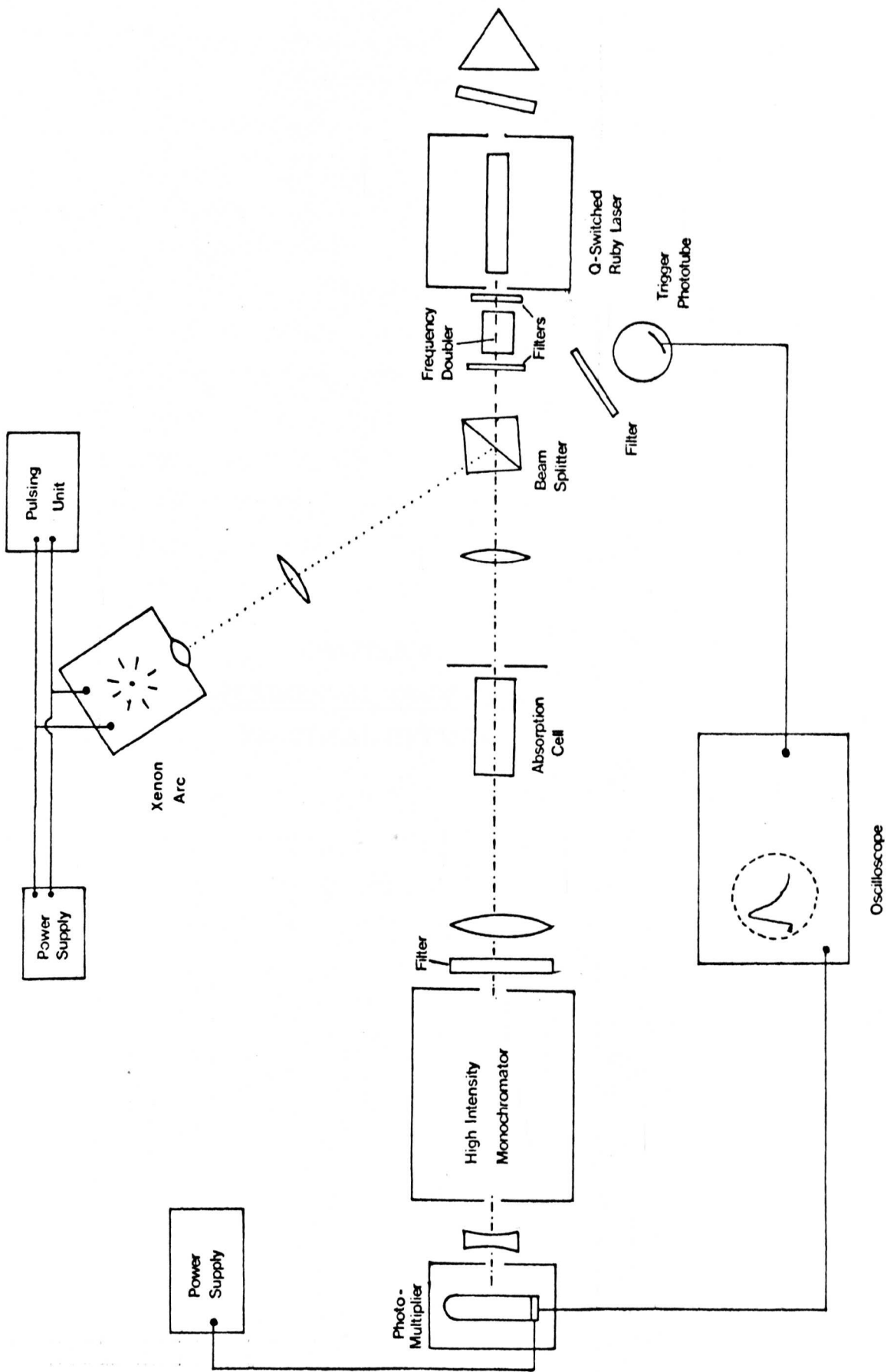
compounds and a frequency doubler (normally a piezo-electric crystal such as ammonium dihydrogen phosphate) is usually coupled with this laser. One of the disadvantages of any laser source is the limited number of wavelengths available for excitation, but the frequency doubled ruby laser ($\lambda = 347.1 \text{ nm}$) is satisfactory for the present work as the uranyl ion can be excited by radiation of any wavelength below $\sim 460 \text{ nm}$.

Laser flash photolysis is commonly used in the kinetic mode and a typical arrangement is shown in figure 3. Monitoring beams must be of high intensity in order to produce a favourable signal to noise ratio and for this purpose flash lamps are often used which, at the peak of output, produce light of virtually constant intensity for up to 100 ns . One of the advantages of the monochromatic nature of laser light is that the monitoring and photolysis beams need not be at right angles and colinear monitoring (as in figure 3) is appreciably more sensitive.

Applications of pulsed lasers in the study of nanosecond transient absorptions, in particular excited singlet states of aromatic compounds, have been reviewed by Moore.¹⁹³

FIGURE 3

A typical laser flash-photolysis apparatus



CHAPTER 4

EXPERIMENTAL TECHNIQUES

PRACTICAL DETAILS

4. EXPERIMENTAL TECHNIQUES PRACTICAL DETAILS

4.1 Electron Spin Resonance

4.1.1 The Spectrometer

The e.s.r. spectrometer used in the present work was a conventional X-band instrument (model X-1, Decca Radar Limited) with a 7 inch electromagnet (Newport Instruments Limited) capable of a maximum field intensity of 600 mT and a general-purpose sample cavity fitted with gold plated ceramic windows and three tuning controls. In most of the experiments the magnetic field was set manually to a point slightly to low field of the radical absorption (invariably ~ 330 mT, corresponding to $g \sim 2$, for organic radicals) and was then swept slowly through the absorption by means of a slow-sweep unit. Typical sweep speeds were 0.1 mT s^{-1} for radicals in solid matrices and 0.02 mT s^{-1} for those in liquid media where slow speeds are necessary in order to resolve the narrow lines characteristic of these radicals. Spectra were displayed as the first derivative of the absorption curve on x-y and x-t pen recorders. To achieve maximum resolution the magnetic field modulation amplitude was kept as small as possible consistent with a reasonable signal to noise ratio. Saturation of the upper spin state (caused by excessively high microwave power) was observable only in a few cases of radicals in the liquid phase. A Biomac 1000 computer-of-average-transients (Data Laboratories Limited) became available in the later stages of this work to enhance the intensity of some of the weaker spectra.

Photolysis of samples was carried out through two slots in the front of the cavity. A standard variable temperature insert (Decca Radar Limited) was used to study radicals statically at temperatures down to 77 K; this employed a flow of cold nitrogen gas over the sample, the temperature being controlled by a platinum resistance thermometer and a feedback circuit to a heating element in the gas flow. In this manner the temperature could be controlled to $\pm 1 \text{ K}^0$. Temperature control during flow experiments is described in section 4.1.5.

The spectrometer was calibrated daily, under all conditions of field sweep speed and recorder settings used, with a dilute alkaline solution of Frémy's salt (potassium peroxyamine disulphonate), the radical dianion of

which exhibits three lines of equal intensity with a splitting of 1.307 mT and a g -factor of 2.0055. A proton resonance probe (Decca Radar Limited) situated in the magnetic field close to the sample cavity was used to operate a marker on the $x - t$ recorder and the remote pen drop of the $x - y$ recorder at a set magnetic field intensity. Thus, a calibration in terms of mT cm^{-1} (with an inherent accuracy of ± 0.01 mT) and of absolute field intensity enabled coupling constants and g -values to be calculated for all radicals studied. Instrumental accuracy was usually high compared to the accuracy of measurement of the spectra.

4.1.2 Spectral Analysis

Analysis of spectra was sometimes difficult for frozen radicals due to line-broadening effects (which obscured some of the smaller splittings) and for radicals in both solid and liquid media due to the presence of more than one paramagnetic species. The use of computer program ESRTT3 (basically similar to the program ESRTT2 written by Dr. O. W. Howarth and listed elsewhere¹⁹⁴) which produces a simulated e.s.r. spectrum from spectral parameters for single or mixed radicals, greatly improved the ease and accuracy of analysis. In this way coupling constants for complicated spectra in the liquid state could be estimated to ± 0.015 mT (almost the instrumental accuracy). Otherwise coupling constants were measured directly from the spectra and converted to millitesla using the Frémy's salt calibration. g -Values were calculated from the value of the magnetic field intensity at the centre of the spectrum, H_c , according to the resonance equation

$$h\nu_o = g\beta_E H_c \quad (\text{page 22})$$

4.1.3 Light Source

The most frequently used lamp was a Philips CSX 900W Xe - Hg point source lamp mounted in a Zeiss-Ikon Xenoblock III unit of the type described in detail by Davidson and Wilson.¹⁹⁵ This was itself mounted in an aluminium housing with a cooling fan and ozone extraction port. The output which was focused by means of a paraboloidal mirror to a spot approximately 3 cm in diameter at the position of the sample cell, passed through two optically flat silica windows between which water was circulated. Usually a Chance-Pilkington OX7 filter (which has $>95\%$ transmission between 230 nm and 405 nm but which removes much of the heat) was immersed in the water. The experiments with

aldehydes were conducted using a filter transmitting only wavelengths greater than 300 nm to prevent direct photolysis of the substrates.

Occasionally a less powerful high pressure Hg compact arc lamp (Hanovia Limited, 100 W), focused by means of a quartz lens, was used for photolysis of frozen samples. This lamp emits 50% of its energy between 290 nm and 360 nm.

4.1.4 Preparation and Examination of Frozen Samples

The "matrix-isolation" technique involves the trapping of reactive species in an inert solid and subsequent examination by ultraviolet, infrared or e.s.r. spectroscopy or other techniques, and is particularly suitable for the present work where the frozen organic substrate also serves as the matrix. Methyl radicals produced in *t*-butanol at 77 K and which disappear to an extent of only 30% in 27 hours¹⁹⁶ are evidence of the effectiveness of this trapping technique. The matrix isolation/e.s.r. method has previously been used extensively for studying such reactions as photo-oxidation by Pb(IV),¹⁹⁷ irradiation of organic compounds with electrons,¹⁹⁸ X-rays^{198,199} and γ -rays¹⁹⁹⁻²⁰² and reactions of organic compounds with $\dot{\text{O}}\text{H}$ radicals²⁰³ and Na atoms.^{204,205}

An ingenious extension of the isolation technique involves the trapping of radicals in matrices of camphane or adamantane^{206,207} which have large voids in which the radicals can rotate relatively freely, producing isotropic e.s.r. signals.

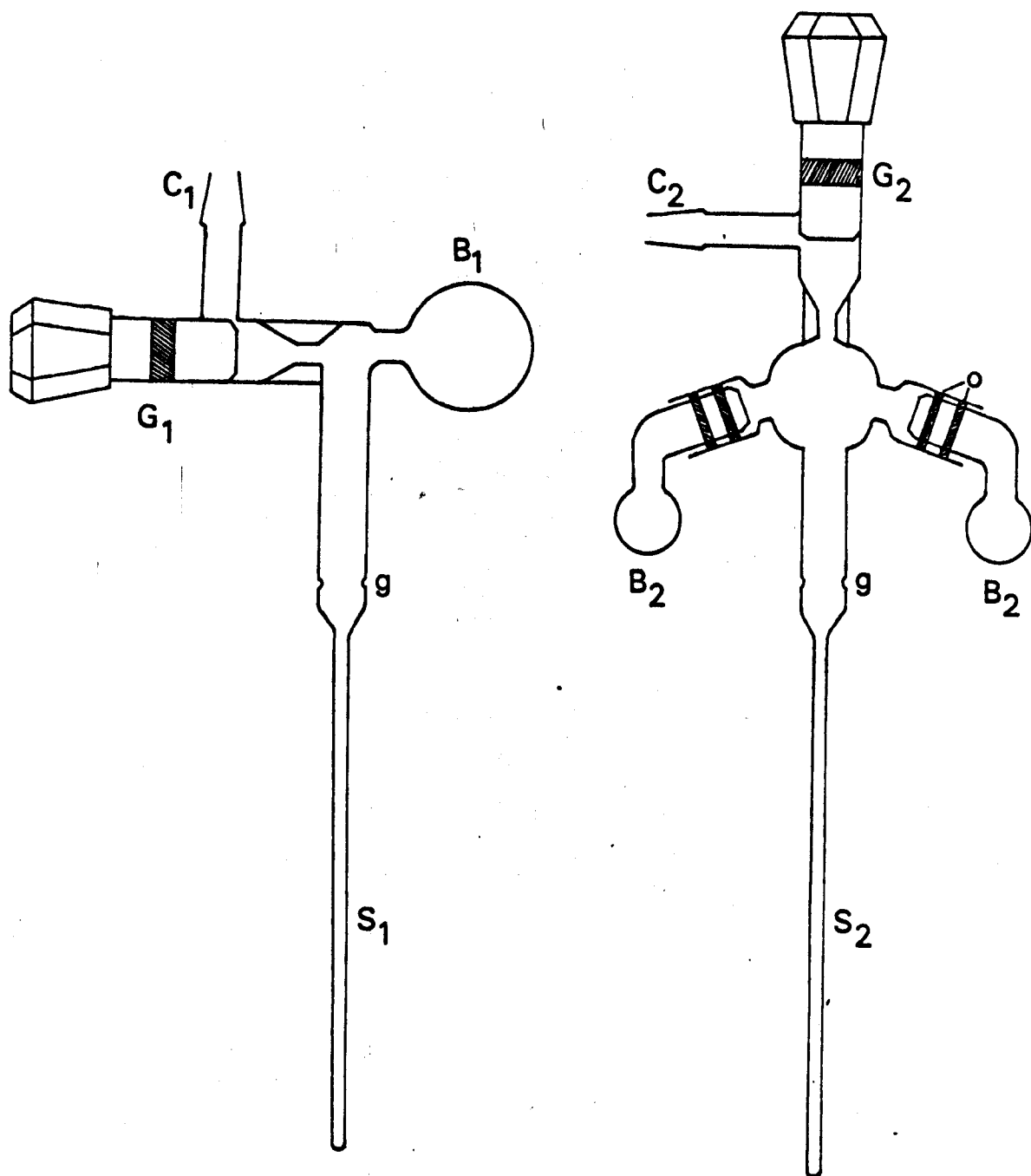
It was necessary to degas every sample prior to photolysis in order to prevent the formation of peroxy radicals by reaction between dissolved oxygen and the photochemically produced radicals (especially when the matrices became "soft" on warming). This was achieved by the use of the cells illustrated in figure 4. Normally the single-bulb cell was used; a sample ($\sim 1 \text{ cm}^3$) of uranyl perchlorate in either neat organic liquid or in an organic-water mixture was placed in the bulb (B_1) and the cell was connected via the B10 cone (C_1) to a high-vacuum line. The sample was degassed by three freeze-pump-thaw cycles after which the stopcock (G_1) was closed, the cell removed from the vacuum line and the sample shaken into the e.s.r. tube (S_1) and frozen in liquid nitrogen, being then ready for photolysis. Occasionally a substrate was encountered that reacted thermally with U(VI) at an appreciable rate or that caused a precipitate to appear gradually. In these cases the two-bulb cell was used and separate aqueous solutions of uranyl perchlorate and organic compound were degassed

FIGURE 4

Cells for degassing and photo-irradiation of frozen samples.

Key

- B_1 and B_2 - sample bulbs
- C_1 and C_2 - B10 cones
- G_1 and G_2 - greaseless stopcocks
- S_1 and S_2 - spectro-sil sample tubes
- g - graded seal
- o - Viton-A "O" ring



in the two bulbs (B_2). Immediately prior to freezing, the two reactants were mixed together vigorously and shaken into the sample tube (S_2).

Solutions were usually of two types, prepared as follows :

Method A - Uranyl perchlorate was dissolved to a concentration of 0.05 to 0.10 mol dm^{-3} in neat organic liquid.

Method B - Uranyl perchlorate was dissolved to a concentration of $\sim 0.1 \text{ mol dm}^{-3}$ in a strong aqueous solution of the substrate ($\sim 70\%$ saturated).

After being transferred to the cavity of the spectrometer, the samples were photolysed; glassy samples normally required ~ 10 s irradiation with the large lamp but opaque, polycrystalline samples needed up to 60 s photolysis before radicals were detectable in appreciable quantities. These times were increased ten-fold when the small lamp was used.

After the spectrum at 77 K had been recorded, the samples were warmed slowly with the illumination off and in several cases the occurrence of secondary reactions was observed. Any suspicion of direct photolysis of the substrate was investigated by irradiation of a sample containing no U(VI).

4.1.5 Preparation and Examination of Samples in the Liquid Phase

The study of liquid-phase photoreactions of the uranyl ion necessitated the use of a (slow) flow system to prevent exhaustion of oxidant and to minimise the effects of secondary reactions. It is also advantageous to reduce the rate of reaction of any radicals produced and to achieve this a low-temperature flow system was used. At the temperatures employed the samples became highly viscous and it was necessary to use mechanically driven syringes to effect the flow.

The motor drive unit devised by Dr. D. L. Greatorrex and described in detail elsewhere¹⁹⁴ was capable of driving two 30 ml glass syringes via a planet-type gearbox at speeds corresponding to flow rates of 0.5 to 15 cm^3 per minute. Early experiments used the glass capillary feed lines and e.s.r. cell described by Greatorrex,¹⁹⁴ but it was found that the glass tubing did not allow sufficient flexibility in the system, resulting in frequent breakage and that ice often formed on the outside surface of the cell in the spectrometer cavity causing serious loss of light at the sample. A new, vacuum jacketed cell and a flexible p.t.f.e. feed line were therefore designed and these are illustrated in

FIGURE 5

Apparatus for photo-irradiation of liquids at low temperature in the cavity of the e.s.r. spectrometer.

Key

- | | |
|-------------|--|
| B | - ball and feed line constructed from p.t.f.e. |
| C | - indented cooling column |
| T | - platinum resistance thermometer |
| TC1 and TC2 | - thermocouples |
| W | - thin window for irradiation of sample |
| e | - evacuated space |
| g | - graded seal; apparatus constructed entirely of silica above this point and entirely of pyrex below |

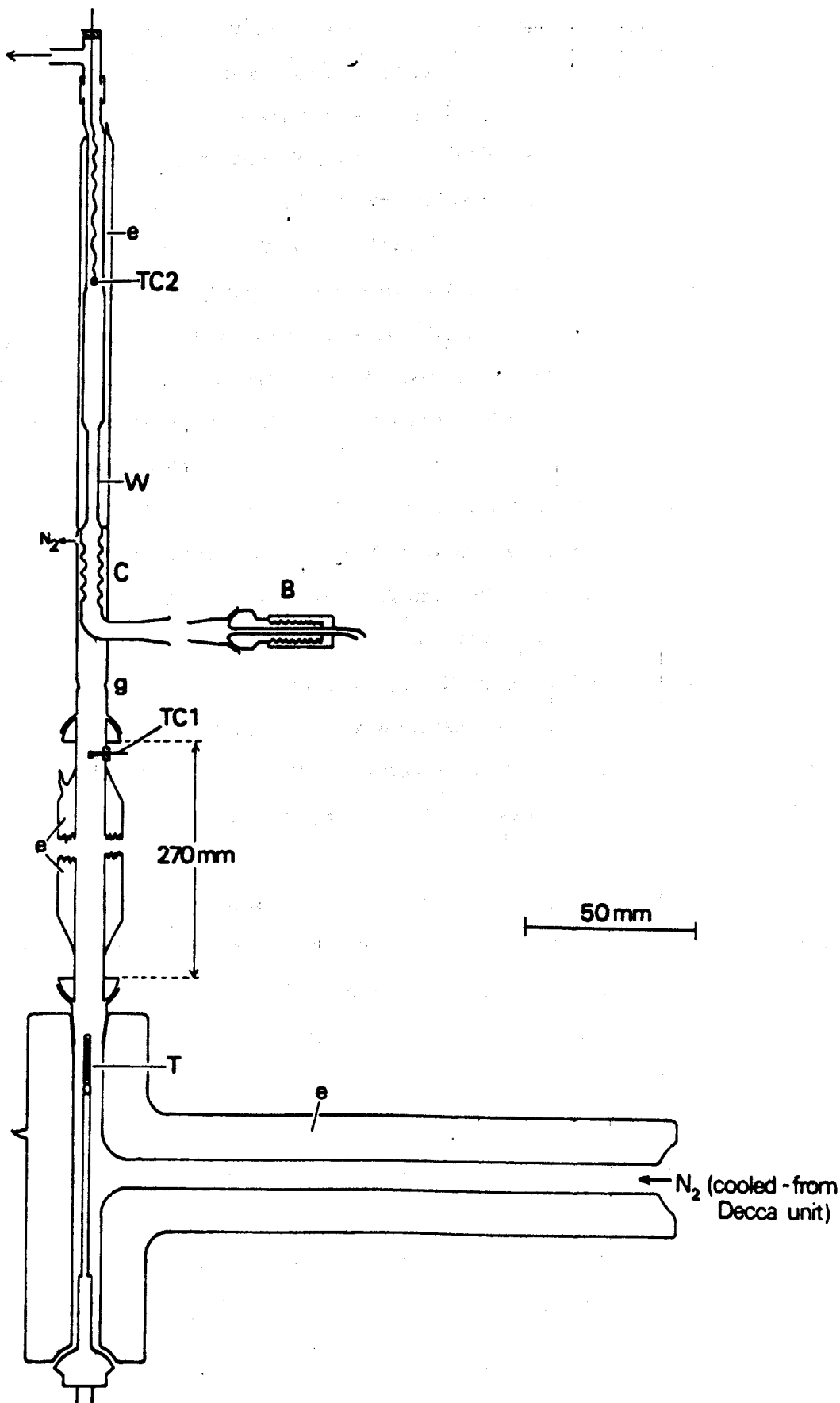


figure 5 together with the cooling unit which is similar to the Decca variable-temperature insert and which uses the same temperature controller.

The main difficulty encountered in the liquid-phase work was the absence of a solvent capable of dissolving both uranyl salts and the organic compound but remaining stable under photolysis (methanol has proved to be very useful in this direction for the study of Ce(IV) photo-oxidations in the flow system).¹⁹⁴ Water fulfils the required conditions and several compounds were examined in this medium but the high dielectric constant necessitated the use of an unusually thin, flat portion of the e. s. r. cell (to reduce loss of microwave power) and radicals could not be produced in sufficient concentrations for detection. Samples almost invariably consisted, therefore, of solutions of uranyl perchlorate ($\sim 5 \times 10^{-3}$ mol dm^{-3}) in neat substrate.

Prior to photolysis, solutions were degassed in the apparatus shown in figure 6. Nitrogen was passed into the sample via the U tube (U), which contained glass wool to trap solid impurities, and the prebubbler (P) which contained a small amount of the sample solution in order to saturate the gas with vapour and prevent loss from the main bubbler. During the degassing operation solution was forced into the syringe (S) by opening tap (G) and closing tap (T) and out again by opening tap (T). After ~ 15 minutes, two syringes were filled and capped by a sealed-off greaseless ball-joint socket while being fitted into the drive unit.

The gas temperature as read by thermocouple TC1 (figure 5) was adjusted to $\sim 1 \text{ K}^{\circ}$ above the freezing point of the solution and the system was allowed to equilibrate for 5 minutes, after which time the cavity was tuned and the sample photolysed. It was found that the temperature of the photolyte, as read by TC2 to $\pm 0.5 \text{ K}^{\circ}$, was usually $\sim 30 \text{ K}^{\circ}$ higher than the gas temperature when this was low ($\sim 180 \text{ K}$) and $\sim 10 \text{ K}^{\circ}$ higher at room temperature. The solution flow rate was adjusted to give maximum signal strength and was normally 2 cm^3 per minute.

4.2 Flash Photolysis

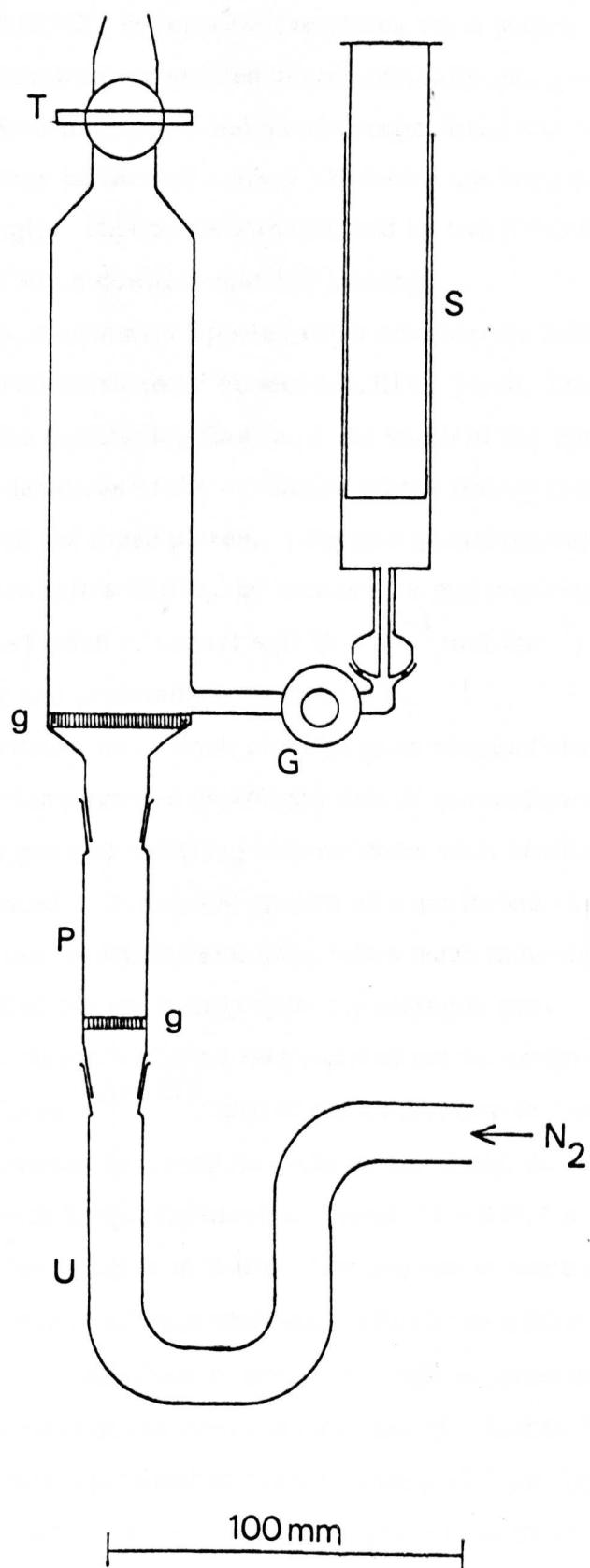
It was found in early experiments that degassing of samples had no effect on the intensity or lifetime of the transient absorptions studied in this work; in this connection the presence of dissolved oxygen is known to have no effect on the luminescence of aqueous uranyl salts^{82, 83, 151, 208} and therefore the samples examined here were used without de-aeration.

FIGURE 6

Apparatus for deoxygenation of liquid samples prior to photolysis
in the flow system

Key

- G - greaseless stopcock
- P - prebubbler
- S - syringe
- T - ground glass tap
- U - U-tube
- g - glass sinter



The microsecond apparatus was a model FP-1D (Northern Precision Company Limited) and transients were either recorded photographically by a second flash on Ilford HP 3 hypersensitive plates via a quartz spectrograph (Hilger and Watts Limited) or studied photometrically using a monitoring lamp, monochromator, photomultiplier and oscilloscope fitted with a "Polaroid" camera. The spectrograph was calibrated using a Cd discharge lamp and all spectra were corrected accordingly. Photolysis was effected by two Kr discharge tubes producing a flash typically of 30 μ s duration and 550 J energy.

The spectra of transient species were constructed from the photographic plates using a microdensitometer (model Mk.III C, Joyce, Loeb and Company Ltd.) and the energy of the monitoring flash and slit width of the spectrograph were chosen so that the optical densities of the developed plates fell on the linear portion of the characteristic curve for those plates. Lifetime quenching experiments were performed by the systematic addition, by means of a microsyringe, of small volumes of quencher to the solution of uranyl salt (5×10^{-3} mol dm⁻³) in the cell, followed by vigorous mixing and photometric examination.

Certain solutions were flash photolysed at reduced temperatures and for this purpose a low-temperature photolysis cell of conventional design was used, cooled by nitrogen gas and featuring end-windows each consisting of a pair of silica plates separated by evacuated spaces of 2 cm in one case and 15 cm in the other. The whole cell assembly and flash tubes were mounted in a thin polythene bag which was flushed out constantly with dry nitrogen gas.

Nanosecond flash photolysis was carried out on equipment at the Royal Institution, London^{209,210} and at the University of East Anglia, Norwich (equipment manufactured by Laser Associates Limited), both of which used a pulsed ruby laser with frequency-doubled output ($\lambda = 347.1$ nm). Solutions of uranyl perchlorate and nitrate in doubly distilled water were used for all the experiments but it was found that whereas a uranyl ion concentration of 2×10^{-2} mol dm⁻³ was sufficient to produce a high concentration of transient species on the apparatus at the Royal Institution, this had to be increased to 0.25 mol dm⁻³ for the equipment at the University of East Anglia (due to the right angled nature of the monitoring system for the latter equipment; see section 3.2). Control experiments using a range of uranyl ion concentrations, however, indicated that there was no self-quenching evident at the higher

concentration.

Quenching experiments were performed in the same manner as described for the microsecond experiments but the relatively small volume of sample solution needed for the nanosecond equipment necessitated the dilution of the more efficient quenchers with water to avoid the inaccuracies associated with measuring excessively small volumes with the microsyringe.

Rate constants for the decay traces produced in both microsecond and nanosecond photolysis experiments were calculated by measuring trace height and time coordinates for several points (typically fifteen) spanning at least $2\frac{1}{2}$ half-lives and processing these with the computer program FPDATA (a slight modification of the program SFDATA written by Dr. D. J. Benton²¹¹ and Dr. P. Moore²¹²). A feature of this program, which is applicable only to first-order reactions, is the capability to calculate rate constants without information about the trace height at infinite time after excitation. Information is given in the form of a graph of log (optical density) against time and a typical output is shown in figure 22 section 6.2. All linear plots (e.g. $k_{\text{pseudo 1st order}}$ against [quencher]) were obtained using the weighted linear least squares analysis program WLLSA written by Dr. P. Moore.

4.3 Fluorimetry and Fluorometry

Luminescence intensity measurements were made on solutions of uranyl perchlorate in doubly distilled water (without de-aeration) in a Farrand Spectrofluorometer Mk.I (Farrand Optical Company Inc., New York). A uranyl ion concentration of 0.1 mol dm^{-3} was found to be optimal, corresponding to complete light absorption and minimal deactivation reactions (e.g. self-quenching). An excitation wavelength of 420 nm was used for all experiments and the luminescence intensity was measured at 514 nm from the spectrum displayed on a chart recorder. Examination of the quenching effects of various compounds was carried out in the same way as in the nanosecond flash photolysis experiments.

As the fluorimeter was not of the double-beam type it was necessary to perform a calibration between every reading using a standard fluorescent block. In addition, at low emission intensities, scattered light at 514 nm could not be neglected and correction was made for this using a blank sample containing only water. Graphs of I_f / I_{f_0} against [quencher] were plotted using the program WLLSA. Although random variations in I_f could be tolerated, it was necessary

for I_{f_0} to be as accurate as possible and therefore the average value obtained from four or five scans of the spectrum was used.

Luminescence lifetimes were measured on the single-photon counting apparatus built by Dr. T. F. Palmer at the University of Nottingham. Samples consisted of uranyl perchlorate at a concentration of $0.114 \text{ mol dm}^{-3}$ in doubly distilled water and quenching effects were studied in the same manner as for the nanosecond flash photolysis and the luminescence intensity quenching experiments. Results for each lifetime measurement were output in the form of 512 numbers corresponding to relative emission intensities at various times after excitation. These were punched on paper tape and processed by the program PTPREP (to subtract the base noise level from the decay trace) and then by the library program AUTOPLOT which gave a plot of log (emission intensity) against time; a typical output is exhibited in figure 23 section 6.2. The required portion of this plot was then selected (rejecting the curvature apparent at the beginning and end of the graph corresponding to scattered excitation light and low luminescence intensity respectively) and these points were processed by program WLLSA 2 (a version of WLLSA modified to ignore the rejected points) to provide a value for the decay rate constant.

4.4 Materials

Unless otherwise stated, all the substrates were of the best quality available and used without further purification.

Uranyl Perchlorate - supplied by Alfa Inorganics

Uranyl Nitrate - B.D.H. Analar grade

Uranyl Sulphate - B.D.H. Reagent grade

Propan-2-ol, Cyclohexanol and Cyclopropanecarboxylic Acid - these were fractionally distilled under reduced pressure

Oxalic and 2-Hydroxyisobutyric Acids - these compounds were recrystallised from water

Acrylic and Methacrylic Acids - inhibitors were removed by vacuum distillation through a column packed with copper gauze^{213a}

2,2,4,4-Tetradeuteropentan-3-one - this was prepared by refluxing a mixture of potassium bicarbonate and diethyl ketone for 24 hours with four successive quantities of D_2O , extracting with ether and fractionally distilling the product.^{213b}

Methanol - spectroscopic grade was used for quenching experiments, otherwise analytical reagent grade was used.

Deuterated Compounds - these were obtained from Ciba and were of > 99% purity.

CHAPTER 5

ELECTRON SPIN RESONANCE RESULTS

5. ELECTRON SPIN RESONANCE RESULTS

5.1 Solid State Studies

Unless otherwise stated all results in this section refer to photolysis at 77 K. Certain experiments were performed by Dr. D. L. Greatorex and are marked thus †.

5.1.1 Primary and Secondary Alcohols (by Method A)

Methanol

A distorted, but recognisable triplet with $a_H = 1.90 \pm 0.20$ mT was obtained, similar to that observed during Ce(IV) photo-oxidation and assigned to $\dot{C}H_2OH$ ¹⁹⁶ for which a coupling constant of 1.9 mT has previously been reported in the solid state.²⁰³

Ethanol †

A five-line binomial spectrum was given with $a_H = 2.10$ mT closely similar to that obtained on photolysis of ethanolic solutions of Ce(IV)¹⁹⁶ and hydrogen peroxide²⁰³ and due to $CH_3\dot{C}HOH$.

Propan-1-ol

The spectrum of the ethyl radical with $a_{CH_3}^H = 2.63 \pm 0.03$ mT, $a_{CH_2}^H = 2.00 \pm 0.03$ mT was produced at 77 K (figure 7a) but disappeared upon warming to 90 K, producing a complex spectrum.

Propan-2-ol †

The spectrum of $\dot{C}H_3$ was the only absorption.

Butan-2-ol

In this case only \dot{C}_2H_5 was produced with $a_{CH_3}^H = 2.67$ mT, $a_{CH_2}^H = 2.10$ mT.

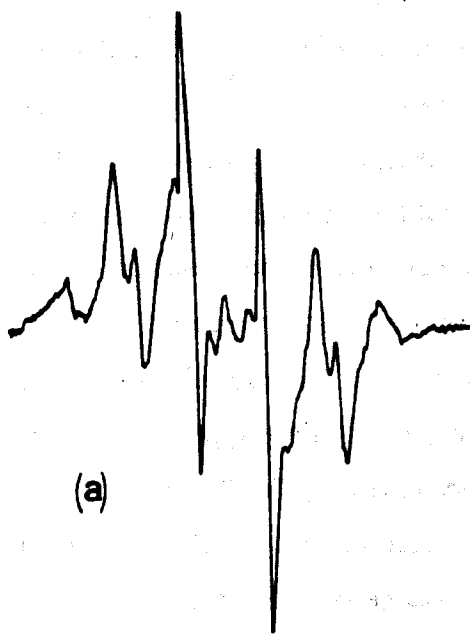
Pentan-1-ol and Hexan-1-ol

These two compounds exhibited similar spectra, the former being analysed as $a_{H(2)} = 2.20 \pm 0.12$ mT, $a_{H(1)} = 6.50 \pm 0.30$ mT (figure 7b) and the latter (only observed at 90 K) as $a_{H(1)} = 1.71 \pm 0.11$ mT, $a_{H(1)} = 3.48 \pm 0.17$ mT, $a_{H(1)} = 5.65 \pm 0.30$ mT (figure 7c). Closely similar spectra, which have been obtained during both Ce(IV) photo-oxidation of butan-1-ol and pentan-1-ol¹⁹⁶ and γ radiolysis of solid hexan-1-ol,¹⁹⁸ have been assigned to radicals of the type $\dot{R}CHOH$. This assignment can be confirmed in the present cases and information about the orientations of the frozen radicals can be deduced as follows :

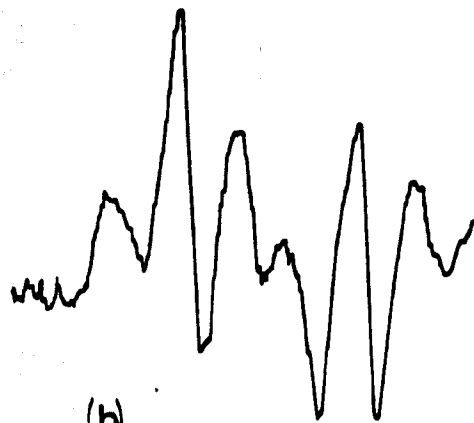
FIGURE 7

E.s.r. spectra obtained upon photo-oxidation of alcohols
by uranyl perchlorate

- (a) Propan-1-ol at 77 K
- (b) Pentan-1-ol at 77 K
- (c) Hexan-1-ol at 90 K
- (d) 2-Methylbutan-2-ol (following warming to 207 K)
- (e) 3-Methylhexan-3-ol at 77 K



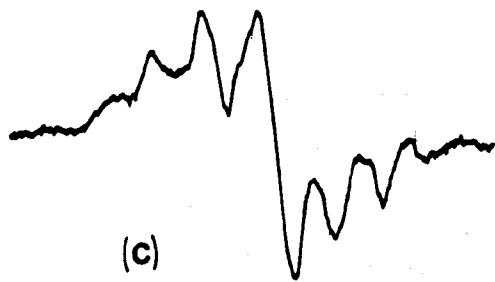
(a)



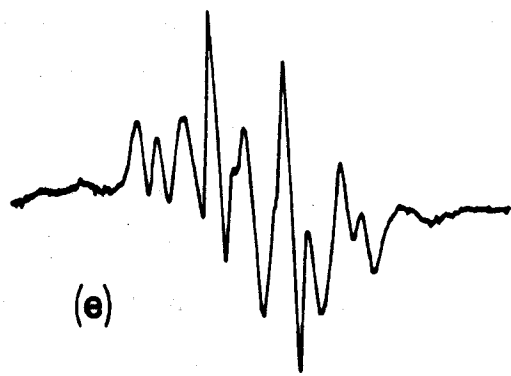
(b)



(d)

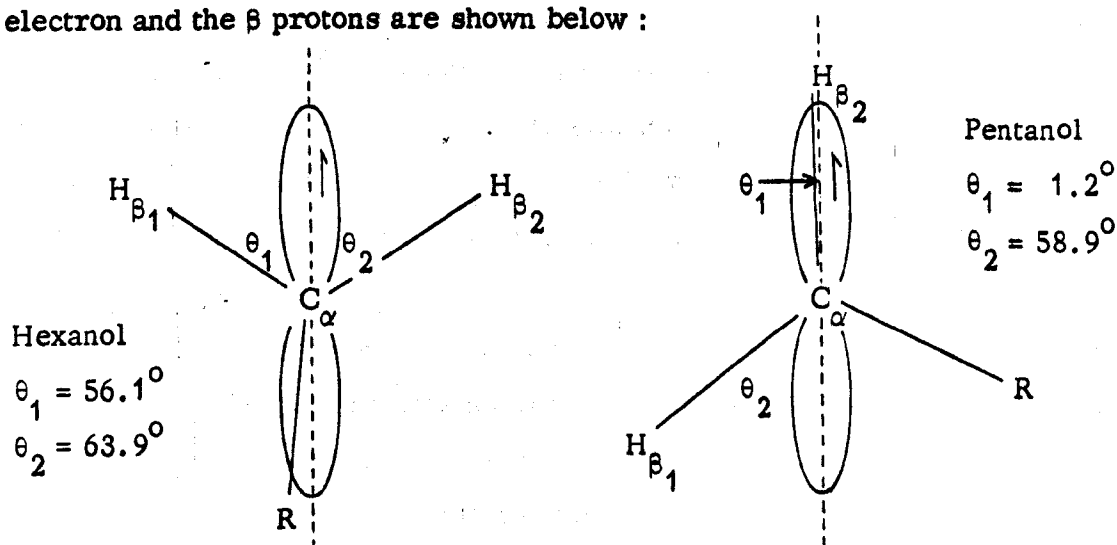


(c)



(e)

ρ_C and Q_{CH} (as in equation (3.10)) are approximately constant in each case of radicals of type $R\dot{C}H_2$, $R_1R_2\dot{C}H$ and $R_1R_2R_3\dot{C}$, irrespective of the lengths of substituents R ¹⁸⁵ and therefore, by analogy with the coupling in the radical $CH_3\dot{C}HOH$ (v. s.), the splittings 2.20 mT and 1.71 mT are assigned to the α protons in the pentanol and hexanol radicals respectively. Applying equation (3.13) to the hexanol radical and assuming the coupling constants of 3.48 mT and 5.65 mT to arise from the β protons and that the dihedral angle between these protons is the normal 120° , a value for $Q_{CCH}\rho_C$ of 6.31 is obtained. Using this value in the application of equation (3.13) to the pentanol radical, one β coupling constant of 2.2 mT predicts the other to be 6.3 mT, in good agreement with the observed value. The dihedral angles between the p orbital bearing the unpaired electron and the β protons are shown below :



Pentan-3-ol

At 77 K a broad 1:3:3:1 spectrum was produced with $a_H = 2.66$ mT which is assigned to the ethyl radical, the broadness of the lines obscuring coupling from the methylene protons. At 175 K, however, a well resolved spectrum of \dot{C}_2H_5 was obtained ($a_{CH_3}^H = 2.67$ mT, $a_{CH_2}^H = 2.13$ mT).

2-Phenylethanol[†]

The e.s.r. spectrum of benzyl radical was produced, behaviour matching that found using $Ce(IV)$ as photo-oxidant.¹⁹⁶ It is possible that the primary reaction is abstraction of the hydroxylic hydrogen atom as the 2-phenylethoxy radical is known to fragment to formaldehyde and the benzyl radical.²¹⁴

5.1.2 Tertiary Alcohols (by Method A)

2-Methylpropan-2-ol (t-butanol)[†]

At 77 K methyl radicals were produced but warming to 120 K caused these

to decay and a new triplet spectrum ($a_H = 2.17 \pm 0.05$ mT) of 1:2:1 character to appear. Photolysis of a fresh sample at 245 K yielded only the triplet for which the radical $\dot{C}H_2C(CH_3)_2OH$ is most probably responsible.

2-Methylbutan-2-ol (t-amyl alcohol)

At 77 K a spectrum of ethyl radical was given but on warming to 180 K a five-line binomial spectrum was produced which, at higher temperatures (e.g. 207 K, figure 7d) became more highly resolved, yielding $a_{H(1)} = 1.99 \pm 0.06$ mT, $a_{H(3)} = 2.43 \pm 0.06$ mT. The secondary radical is believed to be $CH_3\dot{C}HC(CH_3)_2OH$.

2,3-Dimethylbutan-2-ol

A weak six-line spectrum was obtained of approximately binomial intensity distribution and with $a_H = 2.34 \pm 0.07$ mT, probably arising from $(CH_3)_2\dot{C}H$ which has been produced in the solid state at 77 K by γ radiolysis of isobutyric acid ($a_H = 2.45 \pm 0.1$ mT)²⁰² and of isopropyl halides ($a_H = 2.49$ to 2.64 mT).²¹⁵ Warming the sample resulted in replacement of the spectrum by another of five (or possibly seven) lines with $a_H = 2.01 \pm 0.06$ mT, probably originating in attack of the isopropyl radical upon parent molecule to give $(CH_3)_2\dot{C}C(CH_3)_2OH$.

2,3-Dimethylpentan-2-ol

At 77 K a complex spectrum, including that due to $\dot{C}H_3$, was produced, but on warming to 117 K a six-line spectrum with $a_H = 1.36 \pm 0.08$ mT appeared. The number of lines conforms with the radical $CH_3CH_2\dot{C}(CH_3)C(CH_3)_2OH$ produced by attack of $\dot{C}H_3$ on substrate, but the coupling is very low for a radical of this type.

3-Methylhexan-3-ol

Whilst at 77 K a mixture of \dot{C}_2H_5 and a five-line species was apparent (figure 7e), warming to 127 K left only the latter, with $a_H = 2.14 \pm 0.03$ mT, which is ascribed to the radical $CH_3(CH_2)_2C(CH_3)(OH)\dot{C}HCH_3$ formed by attack of \dot{C}_2H_5 upon substrate.

3-Ethylpentan-3-ol

The ethyl radical was produced at 77 K and warming caused this to decay and a broad unanalysable spectrum to appear.

5.1.3 Carboxylic Acids (by Method A)

Formic Acid

A singlet was produced exhibiting g-tensor anisotropy with $g_1 = 2.0047 \pm 0.0005$, $g_2 = 2.0015 \pm 0.0003$ and $g_3 = 1.9951 \pm 0.0005$. This is assigned to the $\dot{C}O_2H$ radical, g-values being in good agreement with those previously reported for

this radical,²¹⁶⁻²¹⁸

Acetic Acid

Two radicals were obtained at 77 K in approximately equal quantities, manifested by a sharp four-line spectrum with $a_H = 2.26 \pm 0.02$ mT, clearly due to the methyl radical and a distorted 1:2:1 triplet with $a_H = 2.15 \pm 0.06$ mT for one of the anisotropic coupling constants. The latter spectrum, which was the sole survivor at 140 K (figure 8a), is assigned to the radical $\dot{C}H_2CO_2H$ by comparison with the closely similar spectra obtained by electron-irradiation of malonic acid²¹⁹ and by γ -radiolysis of acetic acid at 77 K ($a_{H(\perp)} = 2.1 \pm 0.1$ mT, $a_{H(\parallel)} = 3.1 \pm 0.1$ mT).²⁰¹

Propionic Acid

A five-line spectrum of binomial intensity distribution was obtained (figure 8b) with $a_H = 2.35 \pm 0.10$ mT and $g = 2.0025 \pm 0.0007$, which is attributed to the radical $CH_3\dot{C}HCO_2H$, where the difference between $a_{H(\alpha)}$ and $a_{H(\beta)}$ is masked by the line width. Coupling constants of 2.37 mT²⁰² and 2.43 mT¹⁹⁷ have been reported for this radical in the solid state.

n-Butyric Acid

This compound yielded a five-line spectrum shown in figure 8c with $a_H = 2.13 \pm 0.10$ mT and intensity distribution approximately 1:2:2:2:1. An identical spectrum ($a_H = 2.15$ mT) was obtained upon photo-oxidation of Pb(IV)n-butyrate¹⁹⁷ and this was attributed to the radical $CH_3CH_2\dot{C}HCO_2^-$. A reasonable assignment of coupling constants would be $a_{H(\alpha)} = 2.13$ mT, $a_{H(\beta_1)} = 2.13$ mT, $a_{H(\beta_2)} = \sim 4.3$ mT.

iso-Butyric Acid[†]

The seven-line spectrum of $(CH_3)_2\dot{C}CO_2H$ with $a_H = 2.05 \pm 0.10$ mT was produced. The same radical ($a_H = 2.12 \pm 0.03$ mT) has been obtained by γ -irradiation of iso-butyric acid.²⁰²

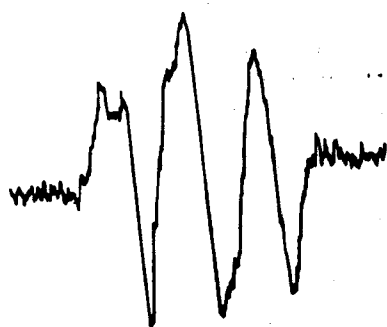
Cyclopropanecarboxylic Acid

An eight-line symmetrical spectrum, shown in figure 8d, was obtained which was not analysable in terms of two sets of two equivalent protons expected from the radical formed by abstraction of the hydrogen atom in the 1 position. It is significant that in a series of γ -irradiated carboxylic acids studied by Ayscough and Oversby,²⁰² the only spectrum not analysed was that obtained from cyclopropanecarboxylic acid and described as "complex."

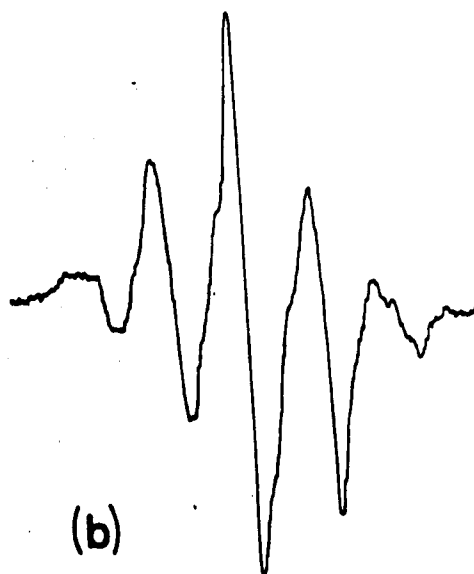
FIGURE 8

E. s. r. spectra obtained during photo-reaction between
carboxylic acids and uranyl perchlorate at 77 K

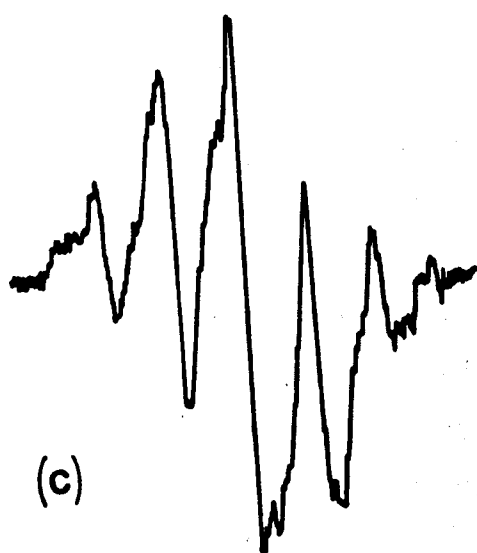
- (a) Acetic acid (following warming to 140 K)
- (b) Propionic acid
- (c) n-Butyric acid
- (d) Cyclopropanecarboxylic acid
- (e) Cyclohexanecarboxylic acid (following warming to 150 K)



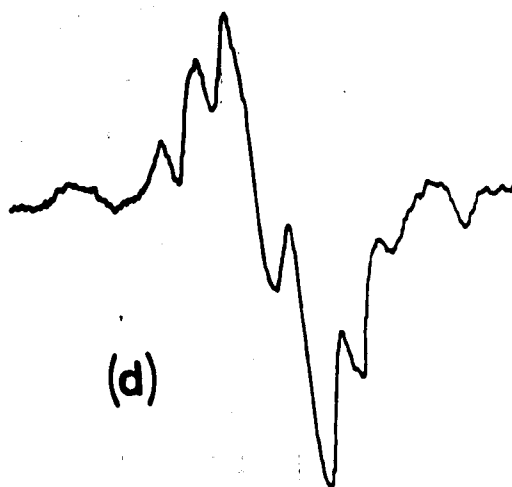
(a)



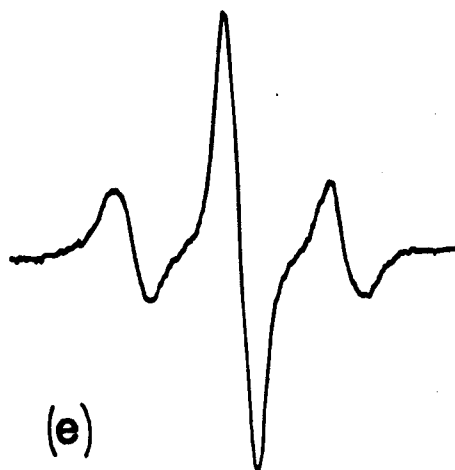
(b)



(c)



(d)

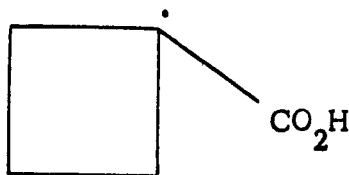


(e)

5.0mT

Cyclobutanecarboxylic Acid

The spectrum from this molecule consisted mainly of a triplet of triplets with $a_{\text{H}(2)} = 3.49 \pm 0.08$ mT and $a_{\text{H}(2)} = 2.64 \pm 0.08$ mT and is shown in figure 9 together with a computer simulation. It was found that a good fit was obtained if a minor species ($\sim 10\%$) producing a 1:2:1 triplet spectrum ($a_{\text{H}} = 4.67$ mT) was included in the simulation. The free radical responsible for the major absorption is believed to be



some support for this view coming from the production of binomial five-line spectra due to this radical, by both Ce(IV) photo-oxidation²¹⁸ and X-irradiation¹⁹⁹ of cyclobutane-1,1-dicarboxylic acid, where $a_{\text{H}(\beta)} = 3.23$ mT and 3.2 mT respectively. The cyclobutane ring is normally slightly buckled²²⁰ and a slight inequivalence of the two pairs of β protons would explain the values of $a_{\text{H}(\beta)}$ being slightly higher and slightly lower than the average value of 3.2 mT.

Cyclohexanecarboxylic Acid

At 77 K a triplet spectrum, together with a smaller species, was obtained but warming to 150 K left only the former (figure 8e) with $a_{\text{H}} = 3.29 \pm 0.05$ mT, $g = 2.0031 \pm 0.0004$, and recooling to 77 K effected no further change. The radical responsible is probably

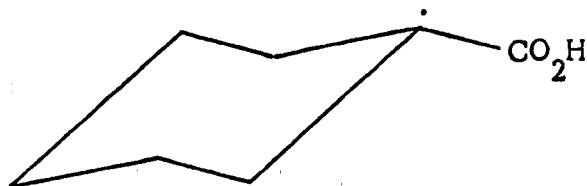


FIGURE 9

E.s.r. spectrum obtained upon photo-oxidation of
cyclobutanecarboxylic acid by uranyl perchlorate at 77 K

(a) Experimental

(b) Computer simulation



5.0mT

an identical spectrum and assignment, with $a_H = 3.35 \pm 0.10$ mT, having been offered by Heusler and Loeliger¹⁹⁷ following photolysis of the Pb(IV) salt in benzene at 77 K and subsequent warming. Leung and Hunt have made a detailed temperature study of this radical²²¹ and quote a g-factor of 2.0029 ± 0.0001 .

5.1.4 Dicarboxylic Acids (by Method B)

Oxalic Acid

A singlet was obtained with $g_1 = 2.0080$, $g_2 = 2.0046$, $g_3 = 2.0007$ (figure 10a). The averaged g-factor of 2.0044 is considerably higher than that expected from free $\dot{C}O_2H$ or $\dot{C}O_2^-$ as found in formic acid oxidation.

Malonic Acid

Comparison of this spectrum (figure 10b) with that given by acetic acid (figure 8a) shows that, in addition to the radical $\dot{C}H_2CO_2H$, characterised by a distorted triplet with $a_{H(1)} = 2.15 \pm 0.09$ mT, another radical is present producing a doublet spectrum with $a_H = 2.17 \pm 0.07$ mT. The absorption is similar to that obtained upon electron-irradiation of malonic acid at 143 K²¹⁹ and analysed as the superposition of a doublet ($a = 2.2$ mT) on a singlet or a triplet. The doublet spectrum is therefore attributed to the radical $\dot{C}H(CO_2H)_2$, for which an isotropic coupling constant of 2.14 mT has been reported in X-irradiated crystals of malonic acid.²²²

Succinic Acid

The behaviour exactly parallels that found for Ce(IV) photo-oxidation,²¹⁸ namely, production of a 77 K spectrum of six lines (total width 8.8 mT) changing at 150 K to a five-line spectrum in accord with the onset of rotation in the radical $\dot{C}H_2CH_2CO_2H$.

Maleic Acid

Only at a high temperature (108 K) was any signal detected upon photolysis. This was the doublet shown in figure 10c with $a_H = 2.25 \pm 0.03$ mT, $g = 2.0025 \pm 0.0005$, assigned to the radical $HO_2\dot{C}C \equiv CHCO_2H$. The trans isomer of maleic acid (fumaric acid) produced no signal.

5.1.5 Substituted Carboxylic Acids

Glycolic Acid - Sodium Salt (Method B)

A doublet spectrum shown in figure 11a was obtained with $a_H = 2.10 \pm 0.05$ mT and this is attributed to $HO\dot{C}HCO_2^-$. A doublet with an isotropic coupling constant of 2.04 mT has been observed for this radical in a γ -irradiated single crystal of

FIGURE 10

E.s.r. spectra obtained during photo-reaction between
dicarboxylic acids and uranyl perchlorate

- (a) Oxalic acid at 77 K
- (b) Malonic acid at 77 K
- (c) Maleic acid at 108 K

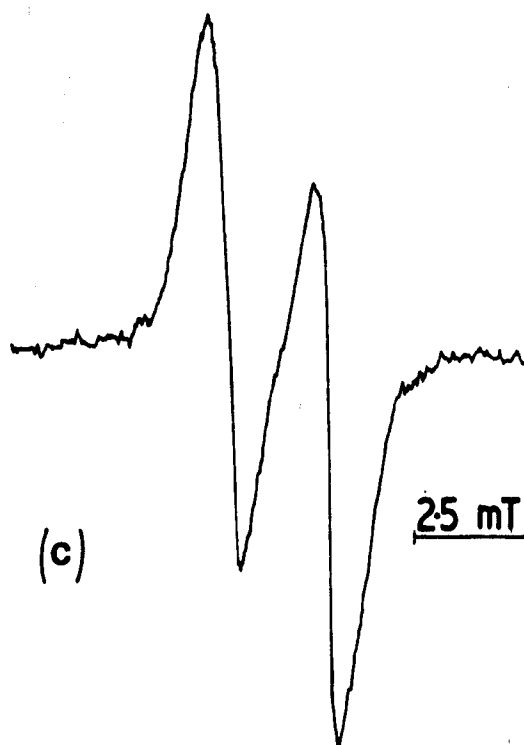
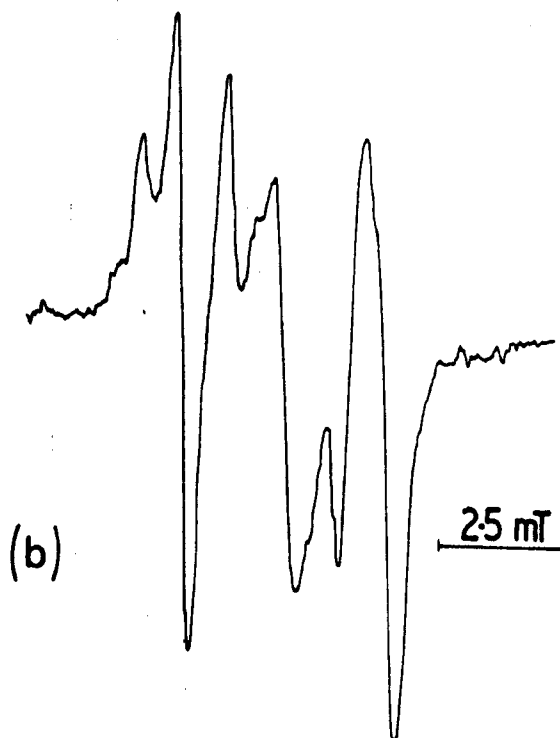
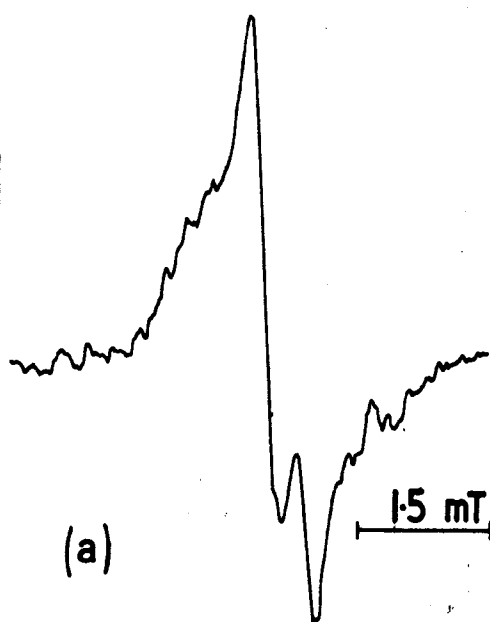
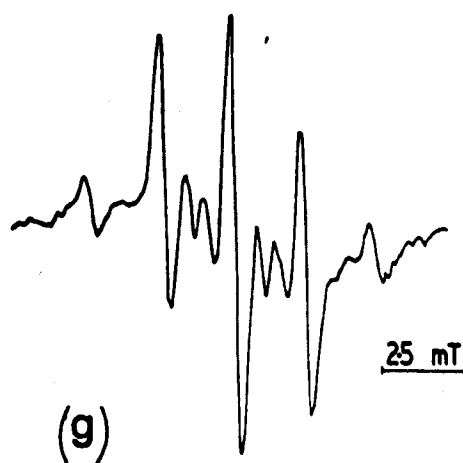
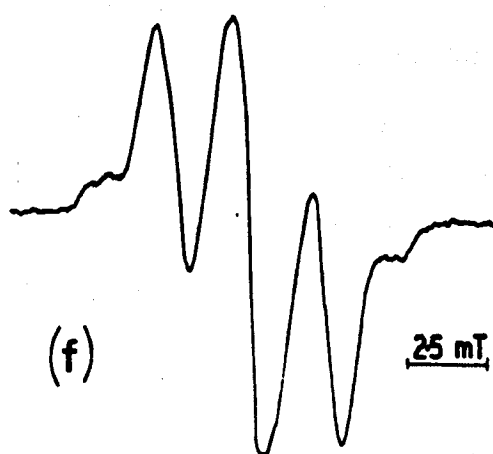
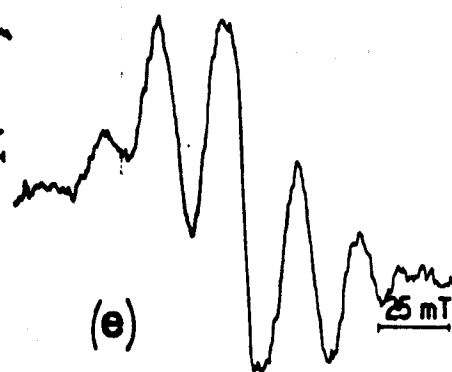
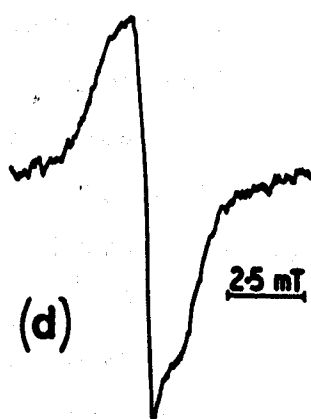
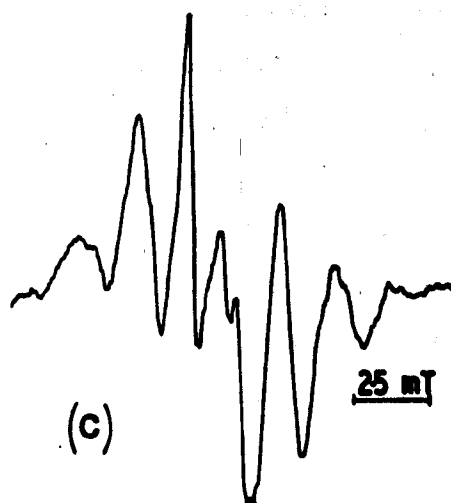
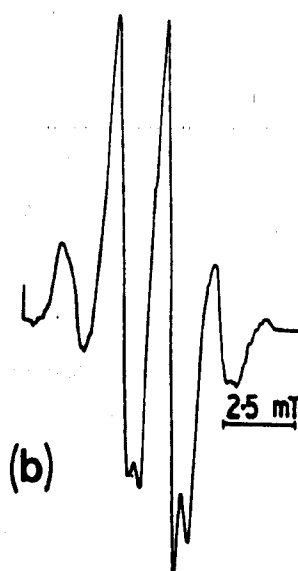
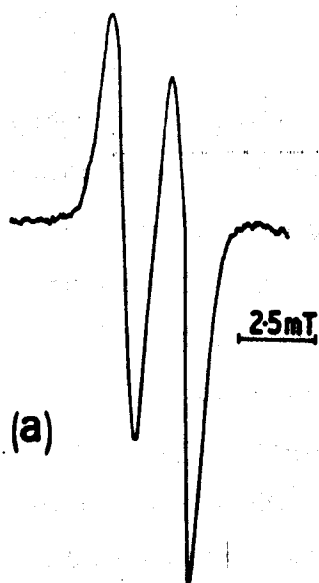


FIGURE 11

E.s.r. spectra obtained during photo-reaction between substituted carboxylic acids and uranyl perchlorate

- (a) Glycolic acid at 77 K
- (b) Lactic acid (pH 1) at 77 K
- (c) Lactic acid (pH 7) at 77 K
- (d) Tartaric acid at 77 K
- (e) Acrylic acid at 165 K
- (f) Acrylic acid at 190 K following warming from 165 K
- (g) Methacrylic acid at 165 K



the acid.²²³

2-Hydroxyisobutyric Acid (Method B)

Photolysis at 77 K produced a singlet ($g = 2.0028 \pm 0.0004$) as the major absorption. A sample adjusted to pH 5.5 with NaOH, however, gave methyl radicals together with a spectrum of intensity distribution 1 : 5 : 1 and $a_H \sim 2.33$ mT. The latter, which was the sole survivor at 168 K, is centred at $g = 2.0023 \pm 0.0005$ and may consist of a binomial triplet and superimposed singlet, a candidate for the radical producing the triplet being $\dot{C}H_2C(CH_3)(OH)CO_2H$ formed by attack of $\dot{C}H_3$ upon parent compound.

Lactic Acid (Sample preparation detailed below)

As a consequence of the report by Sakuraba and Matsushima¹⁴² of different pathways for the photo-oxidation of lactic acid by U(VI) at pH values above and below 3.5, aqueous samples of lactic acid ($\sim 3 \text{ mol dm}^{-3}$) were investigated at pH 1 and 7, pH being adjusted with sodium hydroxide and perchloric acid. The uranyl perchlorate concentration was $\sim 0.1 \text{ mol dm}^{-3}$.

At pH 1 photolysis gave a 1 : 3 : 3 : 1 quartet with $a_H = 1.71 \pm 0.10$ mT, $g = 2.0030 \pm 0.0006$ (figure 11b) probably arising from $CH_3\dot{C}(OH)CO_2H$, for which a solution spectrum gives $a_{CH_3}^H = 1.71$ mT.²²⁴ At pH 7 a mixture of radicals was observed comprising the quartet found at pH 1 and a binomial quintet with $a_H = 2.15 \pm 0.11$ mT, $g = 2.0024 \pm 0.0006$. The latter is similar to the spectra produced from ethanol by Ce(IV) photo-oxidation ($a_H = 2.21$ mT)¹⁹⁶ and $\dot{O}H$ attack ($a_H = 2.2$ mT)²⁰³ and is consequently assigned to the radical $CH_3\dot{C}HOH$ (figure 11c).

Tartaric Acid (Method B)

A broad singlet, possibly due to $HO_2\dot{C}C(OH)CH(OH)CO_2H$, was obtained (figure 11d). β proton coupling constants for this radical in the liquid state²²⁴ and for $DO\dot{C}(CO_2D)CH(OD)CO_2D$ in the solid state²²⁵ are low (0.39 mT and 0.25 mT respectively). The hydroxylic proton coupling is also small (0.16 mT),²²⁴ and these couplings may be masked by the large line-width (~ 2.0 mT).

Chloroacetic Acid (Method B)

An intense, complex spectrum from a mixture of radicals was produced.

Trifluoroacetic Acid (Method A)

Irradiation at 77 K produced the immediate appearance of a spectrum of ~ 27 mT width which was stable up to 160 K and very similar to that obtained by

Loeliger²²⁶ upon photolysis of Pb(IV) trifluoroacetate in hexafluoroethane at 77 K and assigned to $\dot{\text{C}}\text{F}_3$.

Acrylic Acid (Method B but with separate degassing of substrate and oxidant to avoid polymerization)

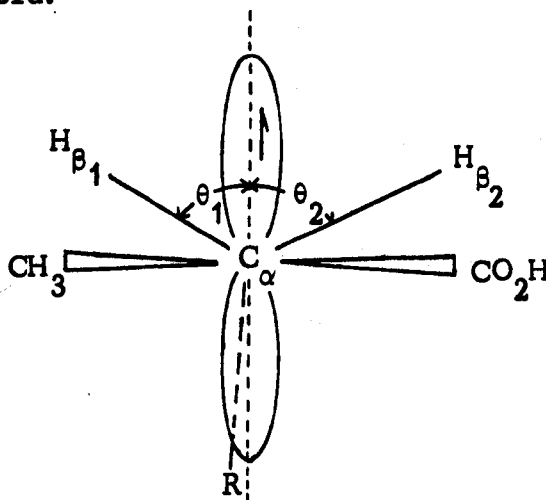
Irradiation at 77 K gave no spectrum but at 165 K a five-line spectrum of approximately binomial intensity distribution but with lines of unequal separation was obtained (figure 11e). Warming to 190 K resulted in the outermost lines almost disappearing to leave a triplet with $a_{\text{H}} = 2.34 \pm 0.06$ mT and $g = 2.0023 \pm 0.0002$ (figure 11f). This behaviour reproduced that reported by Ormerod and Charlesby²²⁷ following γ -irradiation of polyacrylic acid at 77 K and then warming to room temperature; clearly the polymer radical is formed in the present case. Using the expression

$$a_{\text{H}(\beta)} = 4.6 \cos^2 \theta$$

applied by Symons to the poly (methyl methacrylate) radical,²²⁸ dihedral angles (θ) between the β protons and the unpaired electron orbital are calculated to be 44° (producing a coupling of 2.34 mT) and 76° (producing a coupling of 0.27 mT masked by a line width of 1.2 mT).

Methacrylic Acid (Sample preparation as for acrylic acid)

A high temperature (165 K) was necessary to produce the strong absorption spectrum exhibited in figure 11g of the polymethacrylic acid radical which has been analysed by Bamford:²²⁹



Use of Symons' relationship as in the case of acrylic acid gives $\theta_1 = 55^\circ$, $a_{\text{H}(\beta_1)} = 1.47 \pm 0.08$ mT and $\theta_2 = 65^\circ$, $a_{\text{H}(\beta_2)} = 0.83 \pm 0.08$ mT. ($\theta_1 + \theta_2$)

has the expected value of 120° .

5.1.6 Ketones (by Method A)

Acetone

A mixture of two spectra was given at 77 K. These were a sharp four-line spectrum clearly due to $\dot{\text{C}}\text{H}_3$ and a weaker distorted triplet with $a_{\text{H}} = 2.14 \pm 0.09$ mT, $g = 2.0025 \pm 0.0005$, which became the predominant species following the decay of $\dot{\text{C}}\text{H}_3$ on warming to 125 K. This spectrum is attributed to $\dot{\text{C}}\text{H}_2\text{COCH}_3$ for which $a_{\text{H}(\alpha)}$ in solution is variously reported as 1.95 mT²³⁰⁻²³² and 2.03 mT.²²⁴

Methyl Ethyl Ketone[†]

A mixture of $\dot{\text{C}}_2\text{H}_5$ and $\text{CH}_3\dot{\text{C}}\text{HCOCH}_3$ (five-line spectrum, $a_{\text{H}} = 2.06 \pm 0.07$ mT) was obtained at 77 K but warming to 140 K left only the latter radical.

Diethyl Ketone

An intense five-line spectrum, persisting at temperatures of up to 185 K, with $a_{\text{H}} = 2.13 \pm 0.05$ mT was obtained which is assigned to $\text{CH}_3\dot{\text{C}}\text{HCOC}_2\text{H}_5$. Values of 2.05 mT and 2.08 mT were obtained for this radical during Ce(IV) photo-oxidation of the same substrate.²³³ The spectrum is illustrated in figure 12a.

Diethyl Ketone - d_4 (2,2,4,4-Tetradeuteriopentan-3-one)

The four-line spectrum shown in figure 12b with $a_{\text{H}} = 2.20 \pm 0.09$ mT was the major product and this is ascribed to $\text{CH}_3\dot{\text{C}}\text{DCOCD}_2\text{CH}_3$, confirming that α -H, rather than β -H, abstraction is the mode of photo-oxidation of diethyl ketone.

Methyl Isopropyl Ketone

A seven-line spectrum of binomial intensity distribution with $a_{\text{H}} = 1.89 \pm 0.06$ mT was obtained and this is assigned to the radical $(\text{CH}_3)_2\dot{\text{C}}\text{COCH}_3$, a value of 1.99 mT being quoted for the same radical produced by Ce(IV) photo-oxidation.²³³

Dicyclopropyl Ketone

Whilst no resonance occurred at 77 K, at 100 K a five-line spectrum appeared ($a_{\text{H}} = 2.17 \pm 0.05$ mT) which is shown in figure 12c and which probably arises from the radical

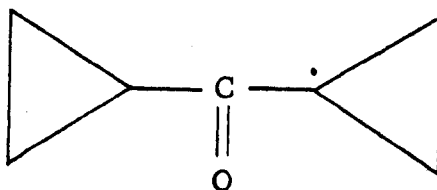
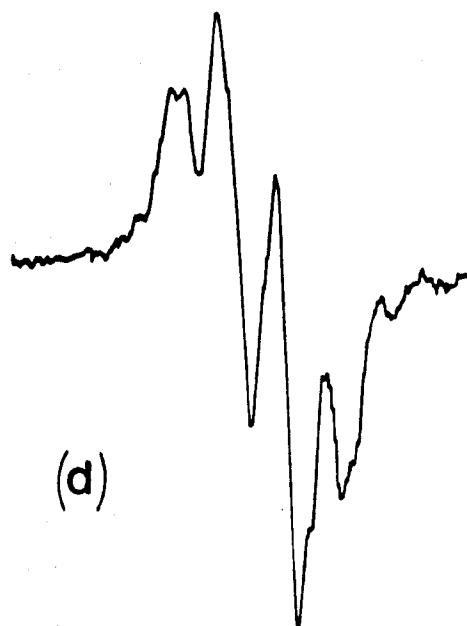
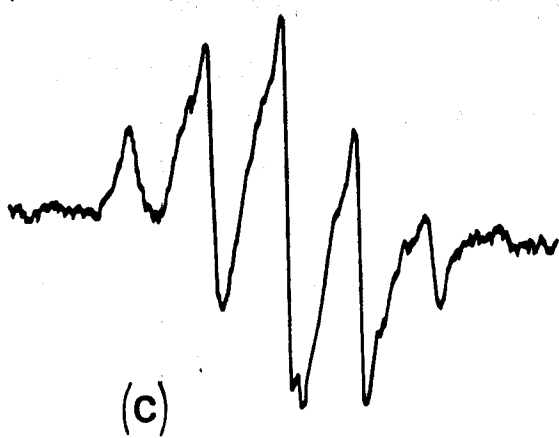
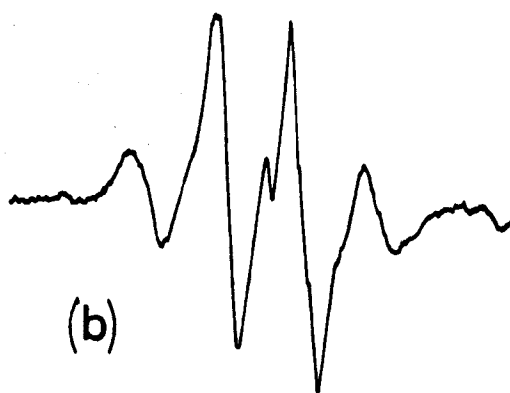
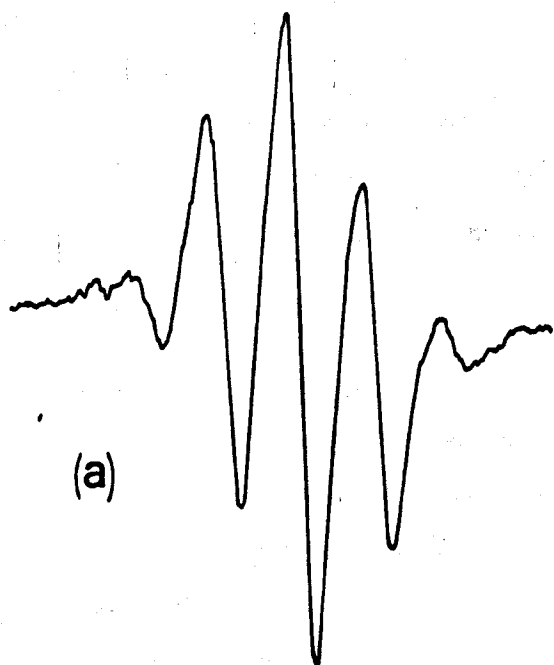


FIGURE 12

**E.s.r. spectra obtained upon photo-oxidation of
ketones by uranyl perchlorate**

- (a) Diethyl ketone at 77 K**
- (b) Diethyl ketone - d₄ at 77 K**
- (c) Dicyclopropyl ketone at 100 K**
- (d) Pent-3-en-2-one at 77 K**

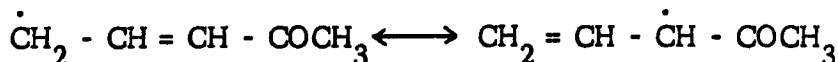


5.0mT

The same radical produced by Ce(IV) photo-oxidation gives a five-line spectrum with $a_H = 2.00$ mT.²³³

Pent-3-en-2-one

A four-line spectrum with the small splittings typical of allylic-type radicals¹⁹⁶ ($a_H = 1.30$ mT) was observed, displaying some resolution of the outermost peaks (figure 12d). The radical responsible is probably



3-Methylpent-3-en-2-one

A complex, asymmetrical spectrum was given which, although unanalysable, displayed the characteristic small couplings of an allyl-type radical.

5.1.7 Aldehydes (by Method A)

Formaldehyde

No absorption was evident at any temperature.

Acetaldehyde

A mixture was obtained of methyl radicals and a species giving rise to a 1:2:1 spectrum with $a_H = 2.15 \pm 0.04$ mT, presumably $\dot{\text{C}}\text{H}_2\text{CHO}$, for which a_H has been reported as 1.90 mT in solution²³² and 2.07 mT in the solid state.²³³ Coupling from the aldehydic proton cannot be resolved even in the liquid state.²³²

Propionaldehyde

The spectrum consisted of a mixture of ethyl radicals and a five-line binomial spectrum with $a_H = 2.33 \pm 0.09$ mT attributable to the radical $\text{CH}_3\dot{\text{C}}\text{HCHO}$ (figure 13a).

5.1.8 Esters (by Method A)

Methyl Formate

The major intense absorption was that of a singlet, but minor peaks from $\dot{\text{C}}\text{H}_3$ and the outermost lines of what is probably a 1:2:1 triplet were also apparent. The singlet displayed ^{13}C coupling of 6.24 ± 0.15 mT whilst $g = 2.0017 \pm 0.0007$, which is compatible with assignment to $\dot{\text{C}}\text{O}_2\text{CH}_3$. Metcalfe and Waters²³⁴ report a solution spectrum of this radical ($g = 2.0005 \pm 0.0003$) upon oxidizing methyl formate with $\text{Ti(III)/H}_2\text{O}_2$.

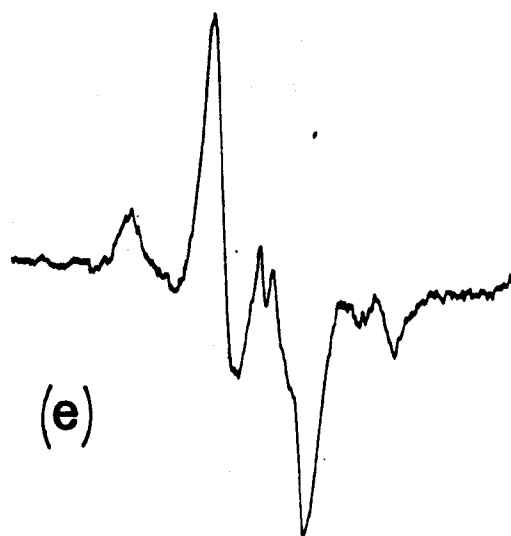
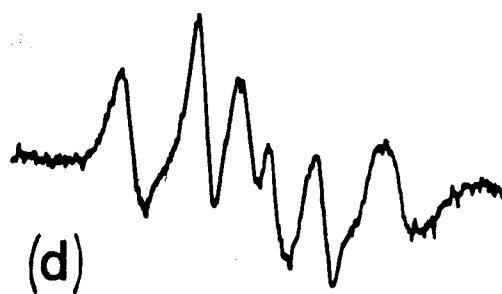
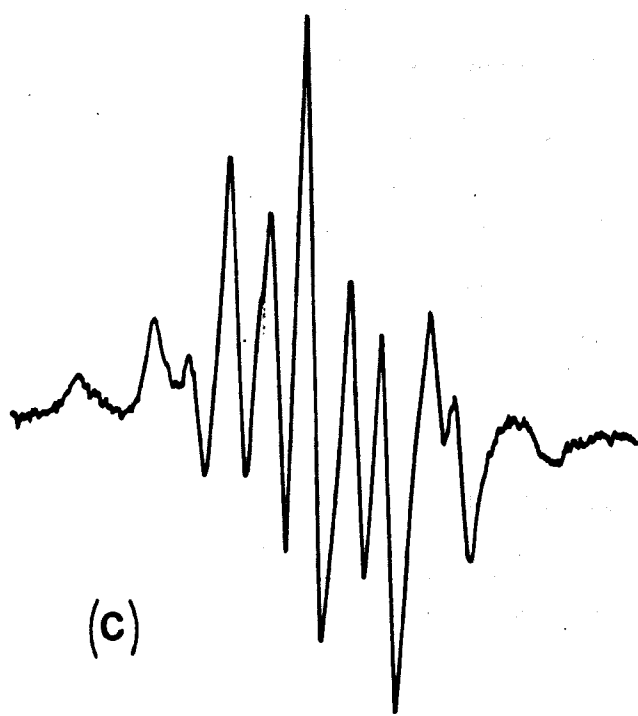
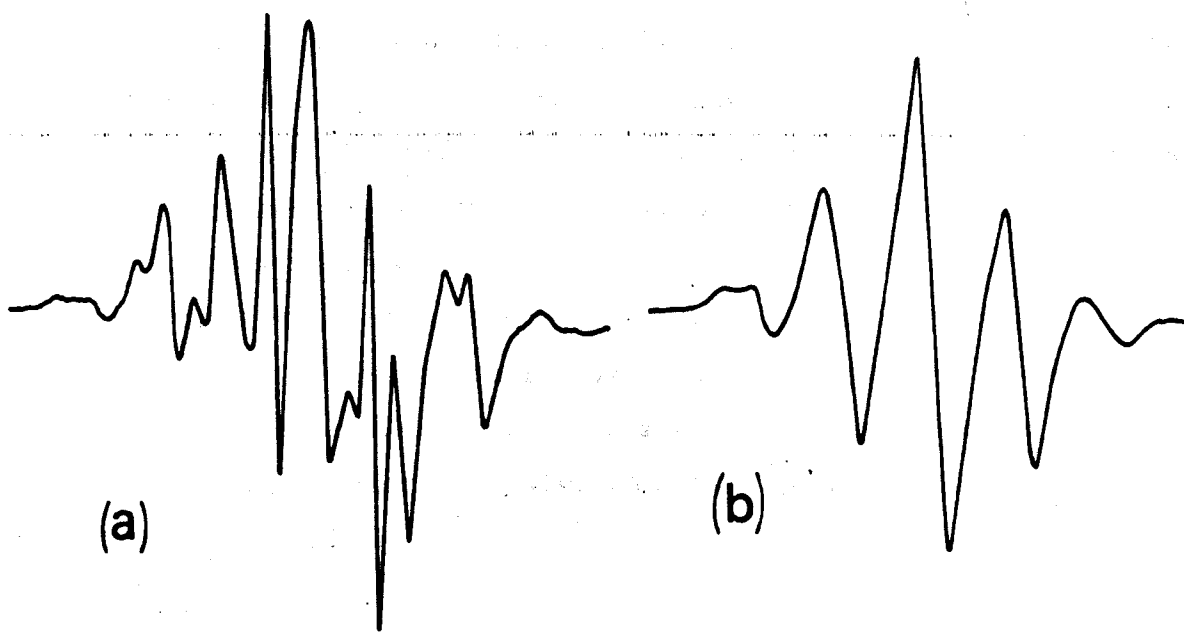
Ethyl Formate

This yielded a singlet with $g = 2.0011 \pm 0.0008$ but of insufficient intensity to exhibit ^{13}C coupling, and a quantity of ethyl radical. Warming the sample

FIGURE 13

E.s.r. spectra obtained during photo-oxidation of
organic molecules by uranyl perchlorate at 77 K

- (a) Propionaldehyde
- (b) Methyl propionate
- (c) Isopropyl isobutyrate
- (d) Formamide
- (e) Cellulose



5.0mT

caused the latter to disappear, the singlet becoming enhanced in intensity. The species responsible for the singlet is presumably $\dot{\text{C}}\text{O}_2\text{C}_2\text{H}_5$, a solution spectrum showing $g = 2.0005 \pm 0.0003$.²³⁴ The behaviour of this sample was very similar to that of the same substrate photolysed directly with light of wavelength $> 300 \text{ nm}$.²³⁵

Methyl and Ethyl Acetates

Both of these compounds gave $\dot{\text{C}}\text{H}_3$ together with a 1:2:1 triplet ($a_{\text{H}} = 2.30 \pm 0.08 \text{ mT}$ in both cases), the latter becoming more intense at the expense of the former on warming. The radicals responsible are presumably $\dot{\text{C}}\text{H}_2\text{CO}_2\text{R}$ ($\text{R} \equiv \text{Me, Et}$) for which other solid state spectra at 77 K give $a_{\text{H}} = 2.14 \text{ mT}$ and 2.13 mT respectively.²³⁵

Methyl Propionate

An intense five-line spectrum with $a_{\text{H}} = 2.30 \pm 0.08 \text{ mT}$ was given (figure 13b) suggesting the presence of $\text{CH}_3\dot{\text{C}}\text{HCO}_2\text{CH}_3$. Previously, values for a_{H} of 2.26 mT and 2.34 mT had been reported for this radical.²³⁵

Isopropyl n-Butyrate

A broad 1:3:3:1 quartet was given with $a_{\text{H}} = 2.26 \pm 0.08 \text{ mT}$, ascribed to the radical $\text{CH}_3\text{CH}_2\dot{\text{C}}\text{HCO}_2\text{C}_3\text{H}_7$.

Isopropyl iso-Butyrate

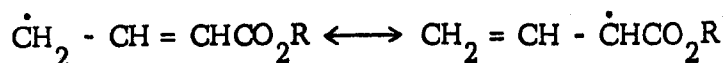
At 77 K were obtained the absorptions of $\dot{\text{C}}\text{H}_3$ and a seven-line spectrum ($a_{\text{H}} = 1.95 \pm 0.05 \text{ mT}$) shown in figure 13c, but at 93 K only the latter was evident; this is assigned to $(\text{CH}_3)_2\dot{\text{C}}\text{CO}_2\text{CH}(\text{CH}_3)_2$.

n-Butyl Lactate

This substrate exactly reproduced the behaviour of lactic acid at pH 1, the quartet ($a_{\text{H}} = 1.69 \pm 0.04 \text{ mT}$) being assigned to $\text{CH}_3\dot{\text{C}}(\text{OH})\text{CO}_2\text{C}_4\text{H}_9$.

Methyl and Ethyl[†] Crotonates

Four-line spectra with $a_{\text{H}} = 1.35 \pm 0.10 \text{ mT}$ were produced of the same type as those formed in Ce(IV) photo-oxidation²³³ and assigned to the allylic radicals



5.1.9 Amides

Formamide (Method A)

A six-line spectrum of $\dot{\text{C}}\text{ONH}_2$ ($a_{\text{H}} = 3.26 \pm 0.08 \text{ mT}$, $a_{\text{N}} = 2.02 \pm 0.06 \text{ mT}$) was produced, identical to that obtained in Ce(IV) photo-oxidation²³³ and with similar coupling constants to that from direct photolysis of aqueous formamide at 77 K when $a_{\text{H}} = 3.1 \text{ mT}$, $a_{\text{N}} = 2.2 \text{ mT}$.²³⁶ The spectrum is shown in figure 13d.

N,N-Dimethylformamide (Method A)

An intense 1:2:1 triplet exhibiting ^{13}C coupling of 8.6 mT was given, with $a_{\text{H}} = 2.05 \pm 0.07$ mT. This was also produced by photo-oxidation at 77 K by Ce(IV) ($a_{\text{H}} = 1.91$ mT)¹⁹⁴ and is assigned to $\text{HCON}(\text{CH}_3)\dot{\text{C}}\text{H}_2$ which has been produced in solution by action of $\text{Ti(III)}/\text{H}_2\text{O}_2$ ²³⁷ and photolysis of solutions containing H_2O_2 ²³⁸ ($a_{\text{H}} = 1.87$ mT and 1.84 mT respectively).

N,N-Diethylformamide (Method A)

A binomial five-line spectrum ($a_{\text{H}} = 2.00 \pm 0.05$ mT) was obtained which is assigned to the radical $\text{HCON}(\text{C}_2\text{H}_5)\dot{\text{C}}\text{HCH}_3$. Electron-irradiation of polycrystalline substrate at 133 K produced the same radical with $a_{\text{H}} = 2.04$ mT.²³⁹

Acetamide (Method B)

This substrate exhibited a mixture of absorptions due to $\dot{\text{C}}\text{H}_3$ and a $\dot{\text{C}}\text{H}_2\text{X}$ species, the latter with $a_{\text{H}} = 2.37$ mT probably arising from the radical $\dot{\text{C}}\text{H}_2\text{CONH}_2$. This radical, with $a_{\text{H}} = 2.3$ mT, has been produced by X-irradiation of acetamide.²⁴⁰

N,N-Dimethylacetamide (Method A)

A similar spectrum to that from acetamide was displayed but in this case the coupling constant for the $\dot{\text{C}}\text{H}_2\text{X}$ species was relatively small (1.90 mT) and this is evidence for assigning the species to the structure $\text{CH}_3\text{CON}(\text{CH}_3)\dot{\text{C}}\text{H}_2$. A similar argument was used by Rogers *et al.*²³⁹ in attributing their triplet spectrum with $a_{\text{H}} \sim 1.8$ mT, obtained from electron-irradiation of N,N-dimethylacetamide, to the same radical.

Propionamide (Method B)

A binomial five-line spectrum ($a_{\text{H}} = 2.51 \pm 0.06$ mT) was displayed and this is almost certainly due to $\text{CH}_3\dot{\text{C}}\text{HCONH}_2$, a similar absorption with $a_{\text{H}} = 2.47$ mT having been observed for this radical in electron-irradiated propionamide.²³⁹

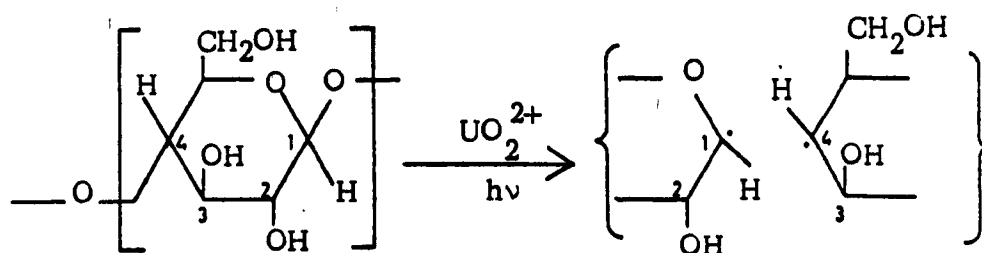
5.1.10 Miscellaneous Organic Compounds

Diethyl Ether (Method A)

This yielded the ethyl radical at 77 K which decayed upon slight warming to 85 K to give instead a five-line spectrum ($a_{\text{H}} = 2.12 \pm 0.15$ mT) suggestive of $\text{CH}_3\dot{\text{C}}\text{HOC}_2\text{H}_5$. The coupling constants in solution for this radical are $a_{\text{H}(\alpha)} = 1.38$ mT, $a_{\text{H}(\beta)} = 2.15$ mT²²⁴ and photolysis of diethyl ether in the far u.v. at 77 K produces the same radical with $a_{\text{H}} = 1.8$ mT.²⁴¹

Cellulose (Cotton wool saturated with uranyl perchlorate ($\sim 0.06 \text{ mol dm}^{-3}$) in 60% aqueous perchloric acid)

This produced the spectrum shown in figure 13e which is very similar to that obtained by Florin and Wall²⁴² on γ -irradiation of purified cellulose in vacuo, although displaying higher resolution. It is assigned to radicals formed from cellulose thus :



5.1.11 Phosphorus (III) Compounds (All g- and a- tensors are uncorrected according to the Breit-Rabi formula)

Sodium Hypophosphite, NaH_2PO_2 (Method B)

An e.s.r. absorption characterized by a spectral width of 60.4 mT was obtained (figure 14a). This spectrum is identical to that obtained by Atkins *et al.*²⁴³ in γ -irradiated polycrystalline magnesium hypophosphite and is analysed in terms of $a_{\text{H}} = 15.5 \pm 0.2 \text{ mT}$, $a_{\text{P}(\perp)} = 46.4 \pm 0.3 \text{ mT}$, $a_{\text{P}(\parallel)} = 62.8 \pm 0.3 \text{ mT}$, $g_{\text{av}} = 2.020$. Following Atkins and also Morton²⁴⁴ the spectrum is assigned to $\text{HPO}_2^{\cdot -}$.

Phosphorous Acid, H_3PO_3 (Method B)

A doublet was produced exhibiting g- and a- tensor anisotropy (figure 14b) which was analysed as follows : $a_{\text{P}(\perp)} = 63.3 \pm 1.0 \text{ mT}$, $g_{\perp} \sim 2.027$, $a_{\text{P}(\parallel)} = 74.1 \pm 1.0 \text{ mT}$, $g_{\parallel} \sim 2.022$. The species responsible is believed to be $\cdot\text{PO}(\text{OH})_2$. Symons²⁴⁵ reports coupling constants for $\text{PO}_3^{\cdot 2-}$, obtained by γ -irradiating various metal ortho-phosphites, of $52.3 < a_{\text{P}(\perp)} < 64.0 \text{ mT}$ and $70.65 < a_{\text{P}(\parallel)} < 81.5$, the exact figure depending on the metal counter-ion.

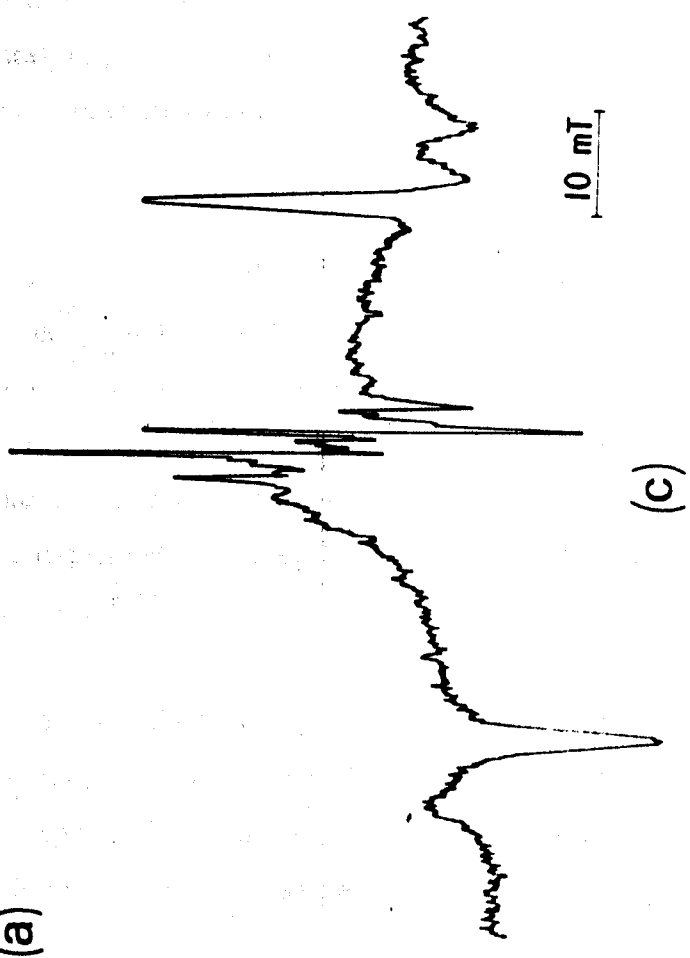
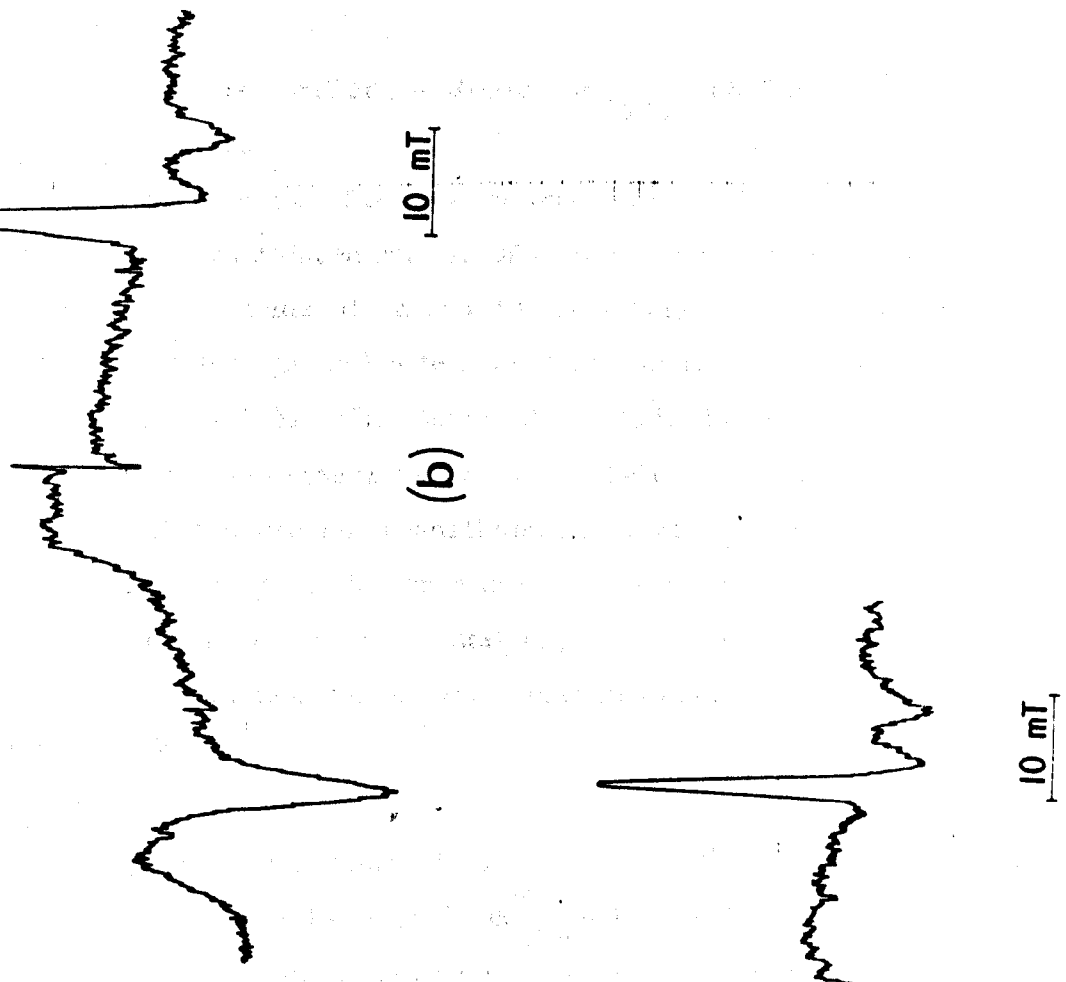
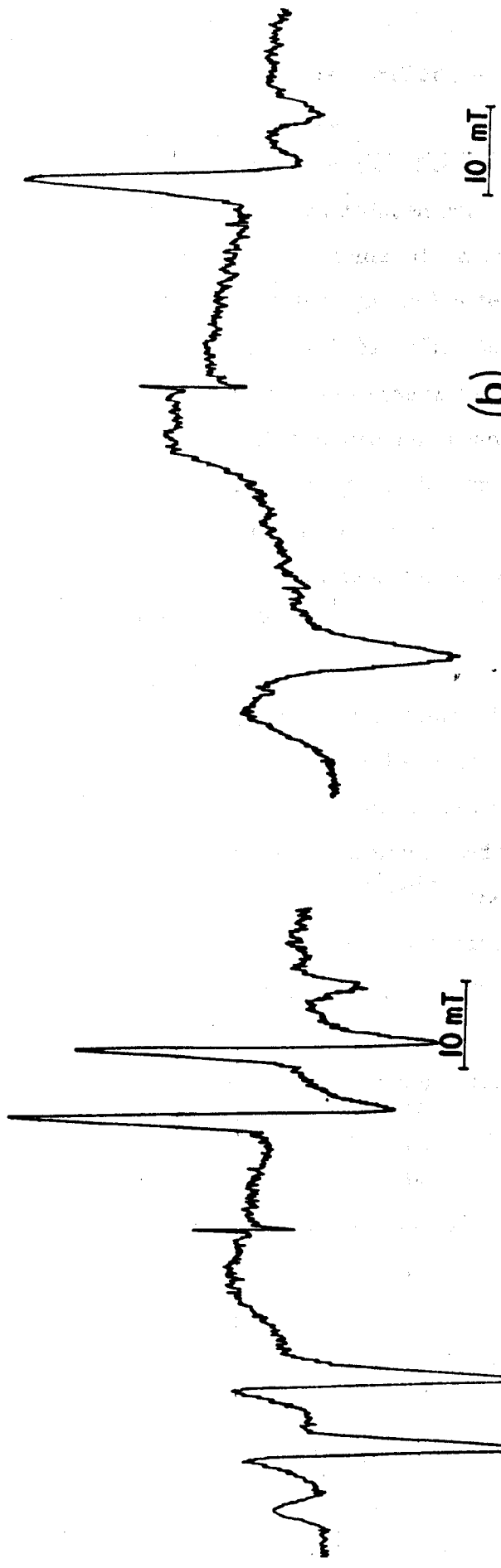
Diethyl Phosphite, $(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{H})\text{O}$ (Method A)

This yielded a spectrum of $\dot{\text{C}}_2\text{H}_5$ as well as a doublet with $a_{\text{P}(\perp)} = 60.5 \pm 1.0 \text{ mT}$, $g_{\perp} \sim 2.034$, $a_{\text{P}(\parallel)} = 71.7 \pm 1.0 \text{ mT}$, $g_{\parallel} \sim 2.017$ (figure 14c) attributed to $(\text{C}_2\text{H}_5\text{O})_2\dot{\text{P}}\text{O}$ in conformity with the result for $\cdot\text{PO}(\text{OH})_2$ and with the solution

FIGURE 14

E.s.r. spectra obtained upon photo-oxidation of P (III)
compounds by uranyl perchlorate at 77 K

- (a) Sodium hypophosphite in aqueous solution
- (b) Phosphorous acid in aqueous solution
- (c) Diethyl phosphite (neat)



spectrum of Davies, Griller and Roberts ($a_{\text{P (av)}} = 68.7 \text{ mT}$).²⁴⁶

5.2 Liquid State Studies

A wide selection of compounds was examined by means of the flow apparatus but relatively few produced spectra of sufficient intensity to enable reasonable assignments to be made, the major difficulty being the inability to run many compounds at the required low temperatures due to the unavailability of a suitable solvent (section 4.1.5). The compounds listed in this section were therefore studied "neat" unless otherwise stated. In the cases of several of the alcohols it was found that addition of a small amount of water (~5%) enhanced the intensity of the resultant spectra. Increase in the concentrations of certain radicals formed by u.v. photolysis of solutions containing H_2O_2 by adding water has also been noticed.²⁴⁷ Coupling constants are quoted to an accuracy of usually $\pm 0.02 \text{ mT}$.

5.2.1 Alcohols

Methanol

An intense, well resolved spectrum of $\dot{\text{C}}\text{H}_2\text{OH}$ (figure 15a) was obtained in the temperature range 195 - 215 K ($a_{\text{CH}_2}^{\text{H}} = 1.76 \text{ mT}$, $a_{\text{OH}}^{\text{H}} = 0.194 \text{ mT}$). Although the relative intensity of the centre doublet decreased as the temperature was lowered, the temperature at which the couplings from the methylene protons became inequivalent^{248, 249} was never reached because of freezing of the solution. A detailed study of the temperature dependence of coupling constants in the hydroxymethyl radical has been made by Krusic.²⁴⁹

Ethanol

The well resolved spectrum of $\text{CH}_3\dot{\text{C}}\text{HOH}$ was produced at 193 K (figure 15b) with $a_{\text{CH}_3}^{\text{H}} = 2.29 \text{ mT}$, $a_{\text{CH}}^{\text{H}} = 1.58 \text{ mT}$, $a_{\text{OH}}^{\text{H}} = 0.156 \text{ mT}$. The coupling from the hydroxylic proton is particularly temperature sensitive, being unresolved at temperatures of 299 K and higher for the same radical generated by photolysis with H_2O_2 , but increasing to 0.113 mT at 206 K.²⁵⁰

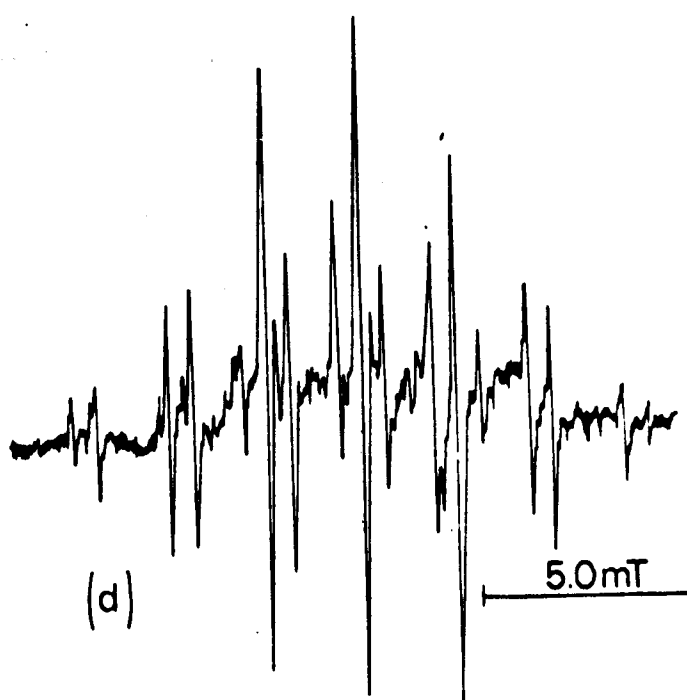
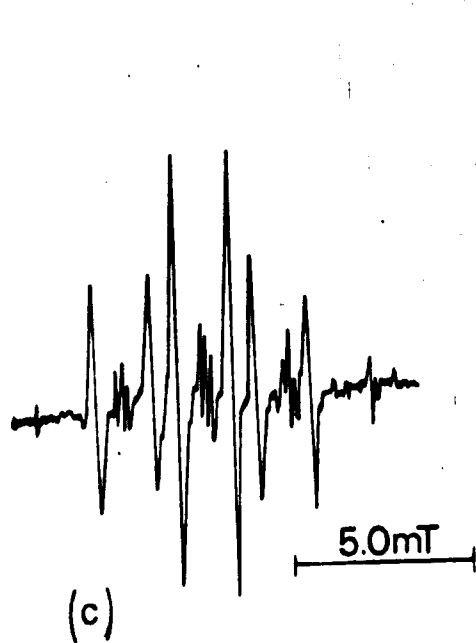
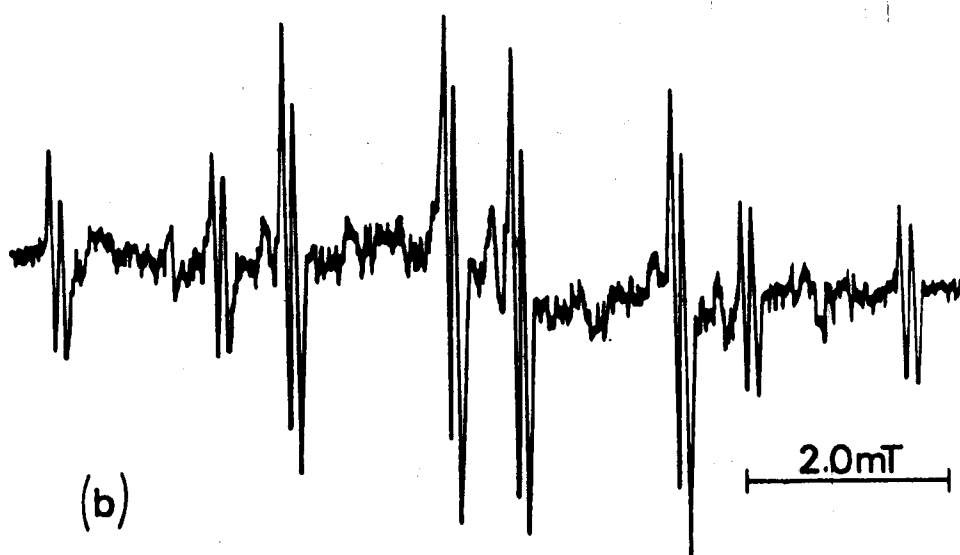
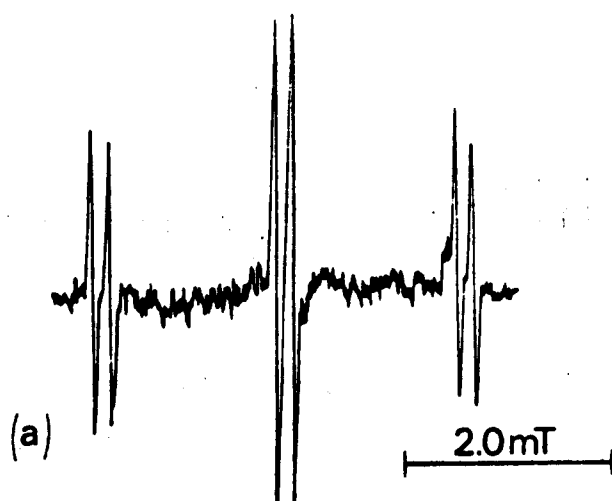
Propan-1-ol

The spectrum at 180 K (figure 15c) consisted mainly of the absorption due to $\text{CH}_3\text{CH}_2\dot{\text{C}}\text{HOH}$ ($a_{\text{CH}_2}^{\text{H}} = 2.21 \text{ mT}$, $a_{\text{CH}}^{\text{H}} = 1.55 \text{ mT}$) together with a number of weaker lines. A similar spectrum was obtained by u.v. photolysis of a solution of H_2O_2 in propan-1-ol²⁵⁰ where the minor species thought to result from β - or γ -hydrogen abstraction was also observed.

FIGURE 15

E.s.r. spectra obtained upon photo-oxidation of alcohols
in the liquid state by uranyl perchlorate

- (a) Methanol at 215 K
- (b) Ethanol at 193 K
- (c) Propan-1-ol at 180 K
- (d) 2-Methylpropan-1-ol at 239 K



Propan-2-ol

At 186 K a weak five-line spectrum was obtained with $a_H = 1.93$ mT. Values of $a_{CH_3}^H$ for the radical $(CH_3)_2\dot{C}OH$ in solution have been reported as 1.96 mT,²⁵⁰ 2.00 mT,²⁵¹ 1.93 mT²⁵² and 1.948 mT²³¹ and this species is thought to be responsible for the spectrum in the present case, the two outermost lines being lost in the base noise.

Butan-1-ol

A complex spectrum was produced which has not been fully analysed but which consists, to the extent of ~50%, of a doublet of triplets attributed to the radical $CH_3(CH_2)_2\dot{C}OH$ with $a_{CH}^H = 1.54$ mT, $a_{CH_2}^H = 1.97$ mT, in good agreement with the values obtained for the same radical by photolysis of butan-1-ol with H_2O_2 ($a_{CH}^H = 1.53$ mT, $a_{CH_2}^H = 2.00$ mT).²⁵⁰

2-Methylpropan-1-ol (iso-Butanol)

The spectrum obtained at 239 K and shown in figure 15d arises from abstraction of a β hydrogen atom, being due to the radical $(CH_3)_2\dot{C}CH_2OH$, with $a_{CH_3}^H = 2.30$ mT and $a_{CH_2}^H = 1.74$ mT.

2-Phenylethanol

The spectrum obtained from this compound at 264 K was analysed, by computer simulation, as $a_{H(2)} = 1.63$ mT, $a_{H(2)} = 0.510$ mT, $a_{H(2)} = 0.177$ mT, $a_{H(1)} = 0.623$ mT (figure 16) and is clearly due to the benzyl radical for which the following assignments have been made : $a_{CH_2}^H = 1.640$ mT, $a_{H(ortho)} = 0.517$ mT, $a_{H(meta)} = 0.177$ mT, $a_{H(para)} = 0.619$ mT.

5.2.2 Carboxylic Acids and Esters

Acetic Acid

The spectrum obtained at 293 K consisted of the triplet shown in figure 17a with $a_H = 2.11$ mT due to the radical $\dot{C}H_2CO_2H$.

Propionic Acid

At 255 K the spectrum of $CH_3\dot{C}HCO_2H$ was obtained, exhibiting $a_{CH_3}^H = 2.44$ mT, $a_{CH}^H = 1.90$ mT (figure 17b).

Lactic Acid

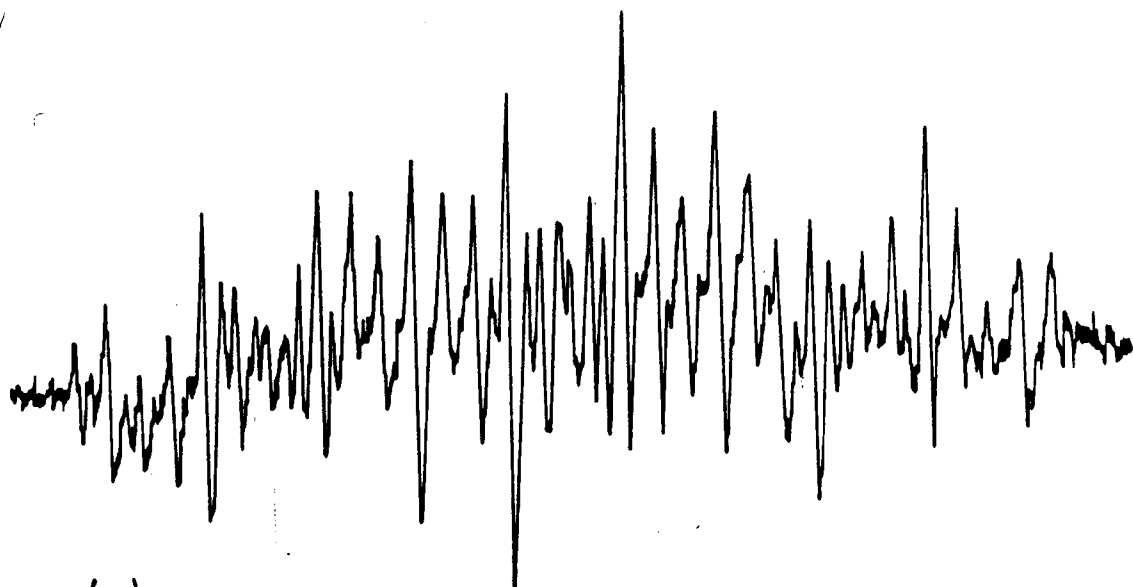
The quartet of doublets shown in figure 17c was produced at 293 K with $a_{H(3)} = 1.66$ mT, $a_{H(1)} = 0.225$ mT. This spectrum is very similar to that of the radical $CH_3\dot{C}(OH)CO_2H$ ($a_{CH_3}^H = 1.71$ mT, $a_{OH}^H = 0.20$ mT) obtained by oxidation of lactic acid by $Ti(III)/H_2O_2$ ²²⁴ and is therefore assigned to this species.

FIGURE 16

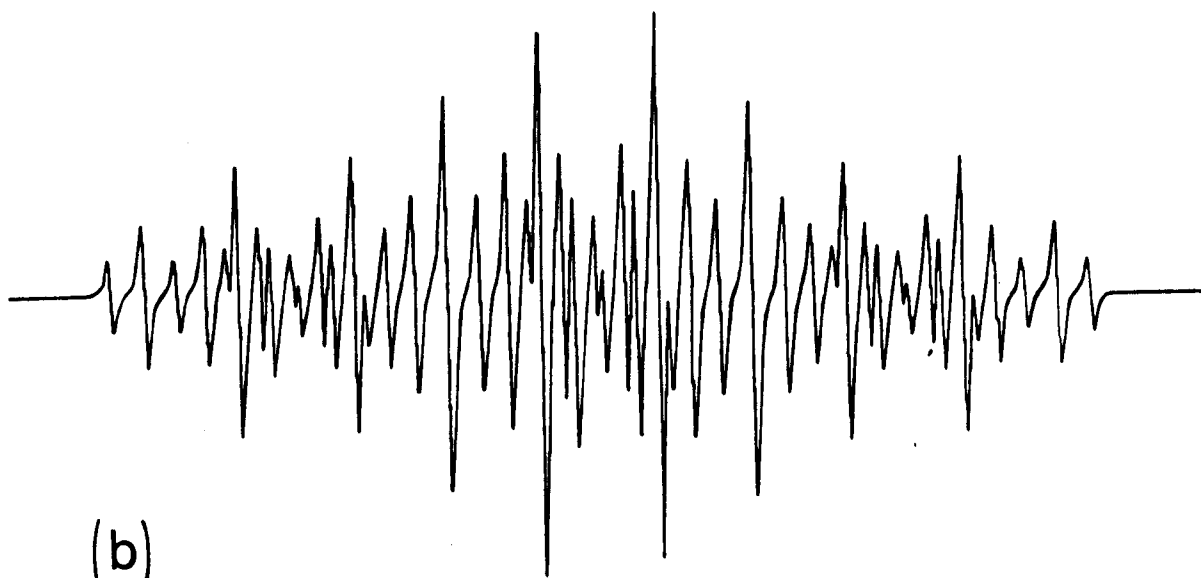
E.s.r. spectrum of the benzyl radical obtained during
photo-reaction of uranyl perchlorate with 2-phenylethanol
in the liquid state at 264 K

(a) Experimental

(b) Computer simulation



(a)



(b)

1.0mT

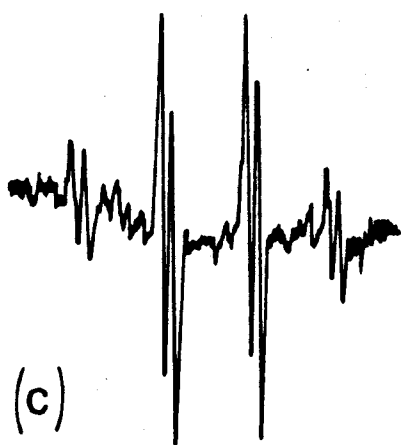
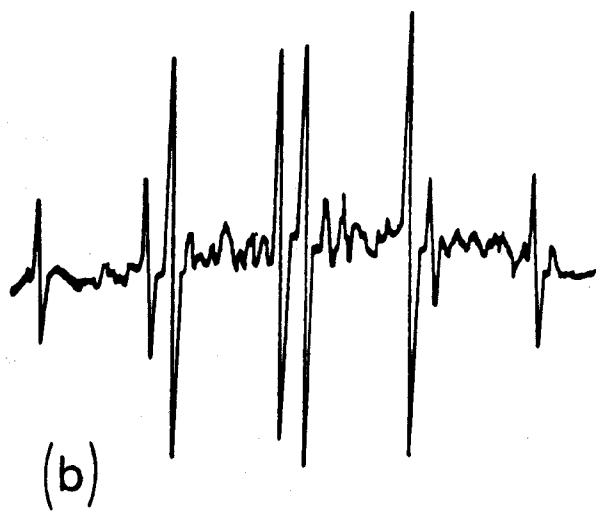
FIGURE 17

E.s.r. spectra obtained upon photo-oxidation of
carboxylic acids in the liquid state by uranyl perchlorate

(a) Acetic acid at 293 K

(b) Propionic acid at 255 K

(c) Lactic acid at 293 K



5.0 mT

Benzilic Acid

Examination of a solution of this compound ($\sim 10^{-2}$ mol dm $^{-3}$) in ethanol at 185 K produced a complex spectrum identical to that obtained by photo-oxidation of the same substrate by Fe(III)¹⁹⁴ and analysed as the benzophenone ketyl radical (C₆H₅)₂ $\dot{\text{C}}\text{OH}$.

n-Butyl Lactate

The intense spectrum produced at 234 K was analysed as due to a mixture of cis- and trans- conformations of the radical CH₃ $\dot{\text{C}}$ (OH)CO₂CH₂CH₂CH₂CH₃ following an analogous interpretation by Fessenden *et al.*²⁵⁴ of the spectrum of the radical CH₃ $\dot{\text{C}}$ (OH)CO₂C₂H₅ produced by photo-reduction of ethyl pyruvate in 2-propanol. The spectrum is illustrated in figure 18 together with a computer simulation based on the following coupling constants :

cis-conformer	$a_{\text{CH}_3}^{\text{H}} = 1.668 \text{ mT}, a_{\text{OH}}^{\text{H}} = 0.265 \text{ mT},$ $a_{\text{CH}_2}^{\text{H}} = 0.165 \text{ mT}$
trans-conformer	$a_{\text{CH}_3}^{\text{H}} = 1.656 \text{ mT}, a_{\text{OH}}^{\text{H}} = 0.236 \text{ mT},$ $a_{\text{CH}_2}^{\text{H}} = 0.116 \text{ mT}$

Fessenden gives the following coupling constants for CH₃ $\dot{\text{C}}$ (OH)CO₂CH₂CH₃ :

cis-conformer	$a_{\text{CH}_3}^{\text{H}} = 1.674 \text{ mT}, a_{\text{OH}}^{\text{H}} = 0.223 \text{ mT},$ $a_{\text{CH}_2}^{\text{H}} = 0.151 \text{ mT}$
trans-conformer	$a_{\text{CH}_3}^{\text{H}} = 1.641 \text{ mT}, a_{\text{OH}}^{\text{H}} = 0.192 \text{ mT},$ $a_{\text{CH}_2}^{\text{H}} = 0.117 \text{ mT}$

Di-ethyl Succinate

The spectrum obtained at 258 K was analysable in terms of coupling from four protons viz. $a_{\text{H}(2)} = 0.15 \text{ mT}$, $a_{\text{H}(1)} = 2.08 \text{ mT}$, $a_{\text{H}(1)} = 0.95 \text{ mT}$, but this analysis cannot be readily assigned to a specific radical.

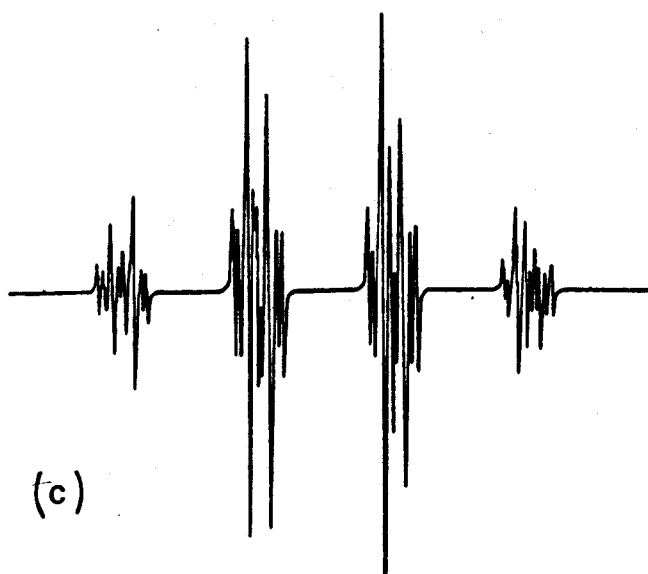
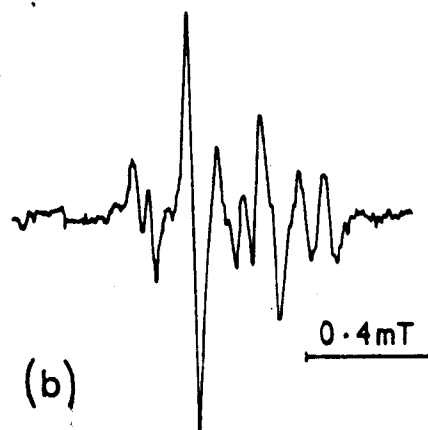
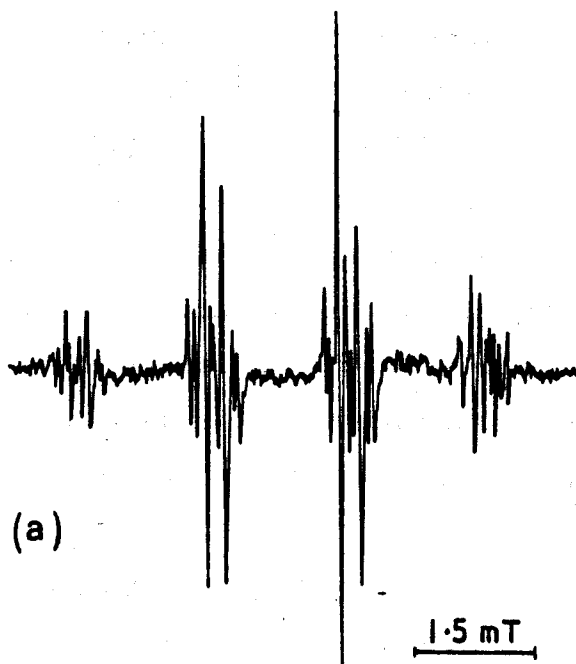
5.2.3 Ethers

1,2-Dimethoxyethane (Uranyl nitrate was used in this experiment instead of the perchlorate as small quantities of water in the latter caused the formation of an emulsion)

At 248 K was obtained a spectrum arising from two species in equal

FIGURE 18

- (a) E.s.r. spectrum of cis- and trans- forms of $\text{CH}_3\dot{\text{C}}(\text{OH})\text{CO}_2\text{Bu}^{\text{n}}$ obtained during photo-oxidation by uranyl perchlorate at 234 K.
- (b) Third group of lines on expanded field scale.
- (c) Computer simulation of (a) based on coupling constants given in the text.



quantities, namely $\dot{\text{C}}\text{H}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$ ($a_{\text{CH}_2(\alpha)}^{\text{H}} = 1.71 \text{ mT}$, $a_{\text{CH}_2(\gamma)}^{\text{H}} = 0.22 \text{ mT}$) and $\text{CH}_3\text{O}\dot{\text{C}}\text{HCH}_2\text{OCH}_3$ ($a_{\text{CH}}^{\text{H}} = 1.73 \text{ mT}$, $a_{\text{CH}_2}^{\text{H}} = 0.81 \text{ mT}$ and $a_{\text{CH}_3(\gamma)}^{\text{H}} = 0.20 \text{ mT}$). The spectrum and simulation according to the above parameters are shown in figure 19a. A similar mixture of radicals was produced from the same substrate by oxidation with $\text{Ti(III)}/\text{H}_2\text{O}_2$ in a flow system²⁵² and these exhibited very similar coupling constants ($a_{\text{H}} = 1.70, 0.21, 1.78, 0.89$ and 0.20 mT respectively). The same results have also been obtained with $\text{Fe(III)}/\text{H}_2\text{O}_2$ in a flow system by Shiga and coworkers²⁵⁵ who discussed in detail the coupling constants in similar types of radicals. In particular, the low value of the methylene coupling constant in the radical $\text{CH}_3\text{O}\dot{\text{C}}\text{HCH}_2\text{OCH}_3$ (the theoretical value is 2.00 mT) can be explained in terms of a preferential orientation of the $-\text{OCH}_3$ group connected to the β carbon atom with respect to the p orbital bearing the unpaired electron.

2-Methoxyethanol

The major species present was $\dot{\text{C}}\text{H}_2\text{OCH}_2\text{CH}_2\text{OH}$, appearing as a triplet of triplets with the centre group relatively broadened at 233 K ($a_{\text{CH}_2(\alpha)}^{\text{H}} = 1.681 \text{ mT}$, $a_{\text{CH}_2(\gamma)}^{\text{H}} = 0.225 \text{ mT}$) but in a normal $1:2:1$ distribution at 273 K ($a_{\text{CH}_2(\alpha)}^{\text{H}} = 1.689 \text{ mT}$, $a_{\text{CH}_2(\gamma)}^{\text{H}} = 0.214 \text{ mT}$). The spectra at these temperatures are presented in figure 19b. The above assignment is confirmed by the production of the same radical by the $\text{Fe(III)}/\text{H}_2\text{O}_2$ couple²⁵⁵ at 298 K which gives $a_{\text{CH}_2(\alpha)}^{\text{H}} = 1.67 \text{ mT}$, $a_{\text{CH}_2(\gamma)}^{\text{H}} = 0.200 \text{ mT}$. Other radicals are evidently present and one of these is probably $\text{CH}_3\text{O}\dot{\text{C}}\text{HCH}_2\text{OH}$ by comparison with the spectrum produced by $\text{Fe(III)}/\text{H}_2\text{O}_2$ ²⁵⁵ which yields $a_{\text{CH}}^{\text{H}} = 1.83 \text{ mT}$, $a_{\text{CH}_2}^{\text{H}} \sim 0.9 \text{ mT}$, $a_{\text{CH}_3}^{\text{H}} = 0.19 \text{ mT}$ while the present spectrum gives $a_{\text{CH}}^{\text{H}} \sim 1.7 \text{ mT}$, $a_{\text{CH}_3}^{\text{H}} = 0.19 \text{ mT}$. The radicals mentioned above have also been produced from 2-methoxyethanol by the $\text{Ti(III)}/\text{H}_2\text{O}_2$ couple in a flow system.²⁵²

5.2.4 Unsuccessful Experiments

The following compounds were examined but determination of any radicals present was not possible for the reasons stated. No paramagnetism was detectable with pentan-2-ol, ethane-1,2-diol, propane-1,2-diol, propane-1,2,3-triol, 1-phenylethanol, 1,2-epoxypropane, dimethoxymethane, ethyl acetate, ethyl cyanoacetate, dimethylformamide, acetone and diethyl ketone. Photolysis at $\sim 233 \text{ K}$, however, of a small sample of uranyl perchlorate dissolved in acetone with the "spin-trapping" agent 2-methyl-2-nitrosopropane (prepared by the method of Holman and Perkins²⁵⁶) at a concentration of $\sim 0.05 \text{ mol dm}^{-3}$

FIGURE 19

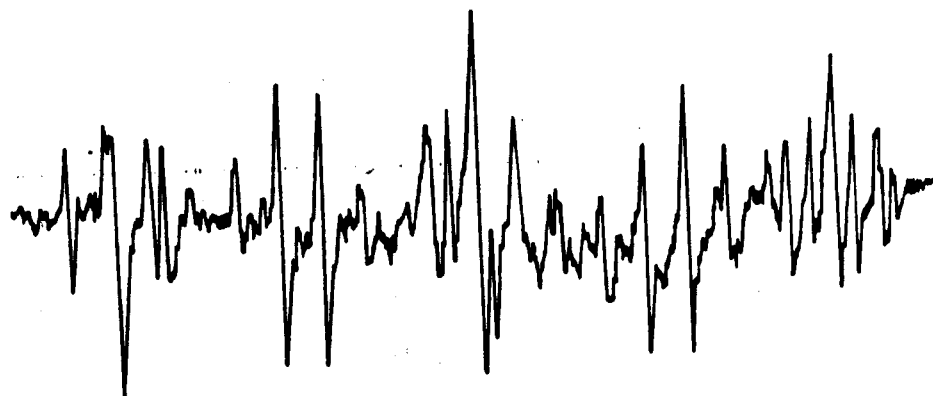
E.s.r. spectra obtained upon photo-oxidation
of ethers by U (VI)

(a) 1,2-Dimethoxyethane/uranyl nitrate at 248 K

- i. Experimental
- ii. Computer simulation

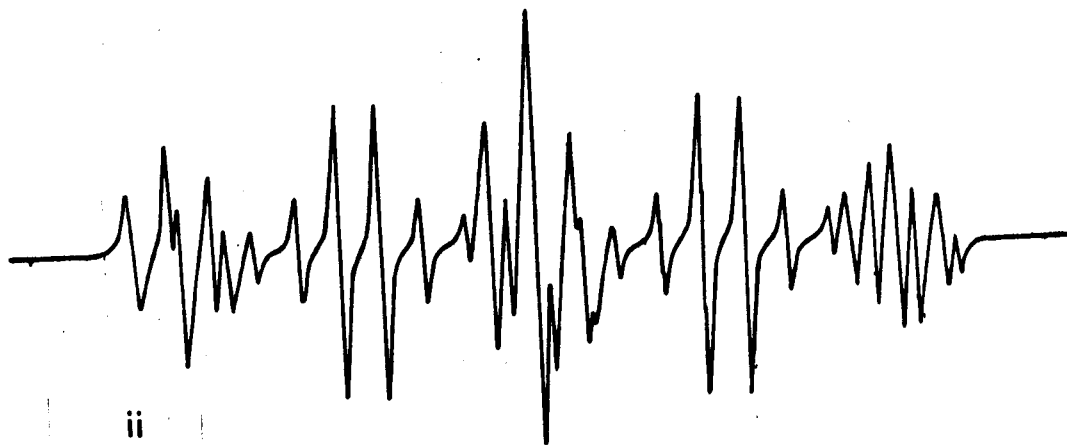
(b) 2-Methoxyethanol/uranyl perchlorate

- i. at 233 K
- ii. at 273 K



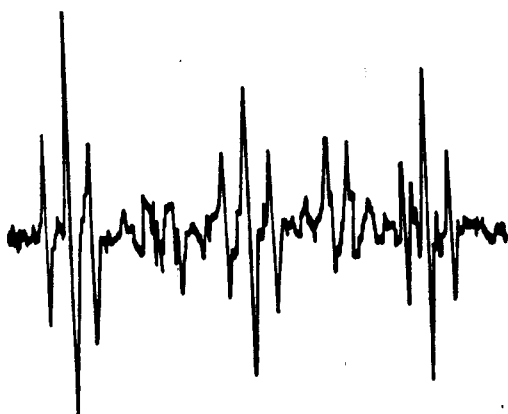
i

1.0mT



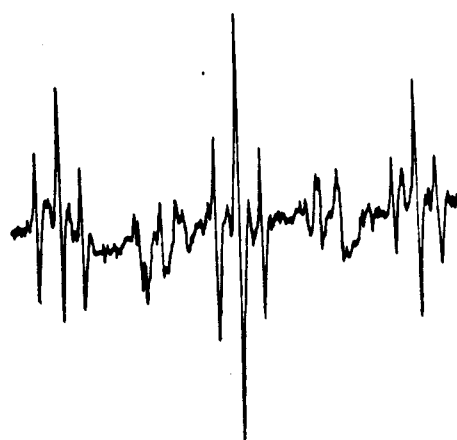
ii

(a).



(b)

i



ii

2.0mT

gave, in addition to the three-line spectrum from direct photolysis of the spin-trap, a set of three doublets with $a_N \sim 2.99$ mT, $a_H \sim 0.45$ mT. This is taken as evidence of α -H abstraction by U(VI) from acetone, the observed spectrum arising from $C(CH_3)_2\dot{N}(\dot{O})CH_2C(O)CH_3$.

Very weak signals were obtained from hexan-1-ol, 3-phenylpropan-1-ol (aromatic type spectrum), methyl acetate, methyl propionate, ethyl n-butyrate, isopropyl isobutyrate, ethyl lactate and dimethyl malonate.

Strong but complex spectra were given by butan-2-ol, pentan-3-ol, 2-methylbutan-2-ol (t-amyl alcohol).

Singlet absorptions were obtained from 2-ethoxyethanol, diethyl malonate, dimethyl maleate and diethyl maleate.

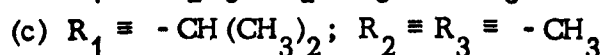
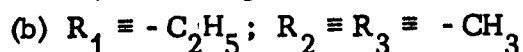
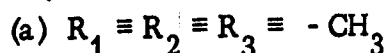
Diethyl phosphite produced a strong spectrum apparently consisting of a doublet ($a \sim 45.6$ mT) and a 1:1:1:1 quartet ($a \sim 9.1$ mT).

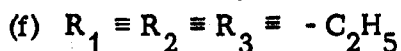
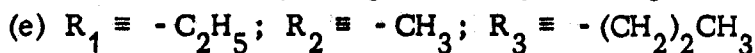
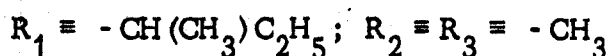
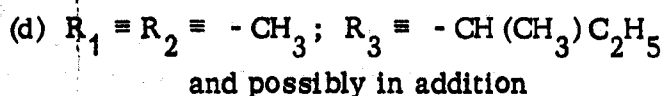
5.3 Discussion

5.3.1 Alcohols

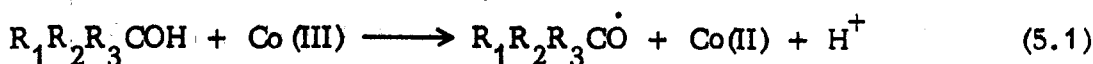
Certain generalisations may be made from the results of U(VI) photoreaction presented in this chapter :

- (i) Photoreactions of primary alcohols in the solid state lead to abstraction of a hydrogen atom from the carbon atom bearing the -OH group. The exceptions to this are the production of ethyl radical from propan-1-ol and benzyl radical from 2-phenylethanol.
- (ii) In the solid state, secondary alcohols undergo C - C cleavage rather than H-atom abstraction. The splitting occurs at the carbon atom to which is attached the -OH group in such a way that an ethyl group is eliminated in preference to a methyl group; thus $(CH_3)_2CHOH$ yields $\dot{C}H_3$ whilst $C_2H_5(CH_3)CHOH$ and $(C_2H_5)_2CHOH$ both give \dot{C}_2H_5 radicals. There is no evidence of secondary thermal reactions of the alkyl fragment.
- (iii) Tertiary alcohols in solid matrices undergo similar primary reactions to those of secondary alcohols, i.e. cleavage of an alkyl group from the tertiary carbon atom. In the series of alcohols $R_1R_2R_3COH$ listed below the \dot{R}_1 radical is produced in each case :

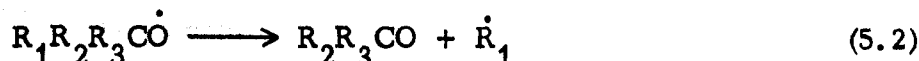




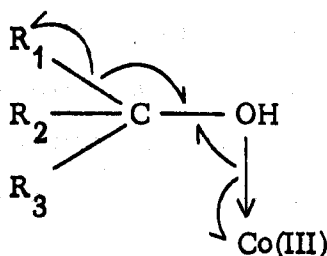
The relative tendencies of the alkyl groups to cleave from the alcohol molecule display much the same trend observed by Hoare and Waters for the thermal oxidation of tertiary alcohols by Co(III).²⁵⁷ These authors believe the primary reaction to be formation of an alkoxy radical :



followed by loss of an alkyl group :



although they noted the possibility of reactions (5.1) and (5.2) being concerted, viz :



The relative rates of elimination for $R_1 \equiv$ isopropyl, ethyl, n-propyl and methyl are 2300, 100, 33.9 and 1.06. This sequence corresponds to the order of stabilities of the alkyl radicals (i.e. to the number of β protons that can be concerned in hyperconjugation) and parallels the order of elimination of alkyl groups in the Fe(II) catalysed decomposition of hydroperoxides²⁵⁸ and in the homolysis of tertiary alkyl hypophosphites.^{259, 260}

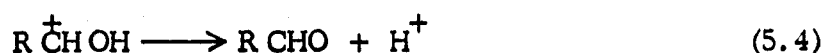
The alkyl groups formed during the photo-oxidation by U(VI) undergo secondary thermal reactions removing a hydrogen atom from the parent molecule in such a way that the most stable radical is produced.

(iv) Photo-oxidation of primary alcohols in the liquid phase appears to parallel the same reactions in the solid state, the product of an α -H abstraction reaction being detected in most cases. The exceptions are 2-phenylethanol which gives benzyl radical as in the solid state and 2-methylpropan-1-ol which yields the radical arising from removal of the β -hydrogen atom. The latter result, although the only example of

β - H abstraction encountered in this work, is not surprising as the radical $(\text{CH}_3)_2\dot{\text{C}}\text{CH}_2\text{OH}$, possessing eight C - H bonds capable of hyperconjugation, is expected to be appreciably more stable than the radical $(\text{CH}_3)_2\text{CH}\dot{\text{C}}\text{HOH}$ which possesses only one such bond. The results of kinetic studies on selectively deuterated 2-methylpropan-1-ol, similar to those presented in the next chapter for other alcohols, would be interesting as they should indicate whether the observed radical is the primary product or whether it is formed via the α - H abstraction product either by rapid isomerisation or by removal of a β -hydrogen atom from a second parent molecule.

The closely similar behaviour between photoreaction of U(VI) with primary alcohols in the solid and liquid states is in direct contrast to the situation with Ce(IV) where it was found that, whilst α - H abstraction occurs at 77 K, alcohols RCH_2OH yield $\dot{\text{R}}$ in liquid media.¹⁹⁴ It would appear that the C - C cleavage reaction possesses a higher activation energy than the C - H fission reaction for photo-oxidation by Ce(IV), but direct comparisons between the two metal ions may not be very meaningful as Ce(IV) reacts exclusively via metal-alcohol complexes¹⁹⁶ while this is probably not the case with U(VI) (see chapter 6).

The hydroxyalkyl radicals observed with primary alcohols are clearly the precursors of the aldehyde products (section 2.3.2) probably reacting as below :



Organic radicals like $\text{R}\dot{\text{C}}\text{HOH}$ with -OH or -OR groups adjacent to the tervalent carbon atom are effective one-electron reducing agents.²⁶¹ The e.s.r. results do not define, however, whether the radicals are produced during the homolytic cleavage of the α C - H bond or whether they result from secondary reactions of alkoxy radicals created by electron transfer to $(\text{UO}_2^{2+})^*$ and subsequent loss of a proton from the alcohol cation radical.²⁶²

The absence of any e.s.r. signal due to alkoxy species does not preclude their existence; these radicals cannot be observed directly by e.s.r. in the liquid state²⁶³ and singlet spectra assigned to radicals of this type obtained by the u.v. photolysis at 77 K of t-butyl hydroperoxide,²⁶⁴ methanol²⁶⁵ and ethanol²⁶⁶ (the latter with an unexpectedly long half-life for an alkoxy radical of "weeks or months") are possibly due to the more stable peroxy radicals.²⁶⁴ Moreover, any alkoxy radical formed would be expected to convert to the more

stable (observed) hydroxyalkyl radical either by rearrangement or, more probably, by hydrogen atom abstraction from an alcohol molecule,^{262, 267} and in the case of 2-phenylethanol in solid and liquid media the observed benzyl radical is known to be a product of fragmentation of the 2-phenylethoxy radical.²¹⁴ Evidence to suggest that U(VI) photo-oxidises simple alcohols in solution by α -H abstraction is presented in chapter 6, along with a discussion of the spin-trapping results of Ledwith *et al.*

A contrast between reaction pathways at 77 K and in liquid media is evident for the secondary alcohol, propan-2-ol. In the solid state C - C cleavage occurs to give the methyl radical, following the general pattern with secondary alcohols as in the case of Ce(IV) photo-oxidation.¹⁹⁶ In solution however, abstraction of the α -hydrogen atom takes place and it is unlikely that this is a secondary reaction involving methyl radicals for the following reasons :

- (i) Methyl radicals (if present) should be detectable in a propan-2-ol medium in the flow apparatus, having been so generated and observed during Ce(IV) photo-oxidation.¹⁹⁴
- (ii) Evidence that the species $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ is the primary radical product in solution includes the spin trapping of this radical under conditions capable of trapping $(\text{CH}_3)_2\text{CH}\dot{\text{O}}$ (section 6.2).
- (iii) There is no reason why a mechanism of C - C cleavage should not predominate at cryogenic temperatures whilst hydrogen abstraction processes are more important at higher temperatures.

The detection of acetone as the product of photo-oxidation of propan-2-ol by U(VI) (section 2.3.2) is consistent with the intermediacy of the $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ radical.

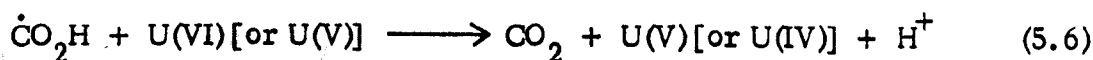
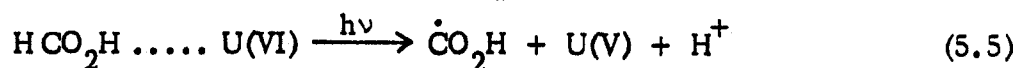
Tertiary alcohols are unable to undergo an α -hydrogen removal mechanism and this is reflected in the relative rates of U(IV) production (approximately 1 : 10) for reaction with t-butanol and the other butanol isomers;⁹⁵ this ratio is by no means large and indicates that at room temperature the energy path for the C - C cleavage reaction (as observed in the present experiments) is only marginally higher than for H-atom abstraction.

5.3.2 Acids

The reactions studied at 77 K are clearly those involving nearest-neighbour molecules, some, but not all, of which will be complexed to the UO_2^{2+} ion. Experiments using frozen dilute aqueous solutions will not record acts dependent upon migration of free $(\text{UO}_2^{2+})^*$ ions which play a rôle in the solution photochemistry of

carboxylic acids via a kinetic-encounter mechanism. However, at the high solute concentrations used in this work and especially in "neat" solvent, even uncomplexed $(\text{UO}_2^{2+})^*$ will have a high probability of reaction with an adventitiously neighbouring solute molecule.

It is evident from the e.s.r. results with simple monocarboxylic acids that α -H abstraction plays an important part in the photoreaction of $\text{R-}\overset{\text{R}_1\text{R}_2\text{CHCO}_2\text{H}}{\text{CO}_2\text{H}}$ with U(VI), $\text{R}_1\text{R}_2\dot{\text{C}}\text{CO}_2\text{H}$ being the exclusive radical detected in all the cases examined except those of formic and acetic acids. The radical obtained from the former is clearly consistent with the following reaction scheme which predicts the main end products to be the observed CO_2 and U(IV) and also the lack of H_2 , viz :

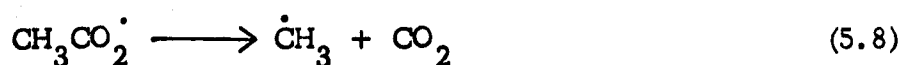
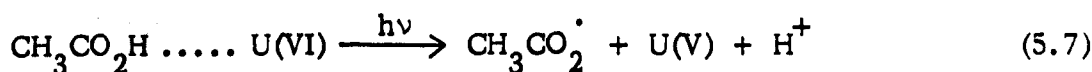


In discussing the correlation between reaction mode (i.e. photo-oxidation or sensitized decarboxylation) and the radicals observed, certain observations are significant :

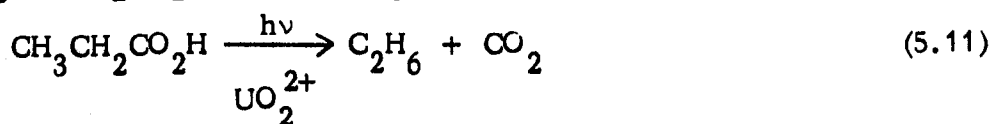
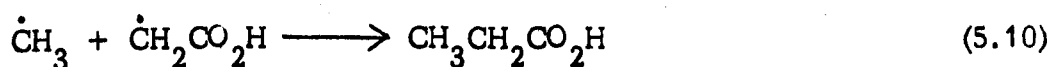
- (i) Of the simple monocarboxylic acids studied, acetic acid is the only one known with any certainty from product analysis to undergo both photo-oxidation and decarboxylation and is the only substrate to produce more than one observable radical (at 77 K), viz. $\dot{\text{C}}\text{H}_3$ and $\dot{\text{C}}\text{H}_2\text{CO}_2\text{H}$. (In this connection it is unlikely that any methyl radicals produced in the flow system would be detectable at the necessarily high temperature employed).
- (ii) The photo-oxidation process, which produces C_2H_6 from acetic acid probably involves the production and dimerisation of methyl radicals. For this to occur in the face of a competitive reaction of H atom abstraction by the methyl radicals, the latter are probably formed in uranyl ion - acid complexes and indeed, this is the mechanism generally accepted for photo-oxidation of acetic acid (section 2.2.1).
- (iii) No alkyl radicals were observed with the higher homologues of acetic acid, although these radicals produced by Ce(IV) photo-oxidation are stable in substrate matrices at 77 K²¹⁸ and consequently it may be assumed that these radicals are

not formed during the primary photochemical act. This, together with the production of $\dot{\text{C}}\text{H}_2\text{CO}_2\text{H}$ from acetic acid, suggests that radicals of the type $\text{R}\dot{\text{C}}\text{HCO}_2\text{H}$ are involved in the primary step of the sensitized decarboxylation process.

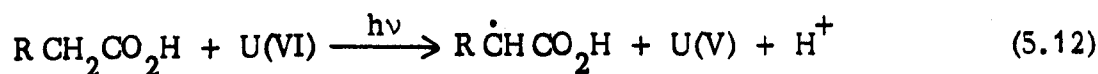
A possible source of methyl radical from photolysed U(VI) - acetic acid is the acetoxy radical $\text{CH}_3\text{CO}_2\dot{\text{O}}$. Removal of the carboxylic hydrogen atom from acetic acid has been suggested as occurring during the photo-oxidation of this compound by Ce(IV) ²¹⁸ and reaction with $\dot{\text{O}}\text{H}$ ²²⁴ both of which produce $\dot{\text{C}}\text{H}_3$ and CO_2 , and therefore the following scheme is proposed for the photo-oxidation of acetic acid by U(VI) :



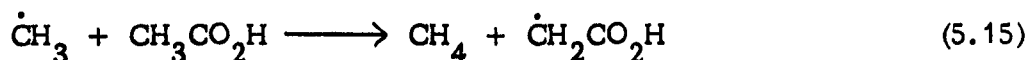
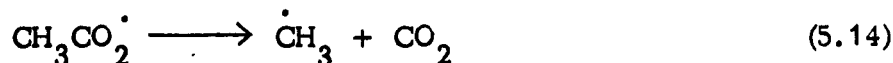
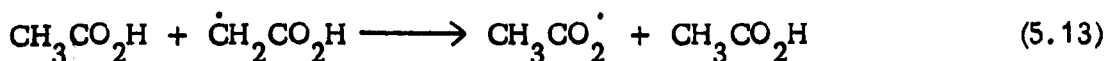
Reaction (5.8) is a well-established reaction of the acetoxy radical.²⁶⁸ An alternative means of producing ethane involves both radical species observed and gives propionic acid which is known to yield ethane upon photoreaction with U(VI) (section 2.2.1) :



It is more difficult to formulate a scheme for sensitized decarboxylation of organic acids. The primary step is one of H-atom abstraction :

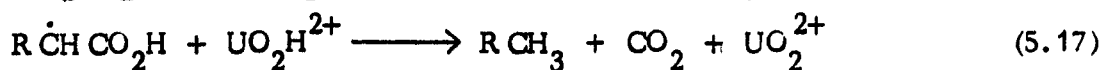
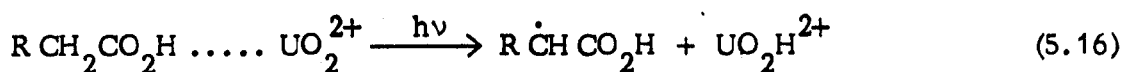


Possible secondary reactions of $\text{R}\dot{\text{C}}\text{HCO}_2\text{H}$ are dimerisation, reduction or oxidation of a uranium species and H-atom abstraction. A dimerisation process does not yield the observed products and reduction of U(VI) or U(V) is unlikely as $\text{R}\dot{\text{C}}\text{HCO}_2\text{H}$ is not a particularly strong reducing agent ($-\text{CO}_2\text{H}$ not being a +M group²⁶¹) and also a process involving oxidation of uranium is sought to account for the lack of U(IV) as product. $\text{R}\dot{\text{C}}\text{HCO}_2\text{H}$ may possibly react in an analogous fashion to $\dot{\text{C}}\text{H}_2\text{CO}_2\text{H}$ at 77 K²⁰¹ :



This chain scheme accounts for production of CH_4 but not for the reoxidation of U(IV) or U(V).

In the absence of a more specific scheme, therefore, the photosensitized decarboxylation of carboxylic acids is represented as follows :

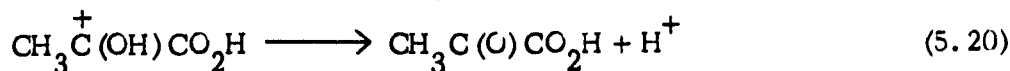
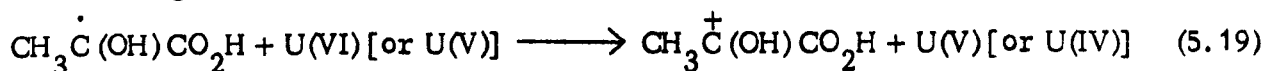
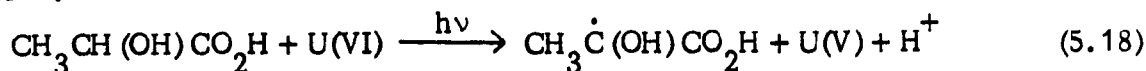


In this scheme the radical $\text{R}\dot{\text{C}}\text{HCO}_2\text{H}$ acts in an oxidising rôle, in contrast to $\text{R}\dot{\text{C}}\text{HOH}$ which is a reducing agent. Waters²⁶⁹ has put forward the concept that two oxidation-reduction potentials, $E_{(+e)}$ and $E_{(-e)}$ may be assigned to any free radical and has shown that the species $\dot{\text{C}}\text{H}(\text{CO}_2\text{H})_2$ has comparable values (~ 1.1 V) for both $E_{(+e)}$ and $E_{(-e)}$, being capable of both reducing Mn(III) and oxidising Mn(II).²⁷⁰ It is justifiable, therefore, to formulate a scheme in which the radical $\dot{\text{C}}\text{H}_2\text{CO}_2\text{H}$, which is expected to be an oxidising agent due to the inductive effect of the carboxyl group, accomplishes the oxidation of U(V) to U(VI) (reaction 5.17) for which the oxidation potential is -0.063 V.

This scheme would also explain the production of CO_2 and $\text{CH}_3\text{CO}_2\text{H}$ and the observation of the radical $\text{HO}_2\text{C}\dot{\text{C}}\text{HCO}_2\text{H}$ with malonic acid. In the absence of reports of other organic products, however, it must be assumed that the radicals $\dot{\text{C}}\text{H}_2\text{CO}_2\text{H}$ and $\dot{\text{C}}\text{H}_2\text{CH}_2\text{CO}_2\text{H}$ observed with malonic and succinic acids respectively are exclusive to reactions in the solid state.

The reactions with lactic acid clearly proceed according to the following schemes :

At pH 1 :

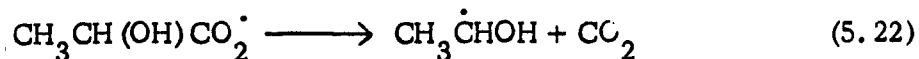
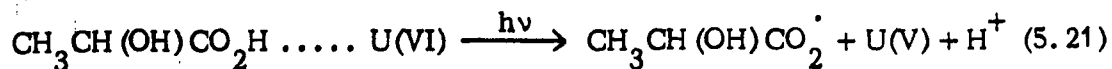


Reaction (5.19) occurs in preference to a reaction similar to (5.17) because the -OH group renders the radical a strong reducing agent.

This scheme also applies to lactic acid in the liquid state and to n-butyl lactate

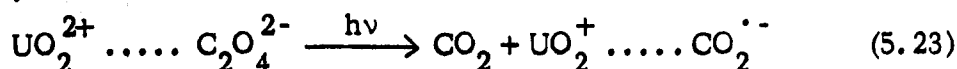
in both solid and liquid states in all of which cases the radical $\text{CH}_3\dot{\text{C}}(\text{OH})\text{CO}_2\text{R}$ was detected.

At pH 7 :



$\text{CH}_3\dot{\text{C}}\text{HOH}$ is then oxidised to CH_3CHO as described on page 56 (reactions (5.3), (5.4)).

The singlet obtained from oxalic acid has a rather high averaged g-value (2.0044) for a σ radical such as free $\text{CO}_2\dot{}^-$; however, Heidt *et al.*¹³³ propose a scheme for the photo-oxidation of oxalic acid in which the primary step produces complexed $\text{CO}_2\dot{}^-$:



The neighbouring heavy U atom may exert a strong g-shift and it is perhaps significant that the g-factor of $\text{CO}_2\dot{}^-$ formed during γ -irradiation of a large number of metal oxalates lies in the range 1.9991 to 2.0053.²⁷¹

5.3.3 Aldehydes and Ketones

It is evident that H-atom abstraction occurs with all the compounds studied from the more highly substituted carbon atom adjacent to the carbonyl function, but that with the lower members both this process and one of C - C cleavage prevail. The unsaturated ketones yield allylic-type radicals by a process of C - H fission.

The results are in contrast to those from Ce(IV) photoreaction which produces acyl radicals from aldehydes and simple ketones.²³³

5.3.4 Esters

These compounds parallel their parent acids in behaviour towards excited U(VI); formates yield $\dot{\text{C}}\text{O}_2\text{R}$ species, acetates produce $\dot{\text{C}}\text{H}_2\text{CO}_2\text{R}$ with some $\dot{\text{C}}\text{H}_3$, while abstraction of an α -hydrogen atom is exclusive for methyl propionate (to give $\text{CH}_3\dot{\text{C}}\text{HCO}_2\text{CH}_3$), isopropyl n-butyrate (to give $\text{CH}_3\text{CH}_2\dot{\text{C}}\text{HCO}_2\text{C}_3\text{H}_7$), isopropyl isobutyrate (to give $(\text{CH}_3)_2\dot{\text{C}}\text{CO}_2\text{C}_3\text{H}_7$), n-butyl lactate (to give $\text{CH}_3\dot{\text{C}}(\text{OH})\text{CO}_2\text{C}_4\text{H}_9$) and methyl and ethyl crotonates (to give the allylic radicals $\dot{\text{C}}\text{H}_2\text{CHCHCO}_2\text{R}$).

The similarity in primary products does not necessarily indicate analogous mechanisms for reactions of acids and esters with U(VI); for example, the production

of $\dot{\text{C}}\text{H}_3$ from methyl and ethyl acetates could not occur by the same process as for acetic acid (reactions (5.7), (5.8)) and in this connection it is worthwhile to note that Ce(IV) photo-oxidises acids and esters in completely different fashions at 77 K, operating by C - C fission in the former case²¹⁸ and mainly by H-abstraction in the latter.²³³

5.3.5 Amides

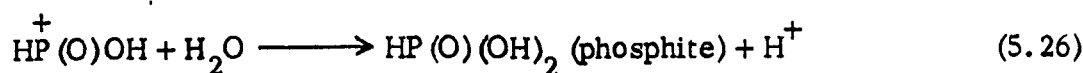
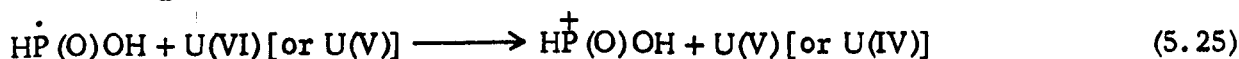
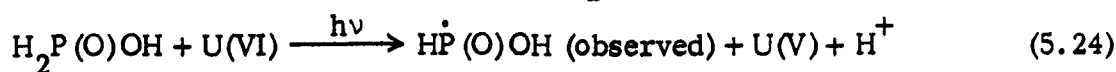
H-atom abstraction is the major mode of photo-oxidation, with a preference for removal of the hydrogen atom from an N-alkyl group when available. Thus, while formamide produces $\dot{\text{C}}\text{ONH}_2$, N,N-dimethylformamide and N,N-diethylformamide yield $\text{HCON}(\text{CH}_3)\dot{\text{C}}\text{H}_2$ and $\text{HCON}(\text{C}_2\text{H}_5)\dot{\text{C}}\text{HCH}_3$ respectively, and while acetamide and propionamide give $\dot{\text{C}}\text{H}_2\text{CONH}_2$ and $\text{CH}_3\dot{\text{C}}\text{HCONH}_2$, N,N-dimethylacetamide produces $\text{CH}_3\text{CON}(\text{CH}_3)\dot{\text{C}}\text{H}_2$. Direct photolysis of formamide, acetamide and N-methyl derivatives of these compounds invariably produces radicals of the type $\dot{\text{C}}\text{ONR}_2$.²³⁶

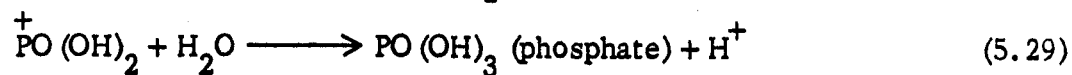
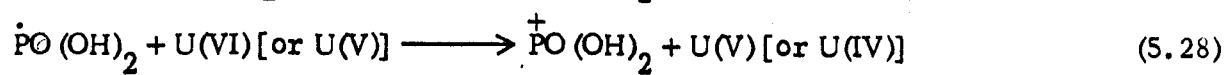
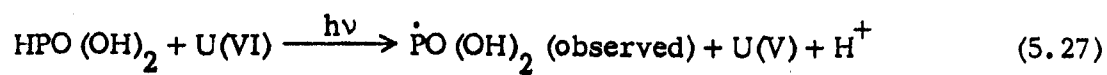
5.3.6 Ethers

These compounds are rather inert to thermal one-electron oxidants of high redox potential but are readily oxidised by excited U(VI) to produce $\dot{\text{C}}_2\text{H}_5$ from diethyl ether in the solid state and products arising from H-abstraction from dimethoxyethane and 2-methoxyethanol in the liquid state. The latter case is of interest as it appears that the ethereal oxygen is a more efficient activator for α -hydrogen abstraction than the hydroxylic oxygen atom.

5.3.7 P(III) Compounds

Phosphorus appears to be an efficient activating atom for H-abstraction by photo-excited uranyl ions, phosphorus-centred radicals derived from reactions of this type having been produced from the three compounds studied. Products of the photoreaction of uranyl salts with sodium hypophosphite in acidic media have been reported as U(IV)^{272, 273} with phosphite and phosphate,²⁷² the reaction probably proceeding according to the following scheme, where $\text{HP}^{\dot{}}(\text{O})\text{OH}$ is equivalent in acid solution to the observed $\text{HPO}_2^{\cdot-}$ plus H^+ :





CHAPTER 6

**STUDIES ON THE PHOTOREACTIVE
STATE OF THE URANYL ION**

6. STUDIES ON THE PHOTOREACTIVE STATE OF THE URANYL ION

6.1 Absorption Spectrum of Excited State UO_2^{2+}

Nanosecond flash photolysis of solutions of uranyl perchlorate and nitrate in water ($2 \times 10^{-2} \text{ mol dm}^{-3}$) at room temperature produced a transient absorption in the range 400 to 700 nm which decayed according to first-order kinetics with a half-life, $t_{1/2}$, of $1.05 \mu\text{s}$ ($k = 6.57 \times 10^5 \text{ s}^{-1}$). A point-to-point spectrum constructed from optical density measurements of the absorption taken immediately after excitation revealed a broad band with $\lambda_{\text{max}} \sim 600 \text{ nm}$. This is shown in figure 20 together with the spectrum obtained spectrographically by flashing aqueous uranyl perchlorate ($2 \times 10^{-2} \text{ mol dm}^{-3}$) in the conventional microsecond apparatus at room temperature. The spectra exhibit the barest semblance of fine structure but this appeared to be reproducible and dilute solutions of uranyl salts in various viscous media were examined under conditions of high resolution in an attempt to improve the spectra. It was found that all the spectra were characterised by, normally, five vibrational bands of approximately constant separation. In the following list these bands are denoted A to E and the separation between two bands is represented by Δ . The uranyl ion concentration was $2 \times 10^{-2} \text{ mol dm}^{-3}$ except in the case of uranyl sulphate in sulphuric acid where it was $5 \times 10^{-3} \text{ mol dm}^{-3}$ and the experiments were performed at room temperature unless otherwise stated.

Uranyl perchlorate / water :

$\lambda_{\text{max}} = 574 \text{ nm}$	$\lambda_{\text{B}} = 551 \text{ nm}$	$\lambda_{\text{C}} = 569 \text{ nm}$
	$\lambda_{\text{D}} = 586 \text{ nm}$	$\lambda_{\text{E}} = 604 \text{ nm}$
	$\Delta_{\text{BC}} = 574 \text{ cm}^{-1}$	$\Delta_{\text{CD}} = 510 \text{ cm}^{-1}$
	$\Delta_{\text{DE}} = 509 \text{ cm}^{-1}$	$\Delta_{\text{av}} = 531 \text{ cm}^{-1}$

Uranyl sulphate / water (figure 21a) :

$\lambda_{\text{max}} = 572 \text{ nm}$	$\lambda_{\text{A}} = 530 \text{ nm}$	$\lambda_{\text{B}} = 548 \text{ nm}$	$\lambda_{\text{C}} = 569 \text{ nm}$
		$\lambda_{\text{D}} = 589 \text{ nm}$	$\lambda_{\text{E}} = 610 \text{ nm}$
	$\Delta_{\text{AB}} = 620 \text{ cm}^{-1}$	$\Delta_{\text{BC}} = 673 \text{ cm}^{-1}$	$\Delta_{\text{CD}} = 597 \text{ cm}^{-1}$
		$\Delta_{\text{DE}} = 584 \text{ cm}^{-1}$	$\Delta_{\text{av}} = 619 \text{ cm}^{-1}$

FIGURE 20

Flash photolysis spectra of solutions of uranyl salts

- Full line - spectrographic recording of absorption from aqueous uranyl perchlorate ($2 \times 10^{-2} \text{ mol dm}^{-3}$) following μs flash
 - X - photoelectrically recorded absorptions upon laser flash photolysis of aqueous uranyl perchlorate ($2 \times 10^{-2} \text{ mol dm}^{-3}$)
 - +
- analogous experiments with uranyl nitrate

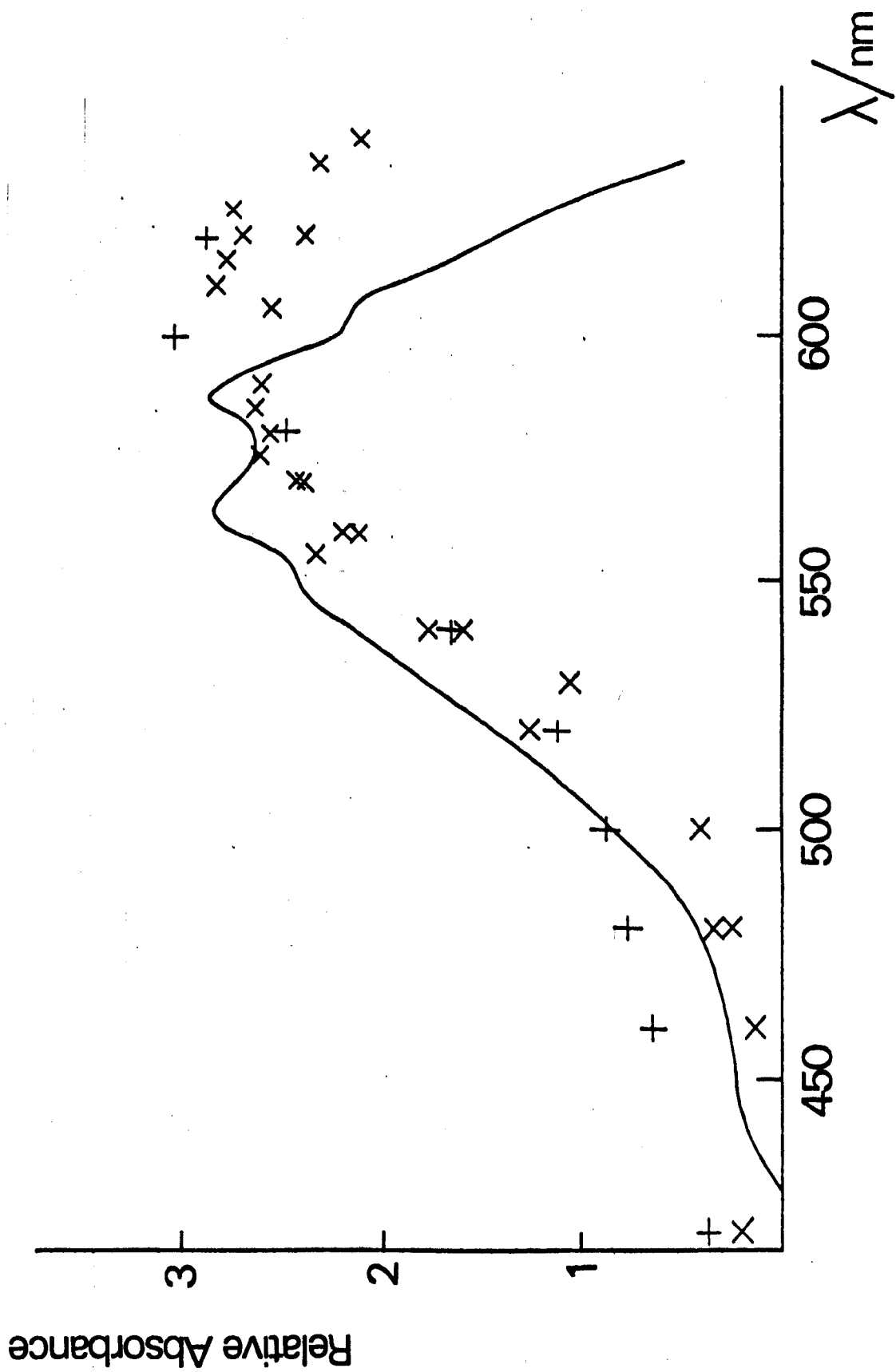
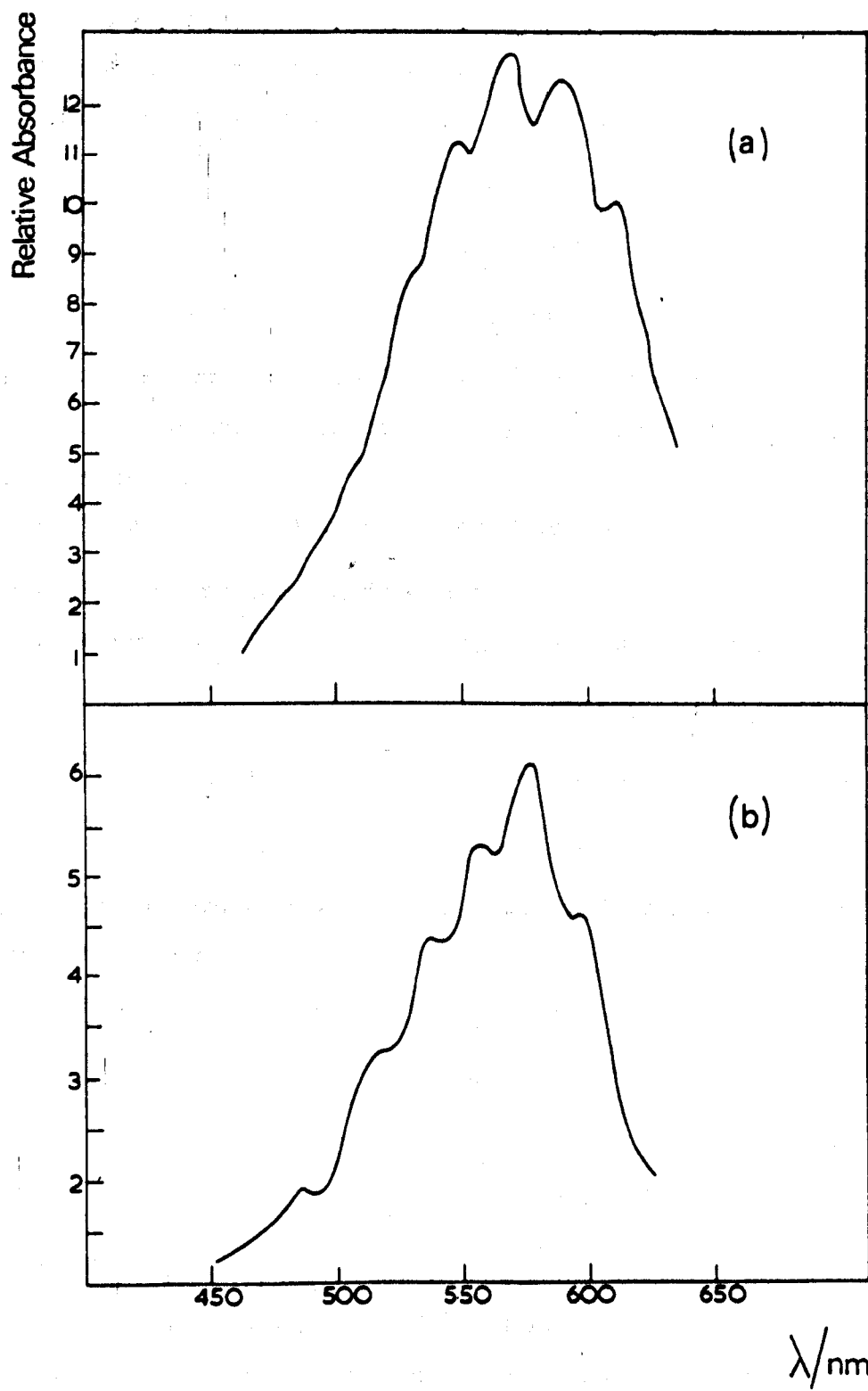


FIGURE 21

Flash photolysis spectra of solutions
of uranyl sulphate ($2 \times 10^{-2} \text{ mol dm}^{-3}$)

- (a) μs (spectrographic) spectrum from aqueous uranyl sulphate
- (b) Low temperature (215 K) μs (spectrographic) spectrum from
uranyl sulphate in 50/50 (v/v) H_3PO_4 - HClO_4



Uranyl perchlorate / water-acetone (50/50) :

Spectral parameters were the same as for uranyl perchlorate / water but the intensity was reduced by ~50%.

Uranyl sulphate / concentrated sulphuric acid :

$$\begin{array}{llll} \lambda_{\max} = 579 \text{ nm} & \lambda_A = 534 \text{ nm} & & \lambda_C = 569 \text{ nm} \\ & & \lambda_D = 589 \text{ nm} & \lambda_E = 611 \text{ nm} \\ & \Delta_{AB} + \Delta_{BC} = 1152 \text{ cm}^{-1} & \Delta_{CD} = 597 \text{ cm}^{-1} & \\ & \Delta_{DE} = 611 \text{ cm}^{-1} & \Delta_{av} = 590 \text{ cm}^{-1} & \end{array}$$

Sodium uranate / concentrated sulphuric acid : (Sodium uranate was made by adding aqueous uranyl sulphate to dilute sodium hydroxide solution and filtering off the precipitate)

$\lambda_{\max} = 578 \text{ nm}$ Fine structure was poorly resolved.

Uranyl sulphate / orthophosphoric acid :

$$\begin{array}{llll} \lambda_{\max} = 555 \text{ nm} & \lambda_A = 524 \text{ nm} & \lambda_B = 540 \text{ nm} & \lambda_C = 557 \text{ nm} \\ & & \lambda_D = 575 \text{ nm} & \lambda_E = 595 \text{ nm} \\ & \Delta_{AB} = 565 \text{ cm}^{-1} & \Delta_{BC} = 565 \text{ cm}^{-1} & \Delta_{CD} = 562 \text{ cm}^{-1} \\ & & \Delta_{DE} = 585 \text{ cm}^{-1} & \Delta_{av} = 569 \text{ cm}^{-1} \end{array}$$

Uranyl sulphate / orthophosphoric acid - 72% perchloric acid (50/50)

at 215 K (figure 21b) :

$$\begin{array}{llll} \lambda_{\max} = 573 \text{ nm} & \lambda_A = 518 \text{ nm} & \lambda_B = 537 \text{ nm} & \lambda_C = 557 \text{ nm} \\ & & \lambda_D = 578 \text{ nm} & \lambda_E = 598 \text{ nm} \\ & \Delta_{AB} = 683 \text{ cm}^{-1} & \Delta_{BC} = 669 \text{ cm}^{-1} & \Delta_{CD} = 652 \text{ cm}^{-1} \\ & & \Delta_{DE} = 578 \text{ cm}^{-1} & \Delta_{av} = 646 \text{ cm}^{-1} \end{array}$$

In addition to the above, a cylinder of soda-glass containing dissolved uranyl sulphate at a concentration of $2 \times 10^{-2} \text{ mol dm}^{-3}$ was examined. The cylinder was approximately 113 mm long and 16 mm in diameter and consisted of three short rods cemented together with Canada balsam and with optically polished ends. It was found that any absorption in the region of 590 nm was masked by the intense uranyl emission which decayed with a half-life of $1.75 \times 10^{-4} \text{ s}$, a value comparable to the range $2.8 \times 10^{-4} \text{ s}$ to $1.1 \times 10^{-3} \text{ s}$ obtained by various authors

in similar media (page 6 and reference 22n).

The overall shape and λ_{\max} of the absorption spectra correspond with those previously reported on flashing inorganic glasses doped with U(VI)^{274, 275} and a recent paper by Rygalov *et al.*²⁷⁶ reports a similar spectrum upon flash photolysis of U(VI) in orthophosphoric acid. None of these spectra, however, exhibit any appreciable vibronic structure and the excited state absorption has not previously been observed in water.

The production of the transient spectrum in each one of the different solvents detailed above and also the similarity in the spacing of the vibrational bands with those of the ground state UO_2^{2+} ion ($\sim 855 \text{ cm}^{-1}$ as manifest by the luminescence spectrum) and the lowest (triplet) excited state ($\sim 715 \text{ cm}^{-1}$, observed in the ground state absorption spectrum)²⁸ suggest that the absorbing species is an excited uranyl ion, the absorption probably involving promotion of an electron to an antibonding orbital to account for the low value of the average separation of the vibrational bands ($\sim 580 \text{ cm}^{-1}$). In addition, the lifetime of this species in water ($1.52 \times 10^{-6} \text{ s}$) is in good agreement with the previously estimated lifetime for uranyl ion luminescence of $1.5 \times 10^{-6} \text{ s}$ ⁸³ (page 8) and addition of a number of organic compounds known to quench the luminescence of aqueous uranyl salts (e.g. methanol, lactic acid) caused shortening of the transient lifetime. The correlation between the quenching of uranyl ion luminescence and of the transient absorption lifetime was therefore studied in greater detail.

6.2 Reaction Kinetics of Excited State UO_2^{2+}

The work described in this section concerns the effects of various organic compounds and their deuterated analogues on the decay characteristics both of the transient absorption and the luminescence of the uranyl ion and of integrated luminescence intensities, and attempts to reveal the nature of the 575 nm transient and the mode of its reaction with organic molecules.

The following nomenclature is used in this section :

methanol - d ₁	≡	CH_3OD
methanol - d ₃	≡	CD_3OH
methanol - d ₄	≡	CD_3OD
isopropanol - d ₇	≡	$(\text{CD}_3)_2\text{CDOH}$
isopropanol - d ₈	≡	$(\text{CD}_3)_2\text{CDOD}$
cyclohexanol - d ₁₁	≡	$\text{C}_6\text{D}_{11}\text{OH}$
cyclohexanol - d ₁₂	≡	$\text{C}_6\text{D}_{11}\text{OD}$

The following studies were made :

Methanol and Methanol - d₃ (Methanol and Methanol - d₄ in H₂O)

Uranyl ion luminescence intensity quenching in H₂O

Uranyl ion luminescence lifetime quenching in H₂O

Transient lifetime quenching in H₂O

Transient lifetime quenching in orthophosphoric acid (the slower decay of the transient in this medium enabled this study to be made on the microsecond flash photolysis apparatus).

Methanol - d₁ and Methanol - d₄ (Methanol and Methanol - d₄ in D₂O)

Transient lifetime quenching in D₂O

Isopropanol and Isopropanol - d₇ (Isopropanol and Isopropanol - d₈ in H₂O)

Uranyl ion luminescence intensity quenching in H₂O

Transient lifetime quenching in H₂O

Cyclohexanol and Cyclohexanol - d₁₁ (Cyclohexanol and Cyclohexanol - d₁₂ in H₂O)

Uranyl ion luminescence intensity quenching in H₂O

Transient lifetime quenching in H₂O

All the decay traces obtained followed strict first-order kinetics, usually for at least three half-lives, and typical analyses of the data from a nanosecond flash photolysis experiment (by the program FPDATA) and of a luminescence lifetime experiment (by the program AUTOPLOT) are shown in figures 22 and 23 respectively. The decays may be represented by the following equations :

$$-d[(\text{UO}_2^{2+})^*]/dt = k'_{\text{tr}}[(\text{UO}_2^{2+})^*] \quad (6.1)$$

$$-d[(\text{UO}_2^{2+})^*]/dt = k'_{\text{lum}}[(\text{UO}_2^{2+})^*] \quad (6.2)$$

where k'_{tr} and k'_{lum} are the pseudo first-order decay constants for the transient absorption and the uranyl ion luminescence respectively.

It became clear that the lifetime of the 575 nm transient was reduced upon addition of alcohols in a way strictly dependent on the alcohol concentration. k'_{tr} , k'_{lum} , and $I_{\text{fo}}/I_{\text{f}}$ were plotted against [alcohol] and in every case a linear relationship was found. The graphs are exhibited in figures 24 and 25 (methanol and methanol - d₃), 26 (methanol - d₁ and methanol - d₄), 27 (isopropanol and isopropanol - d₇) and 28 (cyclohexanol and cyclohexanol - d₁₁). The slopes of these graphs furnished the second-order rate constants k_{tr} and k_{lum} and the Stern-Volmer quenching constant K_{q} where :

FIGURE 22

A typical analysis by the computer program FPDATA of the transient decay during a laser flash photolysis experiment. (In this case the sample was a solution of uranyl perchlorate (0.25 mol dm^{-3}) and methanol ($0.287 \text{ mol dm}^{-3}$) in H_2O).

FPDATA RUN NO 6141

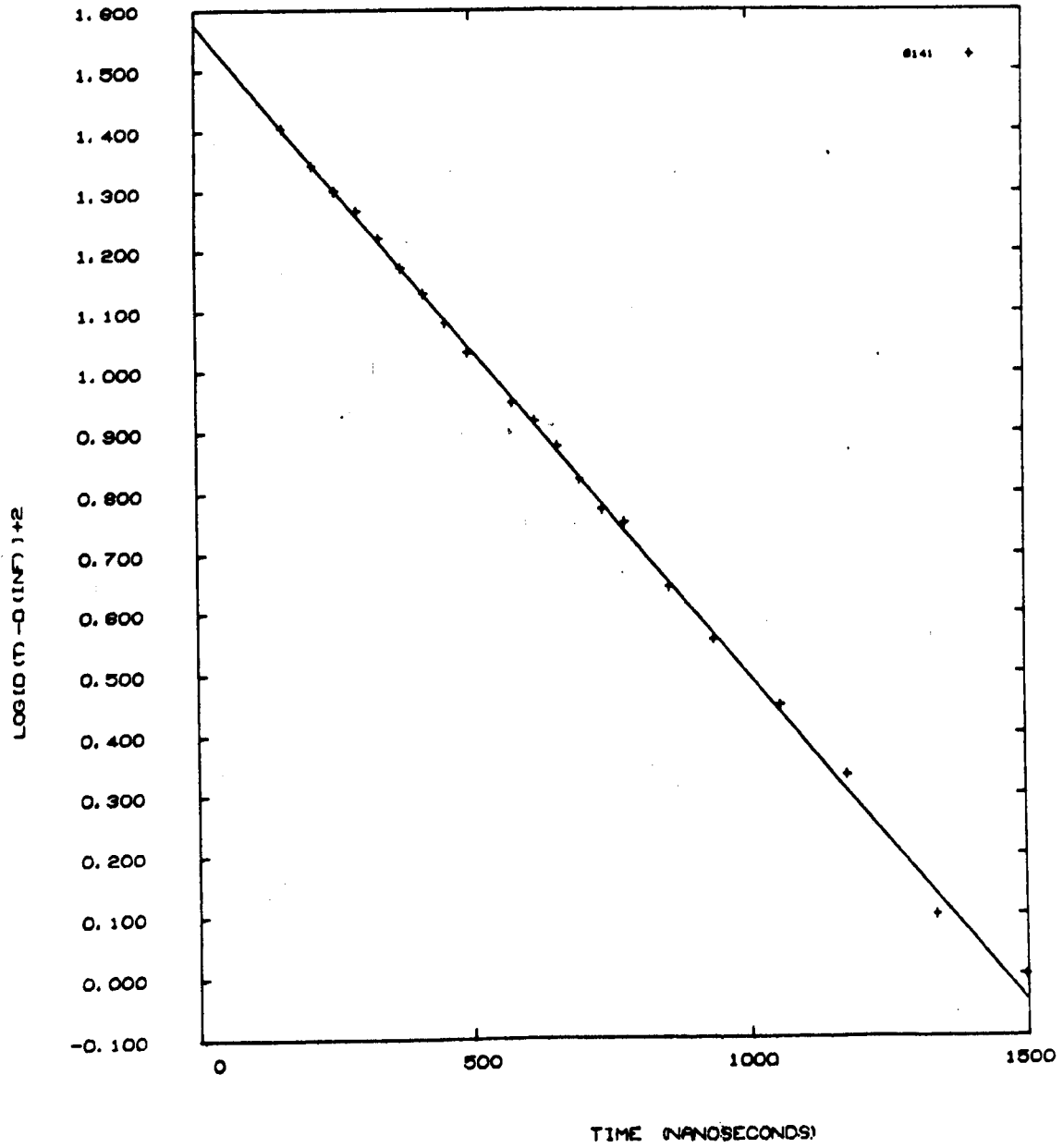


FIGURE 23

A typical analysis by the computer program AUTOPLOT of the luminescence decay during a single photon counting experiment. (In this case the sample was a solution of uranyl perchlorate ($0.114 \text{ mol dm}^{-3}$) and methanol- d_4 (0.69 mol dm^{-3}) in H_2O).

SINGLE PHOTON RUN 5

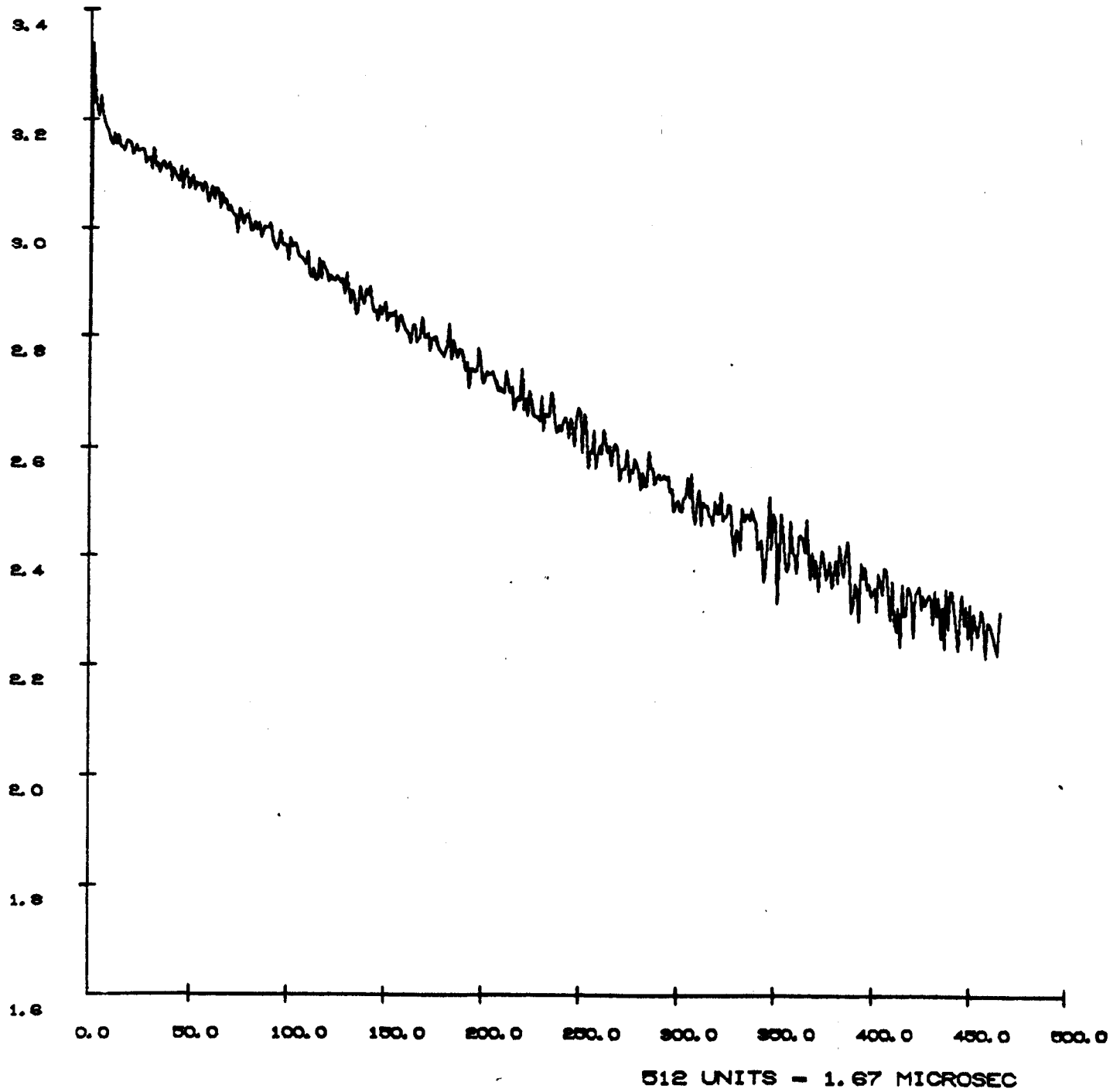


FIGURE 24

- (a) Plot of the first order decay constant (k'_{tr}) for the 575 nm transient versus concentration of alcohol after laser flash photolysis of aqueous uranyl perchlorate in the presence of added methanol (H) and methanol- d_3 (D).
- (b) Stern-Volmer plot for the quenching of the luminescence intensity of aqueous uranyl perchlorate by added methanol (H) and methanol- d_3 (D).

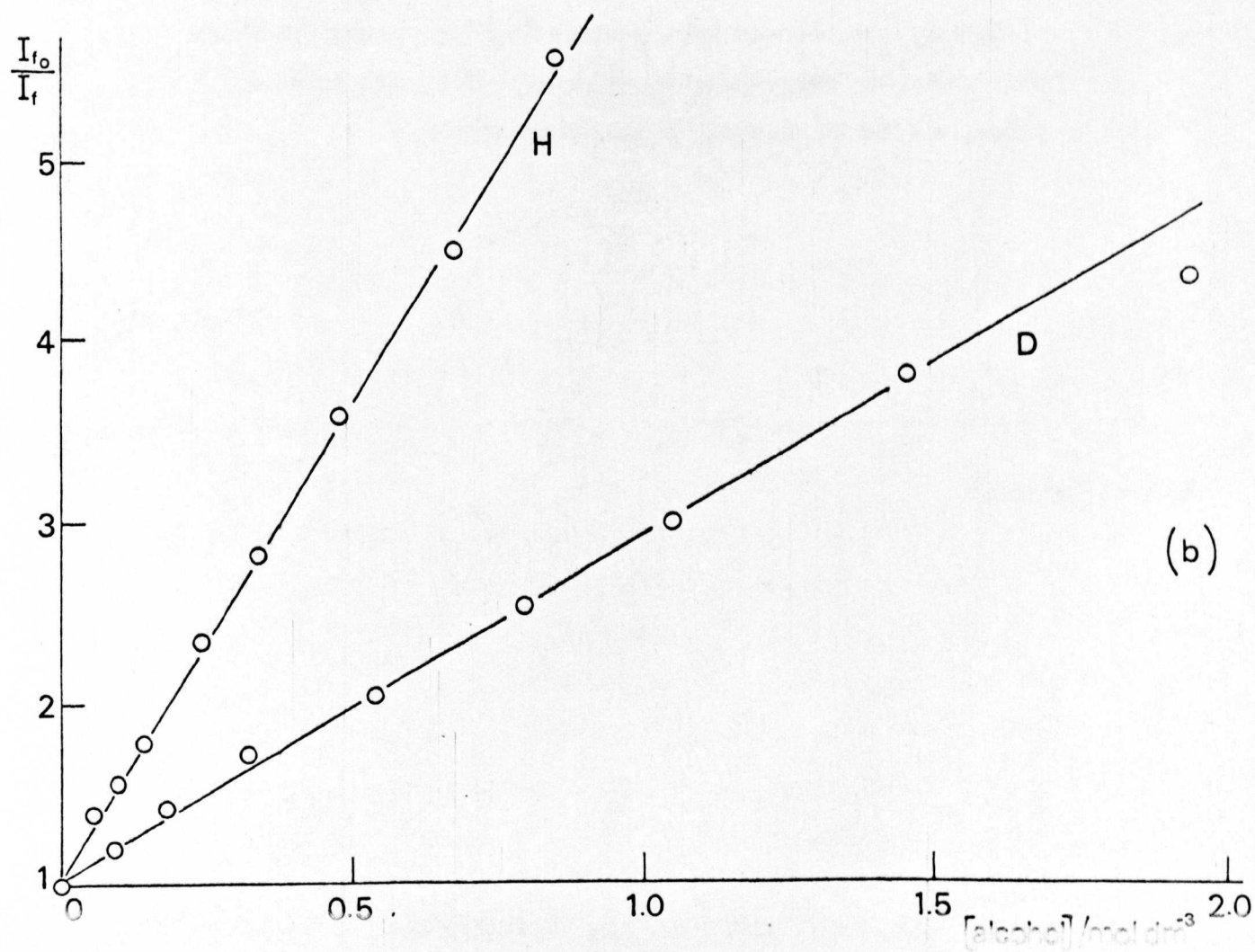
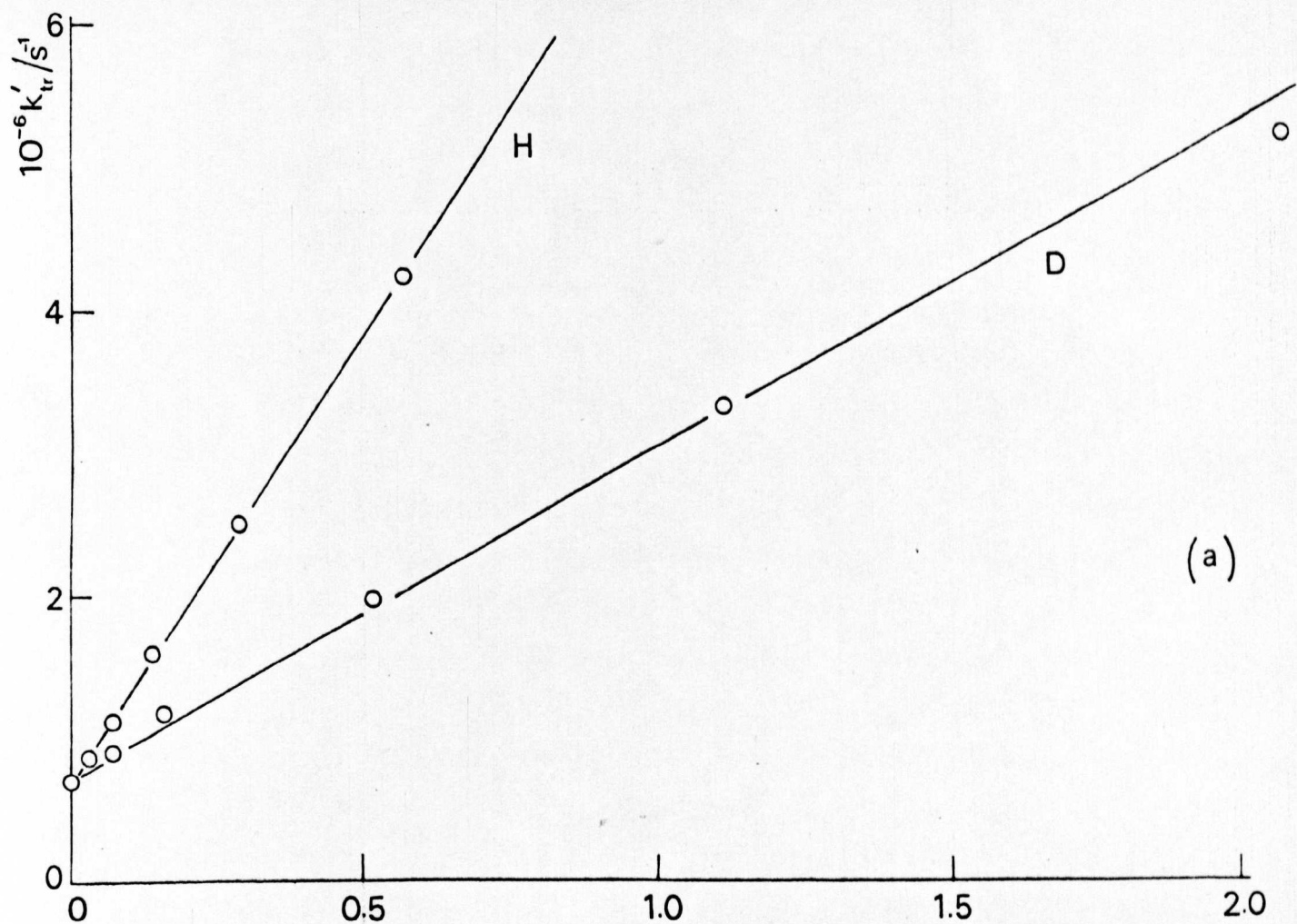


FIGURE 25

Plot of the first order decay constant (k'_{lum}) for the luminescence of the uranyl ion versus concentration of alcohol during the single photon counting experiments on aqueous uranyl perchlorate in the presence of added methanol (H) and methanol- d_3 (D).

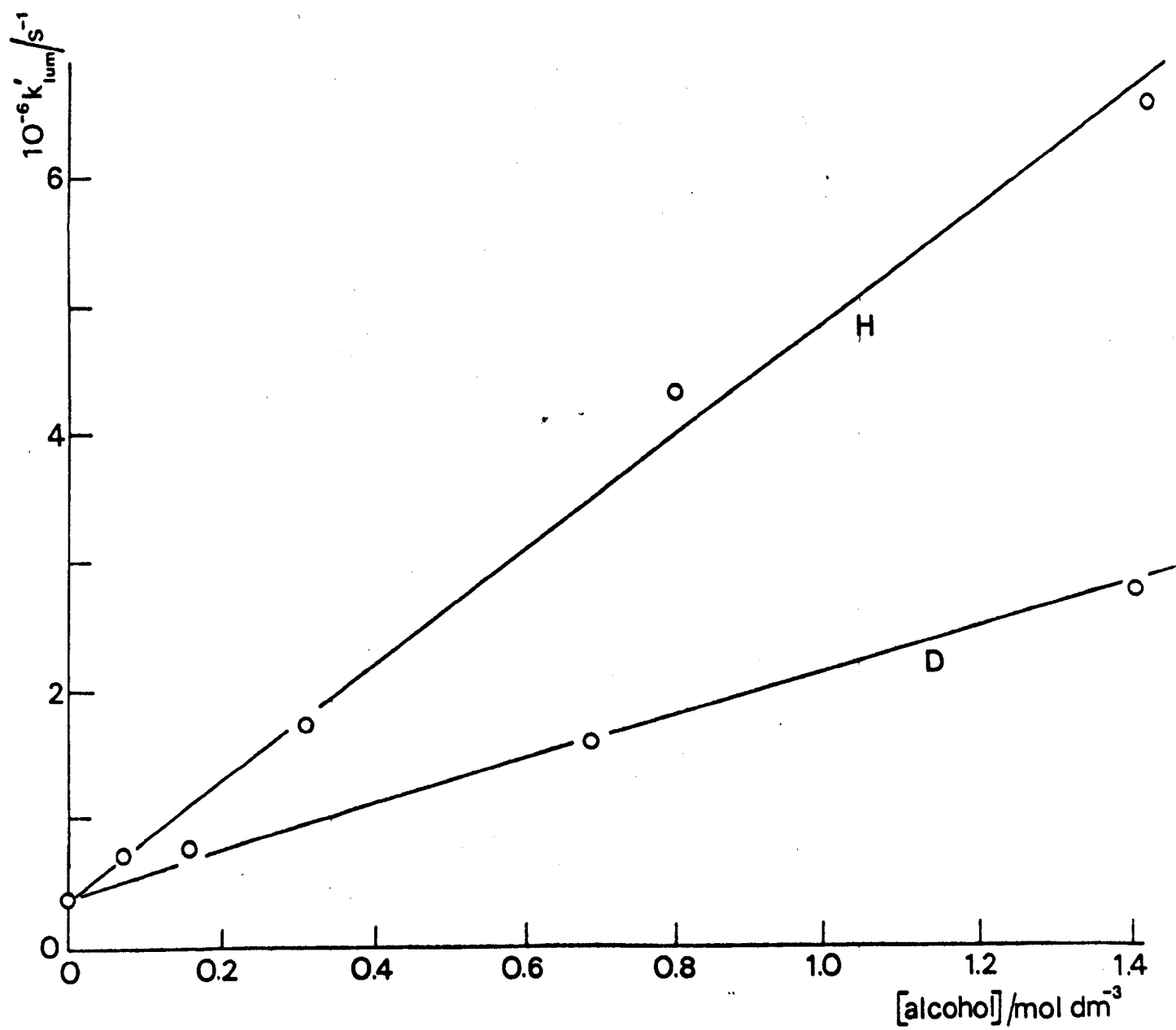


FIGURE 26

Plot of the first order decay constant (k'_{tr}) for the 575 nm transient versus concentration of alcohol after the laser flash photolysis of a solution of uranyl perchlorate in D_2O in the presence of added methanol- d_1 (H) and methanol- d_4 (D).

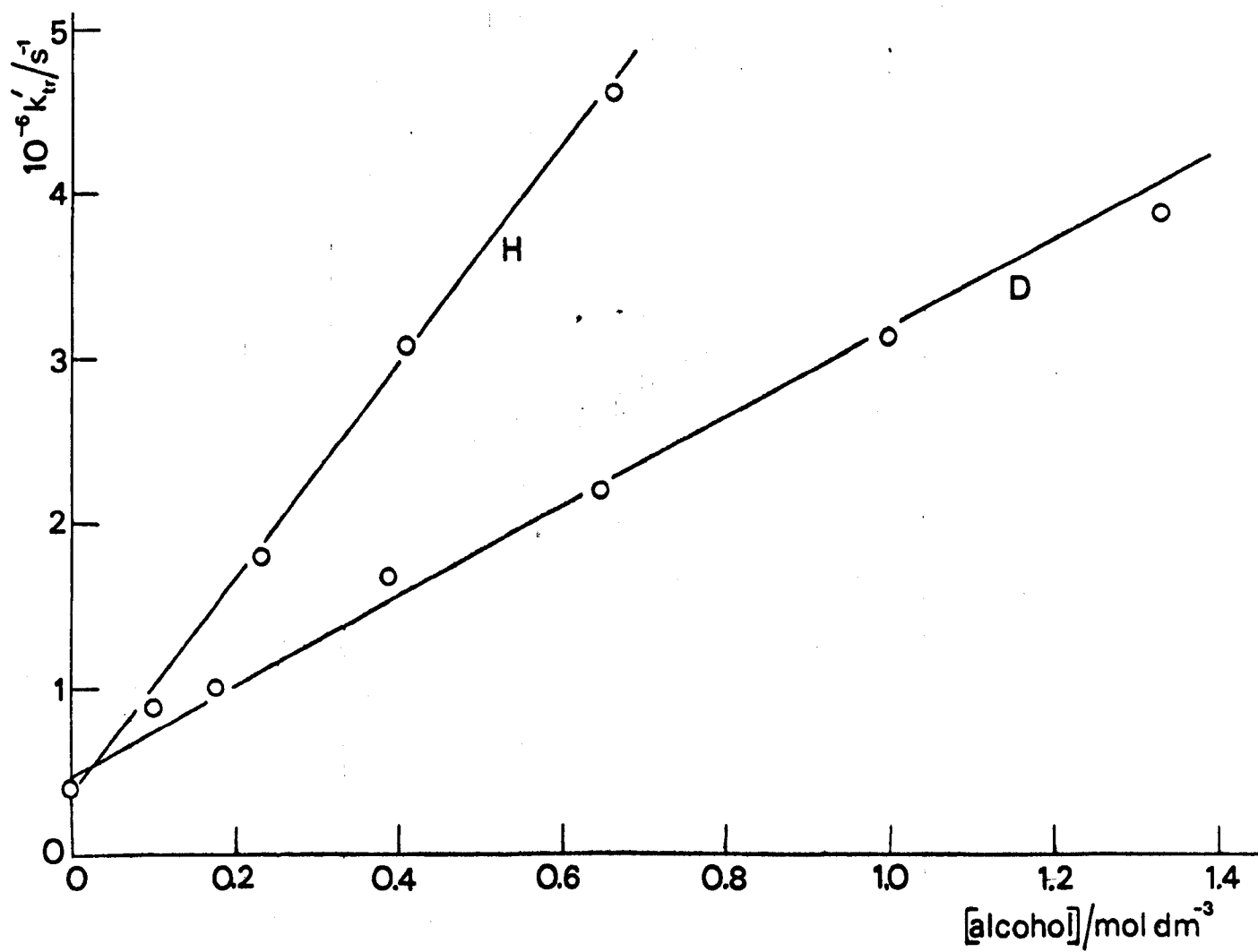


FIGURE 27

- (a) Plot of the first order decay constant (k'_{tr}) for the 575 nm transient versus concentration of alcohol after laser flash photolysis of aqueous uranyl perchlorate in the presence of added isopropanol (propan-2-ol) and isopropanol- d_7 .
- (b) Stern-Volmer plot for the quenching of the luminescence intensity of aqueous uranyl perchlorate by added isopropanol (propan-2-ol) and isopropanol- d_7 .

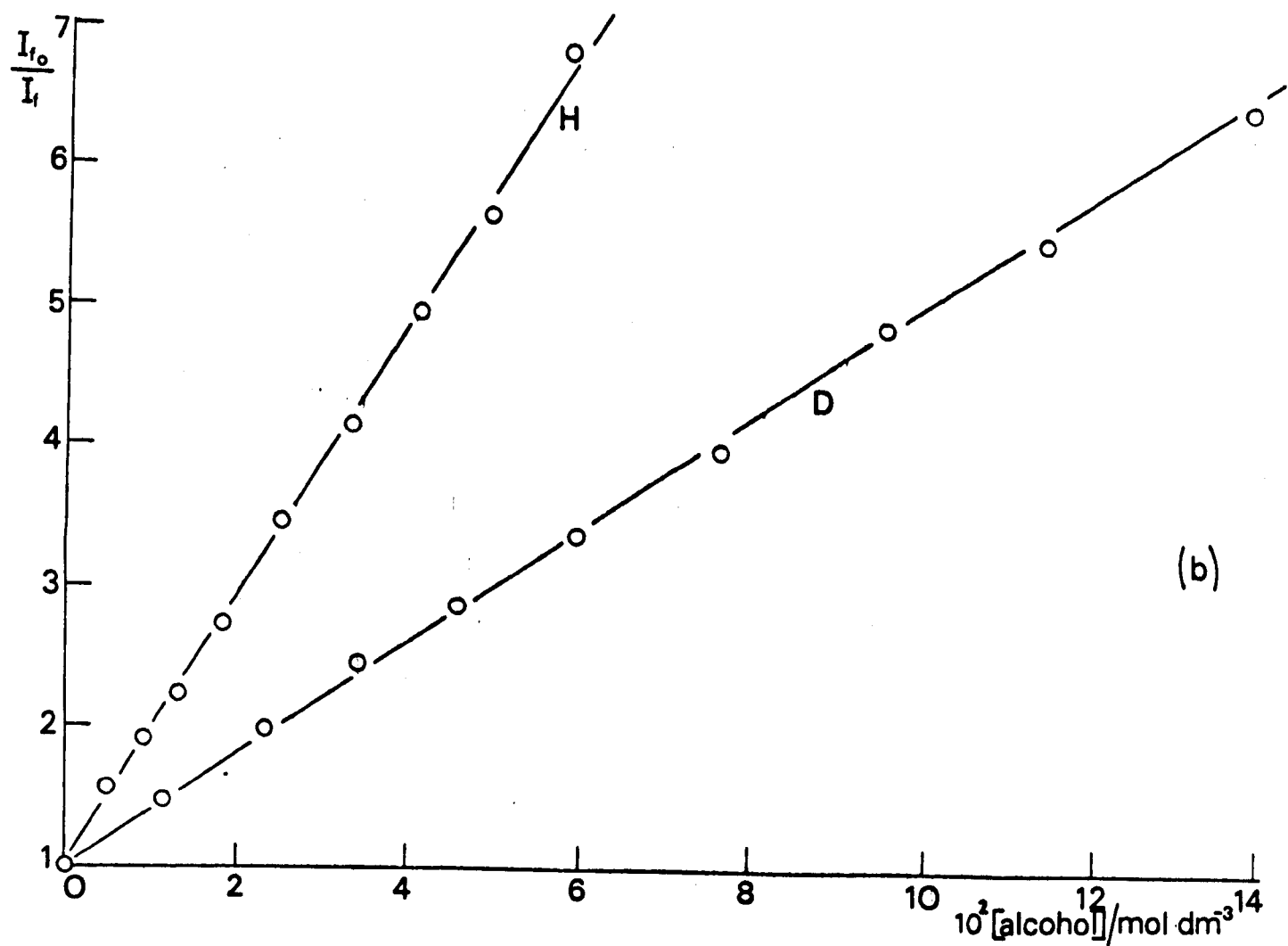
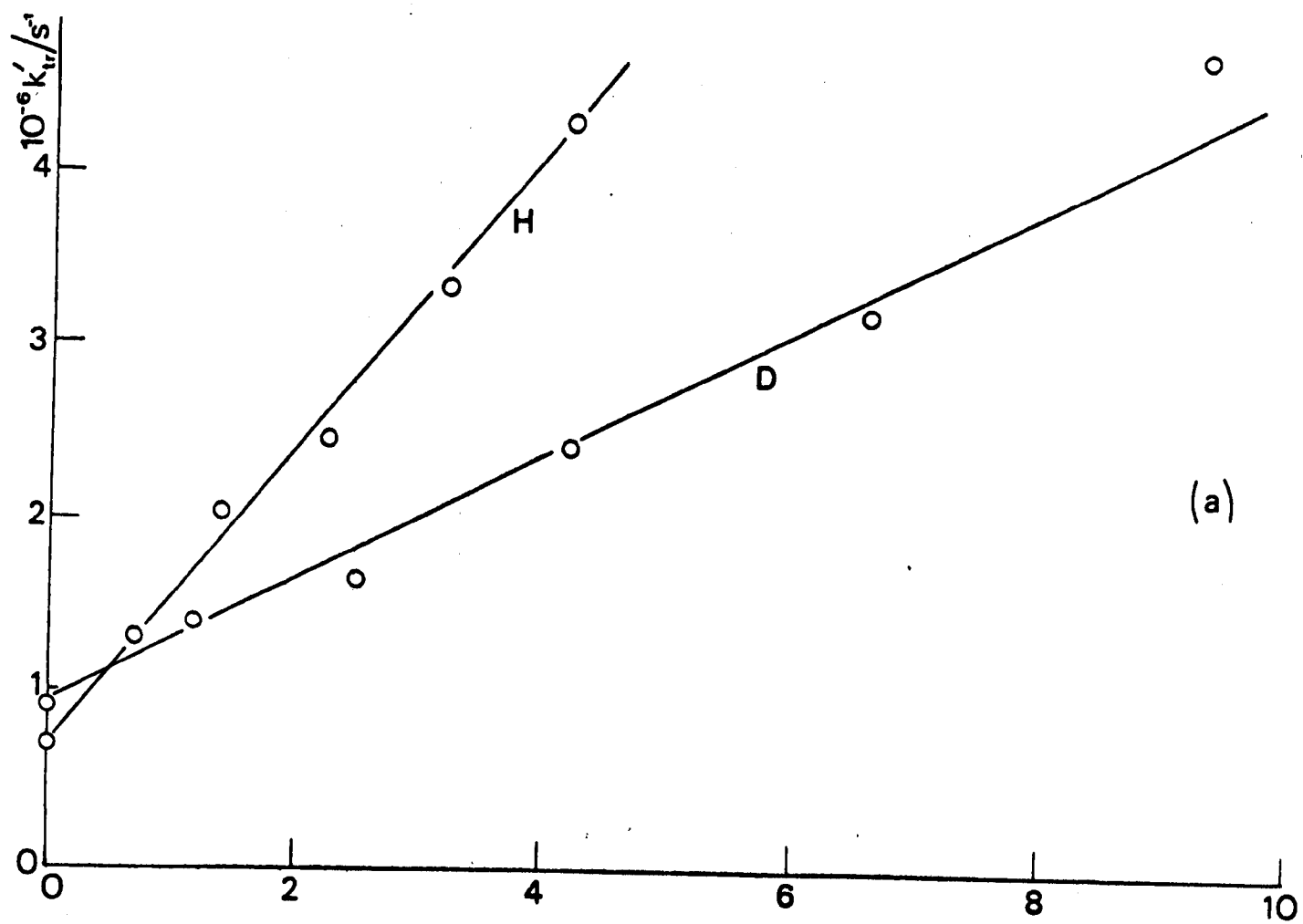
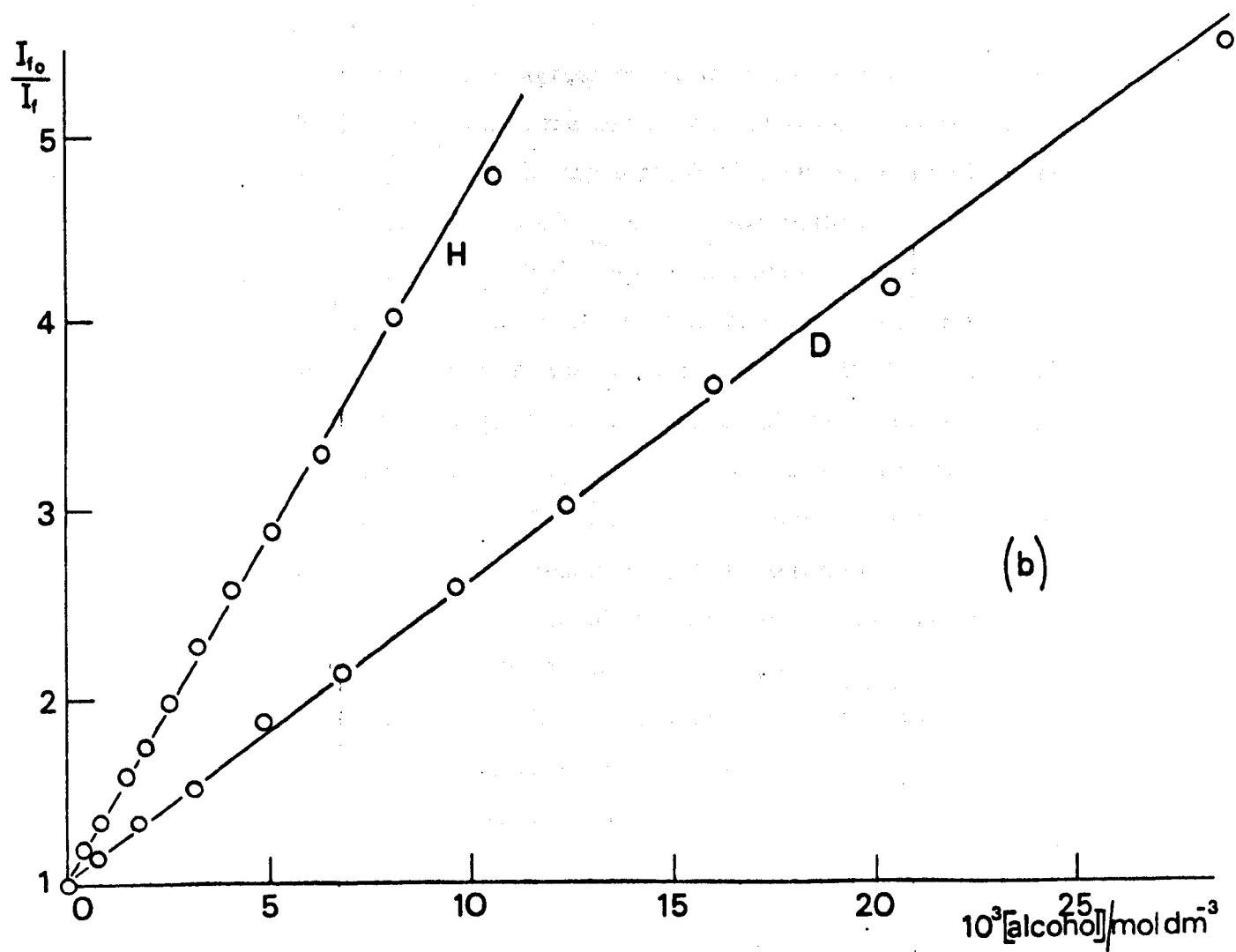
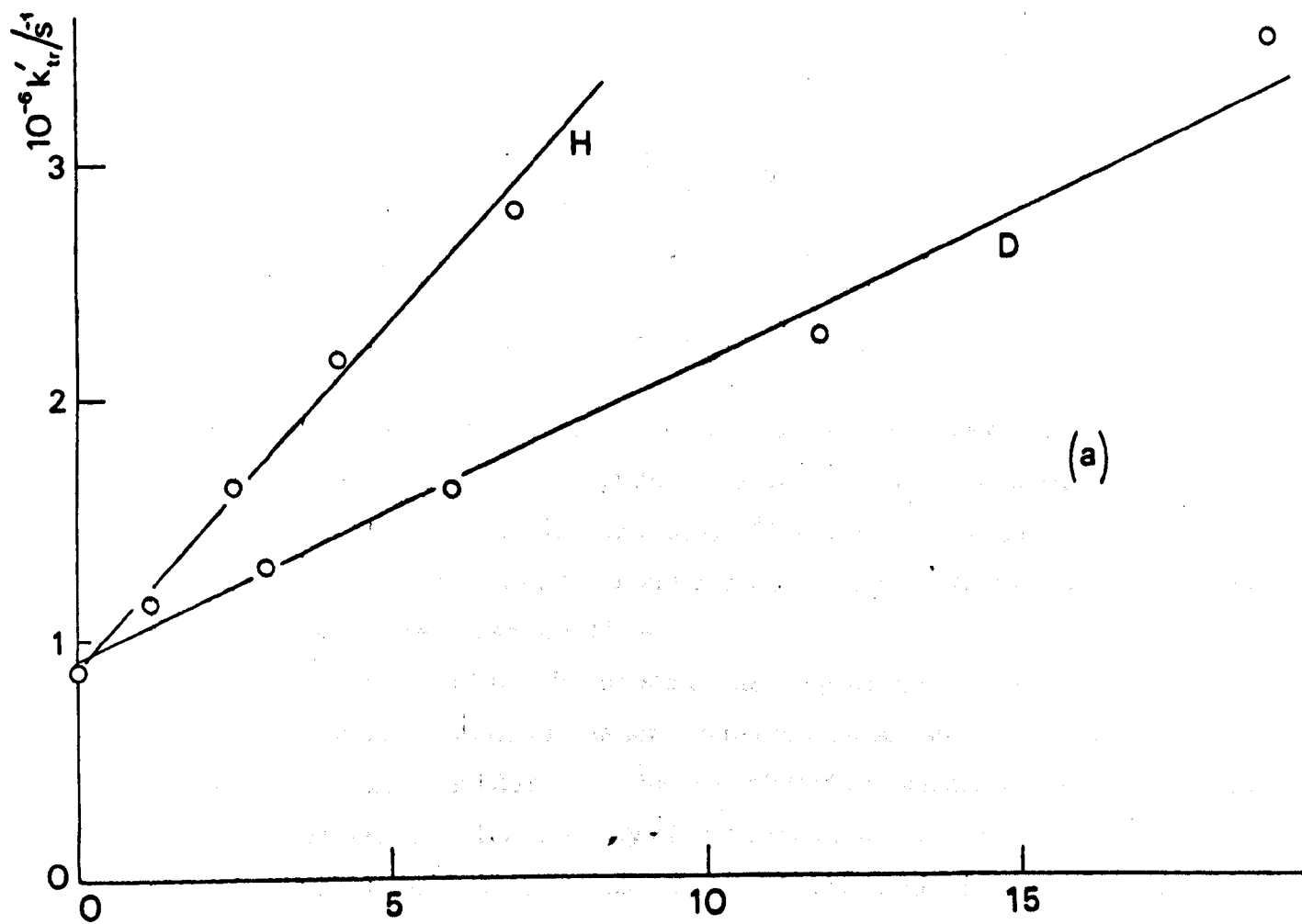


FIGURE 28

- (a) Plot of the first order decay constant (k'_{tr}) for the 575 nm transient versus concentration of alcohol after laser flash photolysis of aqueous uranyl perchlorate in the presence of added cyclohexanol and cyclohexanol- d_{11} .
- (b) Stern-Volmer plot for the quenching of the luminescence intensity of aqueous uranyl perchlorate by added cyclohexanol and cyclohexanol- d_{11} .



$$-d[(\text{UO}_2^{2+})^*]/dt = (k'_{\text{tr}_o} + k_{\text{tr}}[\text{alcohol}])(\text{UO}_2^{2+})^* \quad (6.3)$$

$$-d[(\text{UO}_2^{2+})^*]/dt = (k'_{\text{lum}_o} + k_{\text{lum}}[\text{alcohol}])(\text{UO}_2^{2+})^* \quad (6.4)$$

$$I_o/I_f = 1 + K_q[\text{alcohol}] \quad (6.5)$$

In the above equations the subscript o refers to the absence of added quencher and $*$ represents an excited state of the UO_2^{2+} ion which is not necessarily the same state in equations (6.3) and (6.4). The results of all the quenching experiments are presented in tables 2 and 3 and deuterium isotope effects displayed by these results are shown in table 4.

To confirm that only one state was responsible for the short-lived absorption, the optical density of this absorption in aqueous solution at 520 nm and at fixed time intervals after excitation was plotted against the corresponding optical density at 590 nm. The linearity of this graph implies that only one excited state is involved. The results in tables 2 - 4 strongly suggest that this state, the luminescing state and the photoreactive state are one and the same for the reasons detailed below :

- (i) There is excellent agreement between the deuterium isotope effects on K_q and on the corresponding absolute quenching constant, k_{tr} , for the three alcohols studied and also between the isotope effects on k_{lum} and k_{tr} for methanol.
- (ii) k'_{tr_o} and k'_{lum_o} in H_2O are in reasonable agreement. The luminescence decay lifetime is at the upper limit for reactions suitable for study by the single photon counting technique and it is to be expected that the accuracy of results in this range will not be optimal. k'_{tr_o} for uranyl sulphate in sulphuric acid has the values $7.6 \times 10^3 \text{ s}^{-1}$ at room temperature in conformity with the increased emission lifetime in this medium ($k = 8.0 \times 10^3 \text{ s}^{-1}$). In addition, the solvent isotope effect for the decay of the short-lived transient, $k'_{\text{tr}_o}(\text{H}_2\text{O})/k'_{\text{tr}_o}(\text{D}_2\text{O})$, has a value of 1.9, in fair agreement with the ratio of the integrated luminescence intensities of 1.7.
- (iii) The quenching rate constants k_{tr} and k_{lum} agree fairly well for CH_3OH and CD_3OH .

TABLE 2

First-Order Rate Constants for the Decay
of the Short-Lived Transient (k'_{tr_o}) and of the
Uranyl Ion Luminescence (k'_{lum_o}) in the
Absence of Quencher, at 293K

Medium	k'_{tr_o} / s^{-1}	k'_{lum_o} / s^{-1}
H ₂ O	$8.02 \times 10^5 *$	$3.85 \times 10^5 **$
D ₂ O	4.2×10^5	$2.27 \times 10^5 ‡$
H ₂ SO ₄	$7.6 \times 10^3 ††$	
	$9.7 \times 10^3 ††$	
H ₃ PO ₄	1.75×10^4	
Soda-glass		$4.0 \times 10^3 †$

* This value is the mean of the results from all experiments.

** A value of $6.7 \times 10^5 s^{-1}$ has been calculated by Kropp assuming
 $I_{f_o}(D_2O)/I_{f_o}(H_2O) = 2$. This ratio was found to be, in fact, 1.7 which,
using Kropp's value for $k'_{lum_o}(D_2O)$ of $3.3 \times 10^5 s^{-1} 83$ gives $k'_{lum_o}(H_2O) =$
 $5.6 \times 10^5 s^{-1}$.

† Values for various "uranium glasses" vary between $2.5 \times 10^3 s^{-1}$ and
 $6.3 \times 10^2 s^{-1} 22n$. This experiment was performed with the sample rod
surrounded by a 1 cm thick solution of CoCl₂ in ethanol ($50 g dm^{-3}$) in a
quartz vessel to filter out 590 nm light from the photolysis lamp.

†† Sodium Uranate

‡ Calculated from the decay constant in H₂O and the ratio of luminescence
intensities in D₂O and H₂O which was found to be 1.7 (in general $I_f \propto k'_{lum}^{-1}$).
The decay in D₂O is too slow for direct measurement by the single-photon
counting technique, the limit of the apparatus being reached by uranyl ions
in H₂O. Kropp has measured k'_{lum_o} in D₂O to be $3.3 \pm 1.1 \times 10^5 s^{-1} 83$

‡‡ Uranyl Sulphate

TABLE 3

Rate Constants for Quenching of Excited
Uranyl Ions by Various Alcohols at 293K

Substrate	Medium	$k_{tr} \times 10^{-6} / \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	$k_{lum} \times 10^{-6} / \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	$K_q / \text{dm}^3 \text{mol}^{-1}$	$(K_q / k_{tr}) / \text{s}$
CH ₃ OH	H ₂ O	6.40 ± 0.04	4.48 ± 0.08	5.26 ± 0.03*	0.82 × 10 ⁻⁶
CD ₃ OH	H ₂ O	2.32 ± 0.04	1.73 ± 0.13	1.90 ± 0.02	0.82 × 10 ⁻⁶
CH ₃ OH	H ₃ PO ₄	1.97 ± 0.12			
CD ₃ OH	H ₃ PO ₄	0.68 ± 0.08			
CH ₃ OD	D ₂ O	6.50 ± 0.19			
CD ₃ OD	D ₂ O	2.72 ± 0.04			
(CH ₃) ₂ CHOH	H ₂ O	85.3 ± 1.5		96.46 ± 0.29†	1.13 × 10 ⁻⁶
(CD ₃) ₂ CDOH	H ₂ O	35.4 ± 0.9		39.90 ± 0.15‡	1.13 × 10 ⁻⁶
C ₆ H ₁₁ OH	H ₂ O	294.0 ± 8.9		368.5 ± 1.9	1.25 × 10 ⁻⁶
C ₆ D ₁₁ OH	H ₂ O	126.6 ± 2.9		159.9 ± 0.7	1.26 × 10 ⁻⁶

Literature Values : * 45.7 (ref.82) 12 (ref.81,148) † 400 (ref.82) 113 (ref.81,148) ‡ 41 (ref.81,148)

TABLE 4

Deuterium Kinetic Isotope Effects on the
Quenching of Excited Uranyl Ions by
Alcohol Molecules in Aqueous Solution at 293 K

Substrates	Solvent	$k_{\text{tr}}(\text{H})/k_{\text{tr}}(\text{D})$	$k_{\text{lum}}(\text{H})/k_{\text{lum}}(\text{D})$	$K_{\text{q}}(\text{H})/K_{\text{q}}(\text{D})$
CH ₃ OH CD ₃ OH	H ₂ O	2.76 ± 0.08	2.59 ± 0.24	2.76 ± 0.05
CH ₃ OH CD ₃ OH	H ₃ PO ₄	2.89 ± 0.48		
CH ₃ OD CD ₃ OD	D ₂ O	2.39 ± 0.11		
CH ₃ OH CH ₃ OD	H ₂ O D ₂ O	0.98 ± 0.03		
CD ₃ OH CD ₃ OD	H ₂ O D ₂ O	0.85 ± 0.03		
(CH ₃) ₂ CHOH (CD ₃) ₂ CDOH	H ₂ O	2.41 ± 0.11		2.42 ± 0.02 *
C ₆ H ₁₁ OH C ₆ D ₁₁ OH	H ₂ O	2.32 ± 0.12		2.30 ± 0.02

* Sakuraba and Matsushima^{81,148} report a value of 2.76

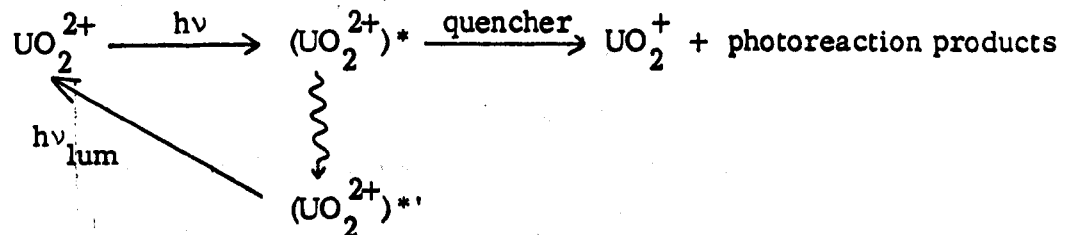
- (iv) The assumption that the 575 nm transient is the luminescent species leads to the relationships :

$$K_q = \tau_o k_{tr} \quad (6.6)$$

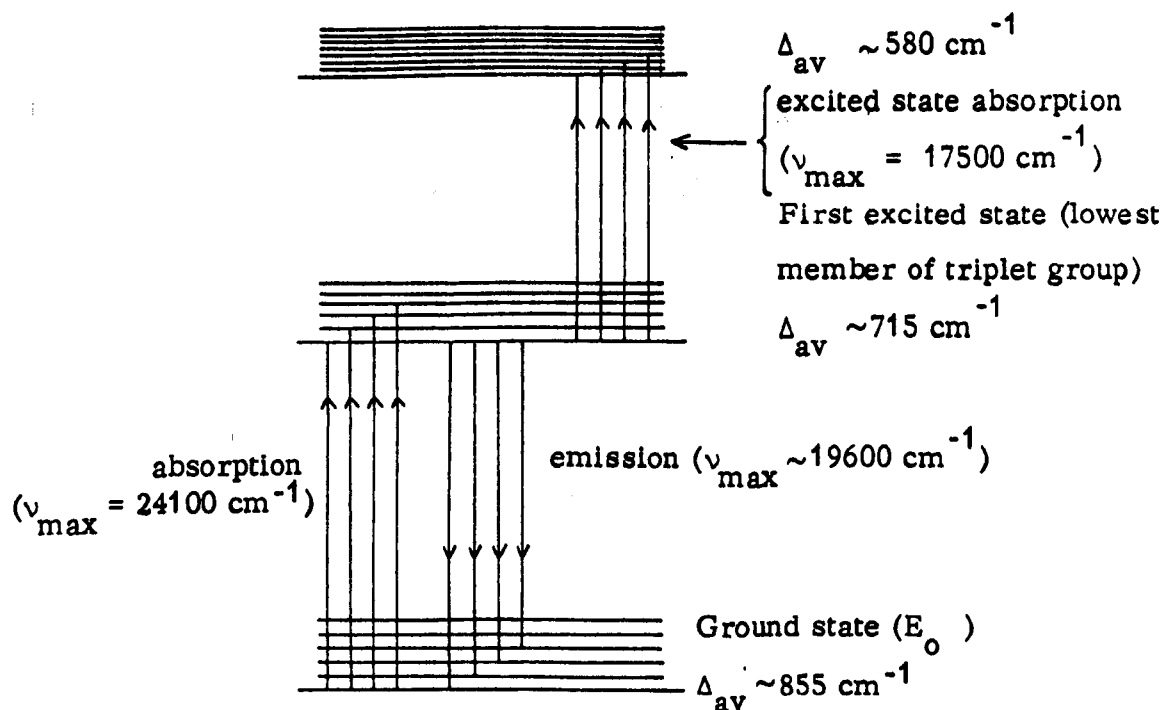
$$\tau_o = 1/k'_{tr_o} \quad (\text{see page 72}) \quad (6.7)$$

The values of K_q/k_{tr} shown in table 3 for the three alcohols studied are close to that for $1/k'_{tr_o}$ which is 1.22×10^{-6} for the decay in H_2O .

By studying the lifetime of excited UO_2^{2+} and the lifetime quenching by organic compounds, it has been possible to show that the photoreactive state of the uranyl ion is the same as the luminescent state. Previous luminescence intensity quenching experiments cannot distinguish between this case and, for example, the following case :



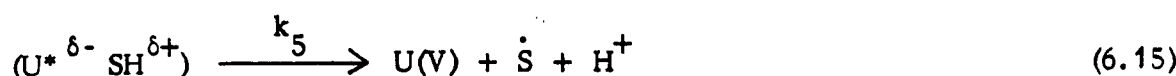
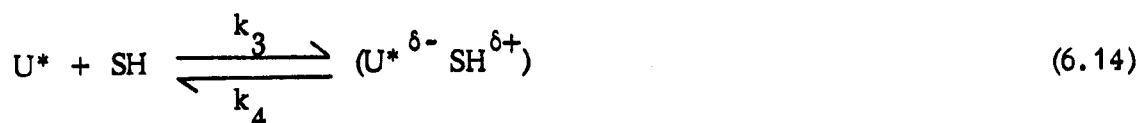
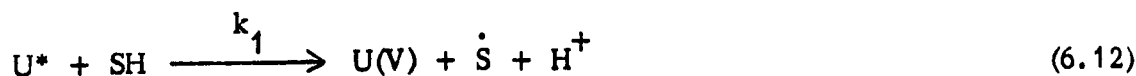
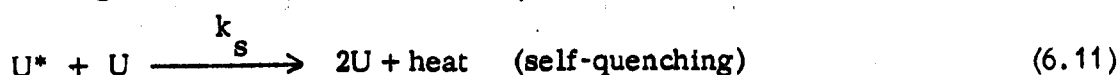
The following energy level scheme may be drawn :

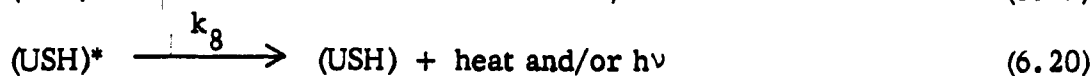
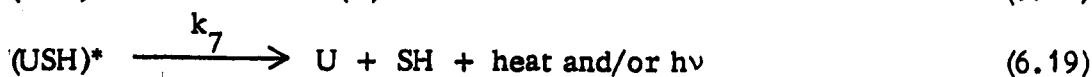
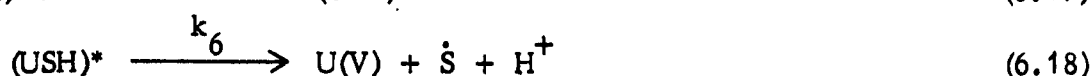


Having established that the 575 nm absorption spectrum is that of the photo-reactive state of UO_2^{2+} , it becomes a valuable means of studying directly the photo-induced reactions of uranyl compounds. Direct determination of quenching rate constants is appreciably more accurate than methods employing steady illumination; a typical study on the U(VI)-isopropanol system at 308 K by luminescence intensity quenching and monitoring of $[\text{U(IV)}]$ gives a value for the second-order quenching constant of $12.5 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ⁸², which differs from the directly measured value at 293 K by a factor of fifteen (the reactions of $(\text{UO}_2^{2+})^*$ exhibit very small temperature dependences; K_q only changes by a factor of ~ 1.5 between 293 K and 308 K⁸¹). Also, dissolved oxygen must be rigorously excluded from any system involving the study of $[\text{U(IV)}]$ as U(V) is readily reoxidised to U(VI)²⁷⁷ instead of disproportionating to U(VI) and U(IV). Regeneration of U(VI) is unimportant in the laser flash photolysis experiments due to the fast time scale of the reaction studied and the small degree of chemical reaction produced by each flash.

The other "direct observation" alternative to flash photolysis is fluorometry; however, the uranyl ion emission intensity is rather low for conventional "flash" fluorometry, especially in the presence of quenching molecules, and the lifetime is too long for accurate study by the single-photon counting technique.

The following schemes describe the possible mode of reaction of $(\text{UO}_2^{2+})^*$ ions with organic molecules :





In these reactions U and SH represent UO_2^{2+} and an organic molecule respectively and USH and $U^{6+} \cdot SH^{\delta+}$ represent a ground state complex and an exciplex respectively. I_a and I_b represent absorption of light in units of einsteins $dm^{-3} s^{-1}$.

Reactions (6.8) to (6.11) are common to all reaction schemes; in addition, (6.12) and (6.13) describe a normal kinetic encounter process, (6.14) and (6.15) represent an encounter mechanism via exciplex formation and reactions (6.16) to (6.20) represent a complex formation mechanism. k'_{lumO} is equivalent to $(k_f + k_d + k_s [U])$.

The rôle of water molecules in the deactivation of $(UO_2^{2+})^*$ is not well understood. As suggested on page 7 the deactivation may be purely physical, with excess energy exciting a high vibrational frequency of the O-H stretching mode in the H_2O molecule. With the lowest excited state of the UO_2^{2+} ion being at $\sim 21,000 \text{ cm}^{-1}$ ^{47,57} and the fundamental O-H vibration at $3,600 \text{ cm}^{-1}$, this would involve excitation of the sixth overtone of the O-H stretching frequency. This is perfectly acceptable according to energy considerations as the analogous quenching of excited Tb^{3+} by H_2O involves excitation of at least the fifth overtone, ⁸⁴ but the large solvent deuterium isotope effects (up to 54) on the deactivation of excited rare earth ions with energy levels not much lower than the luminescent state of UO_2^{2+} ⁸⁴ are in contrast to the relatively small effect (~ 1.7) on the deactivation of the excited uranyl ion. A chemical quenching process, whereby $(UO_2^{2+})^*$ abstracts a hydrogen atom from a water molecule to leave an $\dot{O}H$ radical, would explain this small isotope effect on k'_{trO} and k'_{lumO} . Photolysis of an aqueous solution of uranyl perchlorate ($\sim 0.2 \text{ mol dm}^{-3}$) at 77 K led to no detectable radicals and no end products have been observed for the same reaction. ⁹⁰ This may, however, merely imply rapid back reaction between hydroxyl radicals and U(V) in the solvent cage and radiation chemical studies indicate that this is, in fact, a rapid process. ²⁷⁸

The Stern-Volmer equation

$$I_{f_o} / I_f = 1 + K_q [SH]$$

is generally accepted as applying to collisional deactivation reactions and in the present case, assuming the steady-state approximation for U^* and $(U^* \delta^- SH^{\delta+})$, it takes the following forms :

(a) For a normal collisional mechanism⁹⁵

$$I_{f_o} / I_f = 1 + \{(k_1 + k_2) / (k_f + k_d + k_s [U])\} [SH] \quad (6.22)$$

For quenching by alcohols the physical process (reaction (6.13)) is much less important than the chemical process (reaction (6.12))⁹⁵ and the equation reduces to

$$I_{f_o} / I_f = 1 + \{k_1 / (k_f + k_d + k_s [U])\} [SH] \quad (6.23)$$

$$\text{or } I_{f_o} / I_f = 1 + k_1 \tau_o [SH] \quad (6.24)$$

(b) For an exciplex mechanism⁸¹

$$I_{f_o} / I_f = 1 + \{k_3 k_5 / ((k_4 + k_5) (k_f + k_d + k_s [U]))\} [SH] \quad (6.25)$$

$$\text{or } I_{f_o} / I_f = 1 + \{k_3 k_5 / (k_4 + k_5)\} \tau_o [SH] \quad (6.26)$$

The complex formation mechanism (reaction (6.8) to (6.11) and (6.16) to (6.20)) leads to a similar equation :

$$I_{f_o} / I_f = 1 + (\epsilon_b / \epsilon_a) ([USH] / [U]) \quad (6.27)$$

where ϵ_a and ϵ_b are the molar extinction coefficients of U and USH respectively. The assumption has been made in this scheme that free SH does not quench UO_2^{2+} luminescence.

Using the same approximations the following equations may also be derived :

(a) For a normal collisional mechanism

$$-d[U^*] / dt = (k_f + k_d + k_s [U] + k_1 [SH]) [U^*] \quad (6.28)$$

$$\text{or } -d[U^*] / dt = (1 / \tau_o + k_1 [SH]) [U^*] \quad (6.29)$$

(b) For an exciplex mechanism

$$-d[U^*]/dt = (k_f + k_d + k_s[U] + \{k_3k_5/(k_4 + k_5)\}[SH])[U^*] \quad (6.30)$$

$$\text{or } -d[U^*]/dt = (1/\tau_0 + \{k_3k_5/(k_4 + k_5)\}[SH])[U^*] \quad (6.31)$$

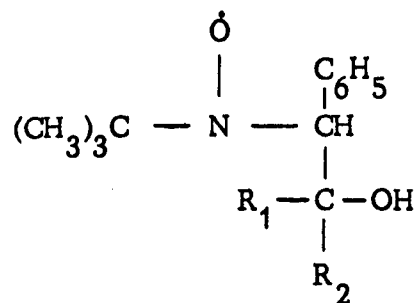
In attempting to distinguish by kinetic means between a collisional and a complex formation mechanism, it is necessary to investigate the many variations of the complex mechanism, e.g. whether the complex is luminescent, whether free substrate quenches free $(\text{UO}_2^{2+})^*$ ions, etc. In the scheme formulated for the 'complex mechanism' (reactions (6.8) to (6.11) and (6.16) to (6.20)) for example, it was assumed that there is no quenching of excited uranyl ions by a collisional mechanism and equation (6.27) indicates that, if the total concentration of U(VI) is high compared to that of the quencher (as occurs with very efficient quenchers), and hence $[SH]_{\text{free}} \propto [SH]_{\text{total}}$, then a linear Stern-Volmer plot will result. The same conditions, however, for linear Stern-Volmer plots require that the lifetime of $(\text{UO}_2^{2+})^*$ be unaffected by added photoreactant. The results of quenching of the luminescence intensity and $(\text{UO}_2^{2+})^*$ lifetime therefore point to a collisional process for the luminescence quenching and photoreduction of U(VI) by alcohol molecules.

It is clear from equations (6.24), (6.26), (6.29) and (6.31) that it is impossible to distinguish by kinetic studies between a normal bimolecular collision process and one involving the intermediacy of an exciplex, the sole difference being between the rate constant k_1 and the compound rate constant $k_3k_5/(k_4 + k_5)$. Arguments forwarded in favour of the collision-complex theory are not as convincing in the case of aliphatic alcohols as in the case of aromatic quenchers.⁸¹ Also, unless such complexes possess very short lifetimes they might be expected to disclose themselves by an absorption spectrum upon flash photolysis or at least by some modification of the free $(\text{UO}_2^{2+})^*$ emission spectrum as in the case of aromatic exciplexes.²⁷⁹ Neither of these phenomena has been observed even though the large quantum yields for photo-oxidation of alcohols and the appreciable deuterium isotope effects presented earlier, which suggest breakdown of the exciplex to be rate-determining, preclude a reaction profile incorporating an exciplex of short lifetime. Moreover, the electron transfer in an exciplex would be expected to originate from the non-bonding oxygen orbitals of the alcohol

molecule followed by loss of the hydroxylic proton, but the substantial primary kinetic isotope effects from the various alcohols (table 4) do not support such an idea.

The evidence presented above indicates that photo-oxidation of alcohols by U(VI) proceeds by a normal bimolecular encounter mechanism and the deuterium isotope effects on the quenching rate constants provide information about the steps involved in this mechanism. The values of k_{tr} follow the trend methanol < isopropanol < cyclohexanol, reflecting the progressive reduction of the energies of the α C-H bonds and intimating that fission of these bonds is the rate-determining step.

The magnitudes of the isotope effects on k_{tr} and K_q follow the general trend that the faster a reaction of a specific type, the smaller the resulting primary kinetic isotope effect due to the closer similarity between reactants and the transition state and the consequent reduction in $\Delta\Delta E^\ddagger$ (the difference between $E_H^\ddagger - E_H$ and $E_D^\ddagger - E_D$).^{280, 281} Considering the large values of k_{tr} , both $k_{tr}(H)/k_{tr}(D)$ and $K_q(H)/K_q(D)$ are large enough to constitute primary isotope effects. This strongly supports the theory that the collisional process involves α -H atom abstraction, in conformity with the e.s.r. results for photo-oxidation of methanol and isopropanol (propan-2-ol) in the liquid state (section 5.2.1). Although the e.s.r. results do not completely discount the intermediacy of alkoxy radicals as explained on page 56, it is unlikely that the primary formation of such radicals would display C-H isotope effects of the magnitudes observed, and this is supported by the absence of any appreciable isotope effect on k_{tr} by substitution of the hydroxylic hydrogen atom by deuterium in CH_3OH and CD_3OH . Also, Ledwith *et al.*¹⁵³ found only radicals of the type



upon photolysis of solutions of uranyl nitrate ($\sim 5 \times 10^{-3}$ mol dm⁻³) and the nitron $\text{C}_6\text{H}_5\text{CH}=\text{N}(\text{O})\text{C}(\text{CH}_3)_3$ (~ 0.1 mol dm⁻³) in 2/1 (v/v) water-methanol, ethanol, butan-1-ol and propan-2-ol. The concentration of nitron is sufficient

to scavenge any alkoxy radicals formed as these were trapped under similar conditions in all the four solvents detailed above, both upon photolysis with paraquat dichloride and upon oxidation by $\text{Ag}^+ / \text{S}_2\text{O}_8^{2-}$. However, the observed nitroxide radicals, which are derived from the trapping of hydroxyalkyl radicals, indicate that $(\text{UO}_2^{2+})^*$ shares with triplet-state benzophenone, hydroxyl and alkoxy radicals a strong propensity to function oxidatively by abstracting hydrogen atoms from activated C-H bonds and it is probable that these reagents share the property of a high spin density near the oxygen atom.

In pure methanol the methoxy radical was, in fact, detected by Ledwith et al. and it appears that the ligand environment is an important factor in determining the reaction of this substrate. The reaction in neat solvent can most readily be interpreted in terms of a CTM transition from coordinated methanol to the uranyl ion, whilst in the water-methanol mixture only water is coordinated to the uranyl ion with the consequence that an intermolecular mechanism must be involved.

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