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**A STUDY OF FREE RADICALS IN LIQUID  
AMMONIA BY ELECTRON SPIN RESONANCE**

**A Thesis submitted for the degree of  
Doctor of Philosophy  
in the  
University of Warwick**

**by**

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## INTRODUCTION

## INTRODUCTION

Electron spin resonance (e.s.r.) investigations of organic free radicals have been mainly concerned with the observation of either stable free radicals which can exist in solution for at least several minutes or unstable radicals whose lifetimes, typically of the order of a few seconds or less in solution, have been extended by freezing the reaction medium once radicals have been formed, or, more usually, by the production of radicals in an already frozen medium by irradiation. E.s.r. observation of radicals in the solid phase suffers from the disadvantage that poorly-resolved spectra are usually obtained. Two methods of producing short-lived radicals in solution in a sufficiently high concentration to be observed by e.s.r. are electrolysis and rapid-flow. The former method is useful for radicals with lifetimes of a few seconds whereas the flow method can yield a sufficiently high steady state concentration of radicals where lifetimes are of the order of a few milliseconds. The rapid-flow technique has been used by a few groups of workers employing an e.s.r. aqueous flat cell mixing device and although excellent work has been carried out with this mixer - in particular the observation of phenoxy radicals and simple neutral radicals from the reaction of the hydroxyl radical with organic compounds - it has the two major disadvantages of a fairly large dead space between mixing and observation and a certain lack of robustness when used with a solvent such as liquid ammonia.

Although the e.s.r. spectra of a very large number of radicals have been described in the literature, there are a number of simple radical-anions which have so far escaped detection using the conventional method of production (reduction by alkali metal in an ether in vacuo). Examples of such hitherto unobserved radical-anions are those from benzamide, styrene, benzoic acid, cyclohexenone and (until recently) pyridine. The



following chapters describe the development and application of a rapid-flow reduction technique designed primarily to observe by e.s.r. radical-anions of such compounds.

Although a somewhat hazardous material, the medium of liquid ammonia was chosen both for its properties as a solvent and because a solution of sodium (or other alkali metal) in ammonia provides a source of solvated electron, an extremely powerful reducing agent. Undoubtedly the greatest difficulty encountered during the work was the design of a robust and efficient mixing cell to cope with rapid temperature changes and high pressures during the initial stages of flowing.

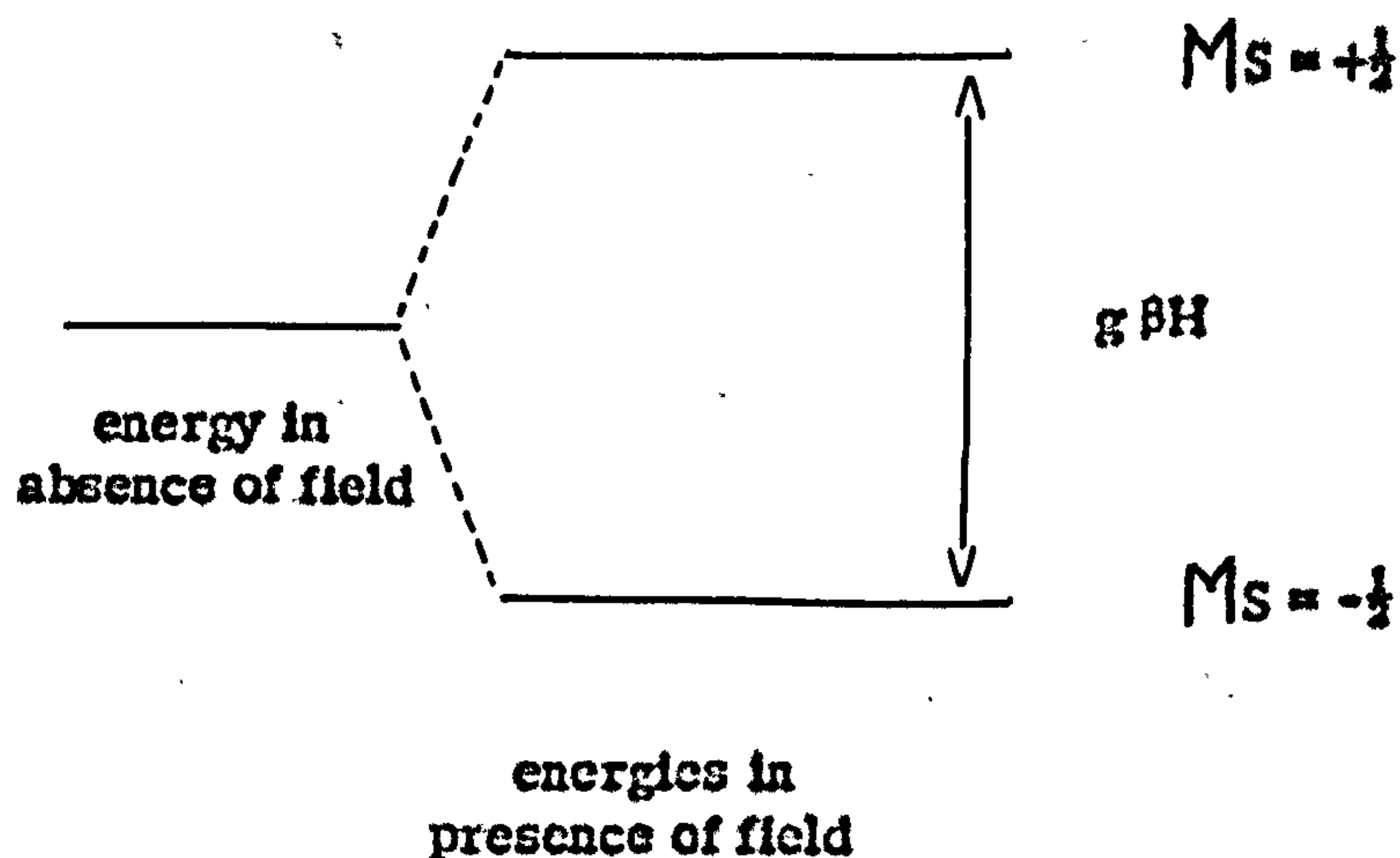
Results obtained from solvated electron reduction of many organic compounds are given in the following chapters where it is seen that although in many instances straightforward addition of an electron occurs to give radical-anions, some results are unexpected owing to secondary reactions (e.g. protonation) taking place or to relatively slow molecular motions (e.g. hindered rotation). Often analysis of the spectra proved at least as difficult a task as production of radicals, especially for styrene and related compounds.



## ELECTRON SPIN RESONANCE

Electron spin resonance (e.s.r.) spectroscopy is used for detecting unpaired electrons, often at very low concentrations, and giving detailed information on their location and energy: it has therefore direct application in the study of organic free radicals. E.s.r. has become a standard technique in the hands of the physical-organic chemist and many articles and reviews have been written.<sup>1-6</sup>

For a free radical containing one unpaired electron, which does not interact with any magnetic nuclei, all directions of the magnetic moment vector of the electron are equally probable and there is no energy difference between them. If this free radical is then placed in a magnetic field then two orientations of the electron magnetic moment become possible, either parallel or antiparallel with the applied field. No intermediate conditions are allowed by the restriction of quantisation since  $S = \frac{1}{2}$ . Those electrons with magnetic moments aligned with the field have a lower energy ( $\frac{1}{2}g\beta H$  less) than in the absence of a magnetic field, and those which are aligned against the field have a greater energy ( $\frac{1}{2}g\beta H$  more).



$H$  is the magnetic field in Oersted,  $\beta$  is a constant and is called the Bohr magneton,  $g$  is the spectroscopic splitting factor which for a free electron has the value 2.0023. However because of the fact that the unpaired electron in a free radical is still slightly bound to paramagnetic atoms causing some interaction with the orbital motion, the  $g$ -factor differs from 2.0023 by small amounts.

The detection of electron spin resonance depends on the difference between the number of electrons in the ground state ( $S = -\frac{1}{2}$ ) and the excited state ( $S = +\frac{1}{2}$ ). This difference is given by the Maxwell-Boltzmann expression

$$\frac{N_1}{N_2} = e^{\frac{-\Delta E}{kT}}$$

where  $N_1$  and  $N_2$  are the electron populations of the excited and ground states,  $\Delta E$  is the energy separation of the two states,  $k$  is the Boltzmann constant and  $T$  the absolute temperature.

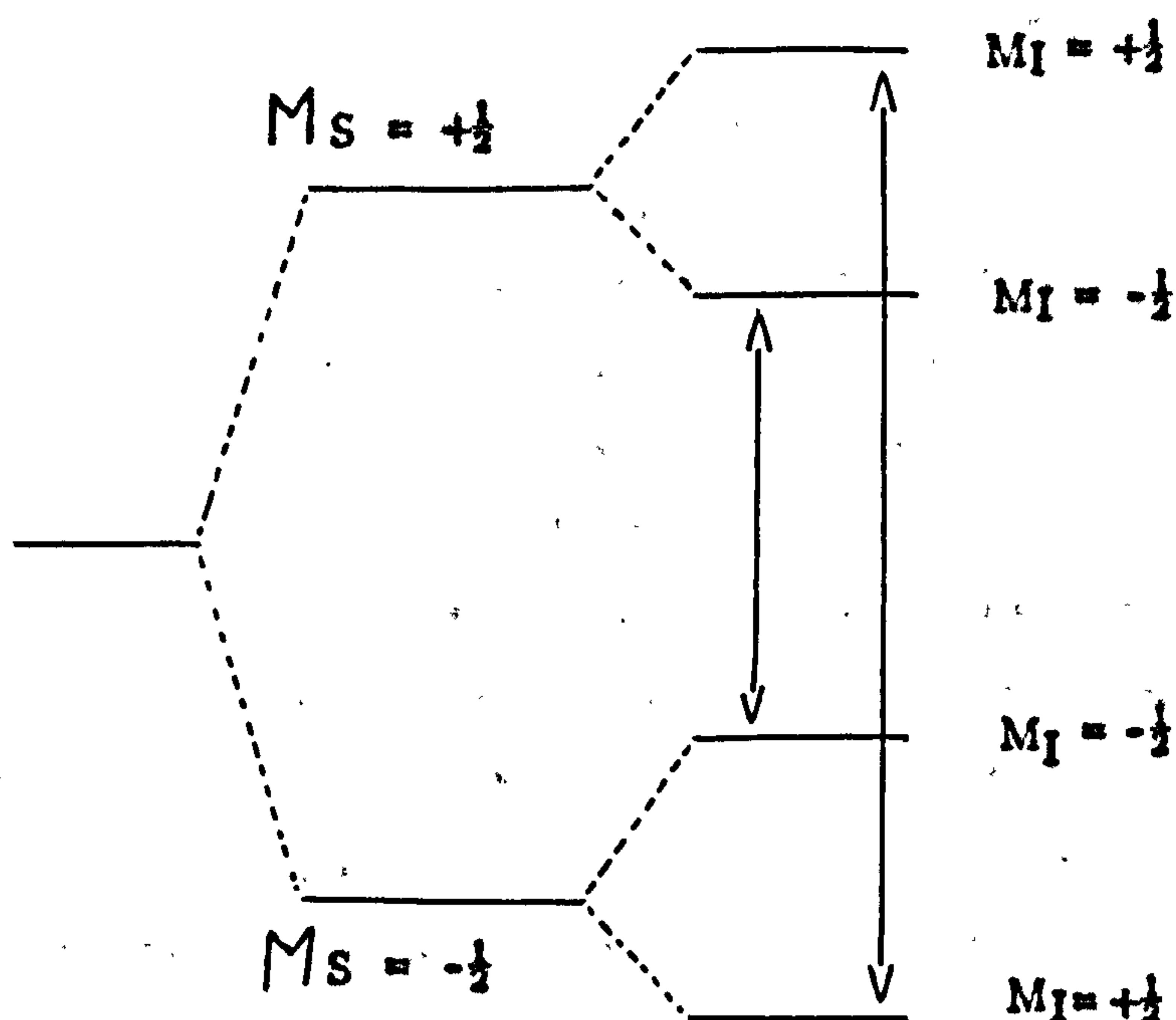
If radiation energy of frequency  $\nu$  is fed to the sample the electron in the lower energy state will be excited to the upper energy level and those having the higher energy will be stimulated to return to the lower level. This only occurs at the resonance condition where

$$h\nu = g\beta H$$

Apart from stimulated emission another mechanism occurs - relaxation - to allow the higher energy electrons to become lower energy electrons. If this did not operate the energy level populations would soon equalise and there would be no further absorption of radiation. It is this absorption of radiation which the e.s.r. spectrometer is designed to

detect. The frequency usually used for organic free radicals is the radar X - band i.e. about 9000 MHz., which after substituting in the above equation requires a magnetic field of about 3000 Oersted.

If the orbital of the unpaired electron encompasses an atom which has a nucleus with a magnetic moment then the energy levels of the electron will be split. For interaction with one proton ( $M_I = \pm \frac{1}{2}$ ) both the upper and lower electronic energy levels will be split into two.



The selection rule  $\Delta M_I = 0$  operates so that there will be two possible transitions, each occurring at a slightly different field value. Therefore in the e.s.r. experiment as the magnetic field is altered two radiation absorptions will be detected at different field values. Interactions with a greater number of magnetic nuclei of varying nuclear spins yield complex multiline spectra. The number of lines is given by



$(2n_1 I_1 + 1) (2n_2 I_2 + 1) \dots (2n_n I_n + 1)$  where  $n$  is the number of nuclei within each group with a nuclear spin of  $I_n$ .

The analysis of a spectrum yields two quantities important in the discussion of results obtained in the present work: a) the  $g$ -value and b) one or more coupling constants which measure the extent of the interaction between the electron and interacting nuclei. The  $g$ -value rarely deviates significantly from the free electron value of 2.0023 for organic free radicals in solution although the presence of some nuclei such as sulphur causes it to alter more than others.

For a small simple molecule where the electron 'sees' only two or three magnetic nuclei the e.s.r. spectrum will consist of just a few lines. The smallest coupling constant will be the distance in Gauss from the first line to the second. Since these two lines may now be reduced to one line the whole number of spectral lines can be reduced by half (for  $I = \frac{1}{2}$ ); this process is repeated until all coupling constants are obtained. As a check of the analysis the coupling constants can be incorporated into a computer program to simulate the spectrum after which minor adjustments can be made to correct for small measurement errors. For most of the spectra actually obtained the pattern is not a simple one. The first lines are not always seen but more usually the difficulty lies in having a large number of lines overlapping so that a guess has to be made as to the location of even the third or fourth lines. In the case of 2-methylpyridine, a comparatively simple molecule, for example, 192 lines are expected and over 900 lines for the dimer produced from further reduction of 2-methylpyridine. Analysis must therefore proceed by inspired and intelligent guesswork. The computer is a valuable aid to interpretation but its extreme

sensitivity to small changes is something of a disadvantage; an error of as little as 0.03 g<sub>au</sub>s in one coupling constant often yields an incorrect simulation.

The hyperfine coupling constants obtained can often identify a particular radical and give precise information on the structure, such as coplanarity of substituent groups and the addition or removal of atoms during reaction, e.g. addition of a proton to pyridine di-acids and removal of fluorine from fluorobenzonitrile (q.v.). How the interpretation of a spectrum has been used to identify and examine other radical-anions is discussed in following chapters.



## THE RAPID FLOW TECHNIQUE

The mechanisms of chemical and biological reactions have long been investigated by the isolation of end-products and by-products, the reconstruction of possible reaction routes, and elimination of some of these routes by further experimentation. This has led to many inspired and often correct interpretations of the behaviour of molecules towards other molecules and biological materials to various substrates.

To find the correctness or otherwise of these reaction paths it is necessary to obtain positive physical evidence for the postulated intermediates; until the early 20th century this was not possible in most cases where these intermediates were not isolable. The problem of the identification of these short-lived intermediates is one of two parts: the production of these transients and their observation.

Transient intermediates may be produced by a variety of methods: two important techniques are electrolysis (e.g. ketyl radical-anions from ketones<sup>7</sup>), and  $\gamma$ -irradiation (e.g. methyl radicals from alkyl halides at 77°K<sup>8</sup>). A particularly novel method of preparing primary radicals has been described by Bennett; alternate layers of substrate and alkali metal are deposited on a rotating cryostat.<sup>9</sup> The flow method, which is widely used, has the advantages firstly that the lifetime of a particular species does not necessarily have to be extended by lowering the temperature or solidifying, thereby changing reaction conditions, and also a steady state concentration of intermediates can be produced at a given place only a few milliseconds after mixing. This was the method used to obtain the results presented in this work,

Possibly the first use of the flow principle for studying reactions was



in 1905 when Raschig<sup>10</sup> followed the NO/ O<sub>2</sub> reaction by allowing each gas to enter one side arm of a T-shaped glass mixer. Following mixing, the products were absorbed after very short time intervals (the shortest 0.025 secs) in a solution which quenched the reaction, the absorbing solution being then analysed. In 1922 a similar study was made<sup>11</sup> on the ethylene - bromine reaction which was monitored manometrically, but the first application of fast mixing of solutions was by Hartridge and Roughton.<sup>12</sup> This experimental procedure was used<sup>13</sup> for the measurement of the rate of oxidation of a dilute solution of reduced haemoglobin with oxygen-saturated water and the rate of reduction of oxy-haemoglobin; the reaction was monitored spectroscopically. Since the experiment of Hartridge and Roughton many modifications have been made to the original technique of fast mixing to suit the enormous range of reactions studied. Some reviews dealing with these modifications and their reasons are given in refs. 14-17. Many oxidation studies have been carried out using the mixer of Dixon and Norman<sup>18</sup> where observation of radical intermediates was by e.s.r. spectroscopy. These include oxidation of phenols,<sup>19-21</sup> aliphatic aldehydes,<sup>22</sup> carbohydrates<sup>23</sup> and esters.<sup>24</sup> Biological applications include experiments on blood pigments,<sup>25</sup> and haemoglobin and lipoate dehydrogenase.<sup>26, 27</sup>

#### Considerations in Design of a Fast Mixing Apparatus

The production of an efficient mixer necessitates a consideration of both the method of introducing the separate solutions to the point of mixing and the behaviour of the mixing solutions.

It is essential for equal or almost equal volumes of each solution to arrive at the mixing point. This can be achieved in a slow flow apparatus by pressing down on a platform to operate two syringes. For faster flow

rates a constant pressure head of gas, inert to the solutions being used, is usually employed. When two flowing solutions are suddenly placed together in a tube there is a finite length in which mixing is taking place. An ideal mixer would keep this length negligible with respect to the reaction and the method of observation. To keep this mixing length as small as possible in practical mixers it is necessary to consider fluid properties such as mass-flow, turbulence and cavitation.

Once in the observation tube the solution must be as near mass-flow as possible, that is, the solution velocity at the centre must be as close as possible to that at the periphery. This does not usually present a problem since deviations from mass-flow are negligible for solutions travelling above the critical value for turbulence which in turn is a prerequisite for efficient mixing. Turbulent flow is caused by radial components due to eddying and the minimum velocity,  $u_c$ , is given by Reynold's equation:

$$u_c = \frac{1000 \eta}{\rho \times r}$$

where  $\eta$  is the viscosity in poises,  $\rho$  the density of the solution and  $r$  the radius of the tube in cm. For water at 20° C in a tube of 1 mm diameter  $u_c = 200$  cm/sec or 1.6 ml/sec.

Cavitation is caused by variations in the hydrostatic pressure of the streaming liquid at different parts of the observation tube giving rise to a stream of bubbles. This only occurs at very high flow rates and is enhanced by the presence of soluble gases.<sup>28</sup>

The results presented in this thesis were obtained with a rapid-mixing device and the application of the above criteria in the development and construction of this mixer is described in the experimental chapter.



## THE SOLVATED ELECTRON AND REDUCTION IN LIQUID AMMONIA

The fact that alkali metals dissolve in liquid ammonia has been known for over a hundred years<sup>29</sup> and that the blue solution contains solvated electrons was postulated as early as 1908 by Kraus.<sup>30</sup>

Kraus postulated that the metal dissociated in ammonia solution to give both solvated cations and solvated electrons,

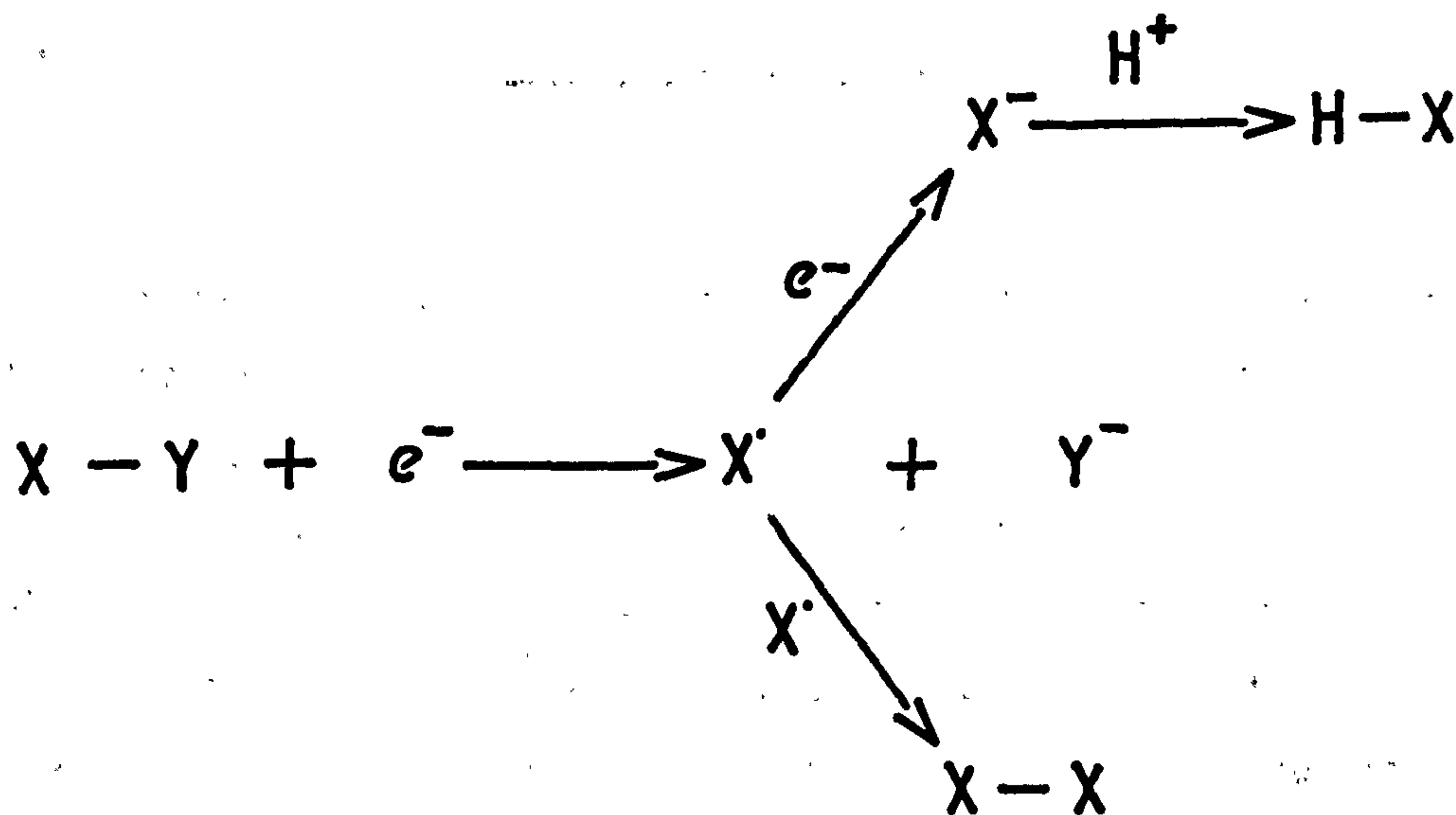


Although solvated electrons are still thought to be present in alkali metal - ammonia solutions the exact nature of the solvation cloud is still uncertain. It is thought<sup>31-33</sup> that the electrons of the solvent molecules are displaced to form a cavity, the unpaired electron being at the centre. Supporting evidence for this is that on dissolving, for example, sodium in ammonia there is an increase in volume greater than expected, i.e. 60 - 80 ml/mole of sodium instead of 23 ml/mole.<sup>34-38</sup> The effect of temperature and pressure on light absorption also indicates that  $e^{-}$  is in a cavity.<sup>39</sup> Knight shift measurements<sup>40, 41</sup> indicate that the metal cation is not totally separated from the electron; possibly the polarised solvent molecules in turn polarise the  $M^{+}$  ions.<sup>42</sup> This model of one electron in a solvent cavity appears to be true only for dilute solutions (less than 0.05 M). At higher concentrations (0.05 - 1M) the cavities appear to contain electron spin-compensated pairs and at higher concentrations still the solution takes on metallic properties such as high conductivity and metallic lustre, viz:

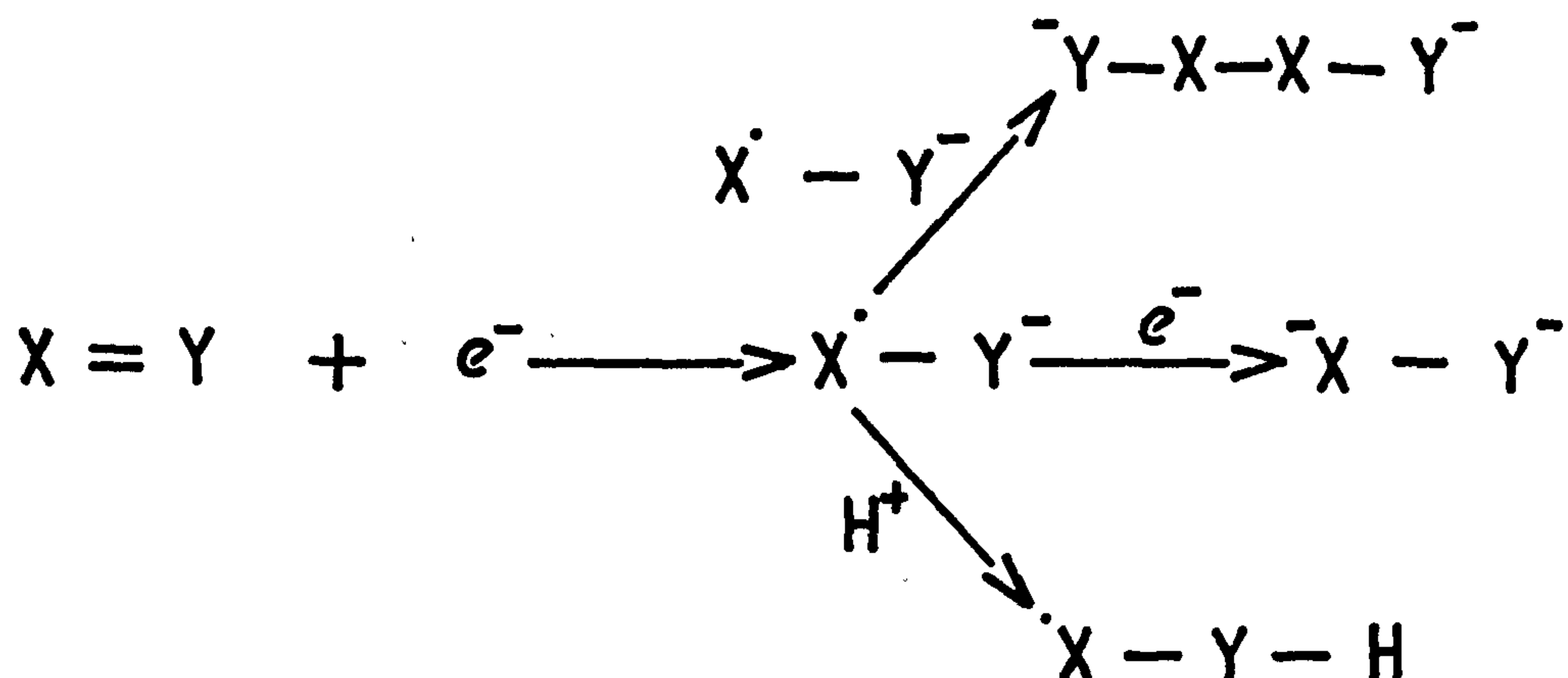
$$e^{-} \rightleftharpoons \frac{1}{2} e_2^{2-} \rightleftharpoons e_{\text{met}}^{-}$$

Whether a single unpaired electron or an electron pair reacts with an organic compound may affect the reduction path in sodium/liquid ammonia.

The initial process of reduction was thought to be the action of nascent hydrogen<sup>43</sup> but this was rejected on the basis of the high product yields sometimes obtained.<sup>44</sup> Willstätter<sup>44</sup> proposed that the first stage was the addition of alkali metal followed by solvolysis. There were other theories<sup>45</sup> but the most successful is that of an initial one or two electron addition<sup>46</sup> to form either a radical-anion or a dianion which subsequently undergo further reaction with either electrons, solvent or substrate. The addition of electrons to a molecule may cause bond cleavage,



or opening of a double bond,

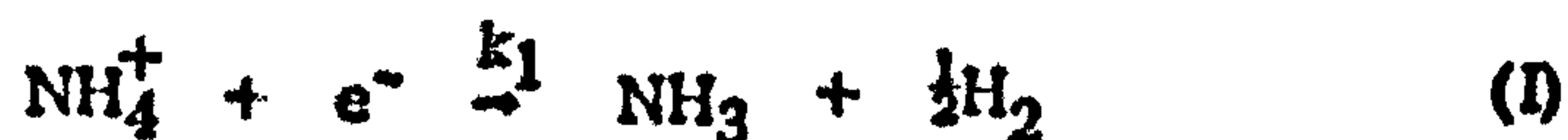


It is not obvious chemically whether one or two electrons are added in the initial step but it is by e.s.r. since  $2e^-$  addition gives diamagnetic products (unless further reactions give a radical). It is possible to distinguish whether anionic or radical intermediates are present by altering substituents, e.g. increasing alkylation (in place of H) may decrease reaction rates<sup>47</sup> (due to increased heats of formation) whereas any increasing extent of substitution stabilises radicals<sup>48, 49</sup> and hence increases the reaction rate.

Product analysis provides little evidence but certain factors such as the presence, or especially the absence, of dimeric products may indicate presence or absence respectively of radical reactions.



The observation of short-lived free radicals even by a fast-flow method demands radical lifetimes of at least a few milliseconds. As will be seen in later chapters the initial uptake of an electron may not produce the first radical observed by e.s.r.; the radical observed may be the second or third in a chain of events as in the reduction of aryl halides. Competing reactions may also occur to reduce the concentration of  $e^-_{\text{solv}}$ . This is the case when protons are deliberately introduced, as for ethanol/substrate mixtures, or incidentally introduced as for carboxylic acids which ionise to produce protons. In these cases either the protons reduce the available concentration of electrons so that no reaction between  $e^-_{\text{solv}}$  and organic substrate can occur, or the radical produced is protonated and this protonated species may be the first radical observed. Protons in ammonia will exist as  $\text{NH}_4^+$  and the rate constant for



is about  $10^{10} \text{ m}^{-1} \text{ sec}^{-1}$ .<sup>50</sup> This is of the same order as  $k_2$  in the reaction



In reaction (I) the formation of atomic hydrogen is inconsistent with rate constants in liquid ammonia<sup>50</sup> and probably the rate determining process is





then



There are many other reactions which account for the non-observation of radicals and these will be discussed as they occur.

REDUCTION OF PYRIDINE

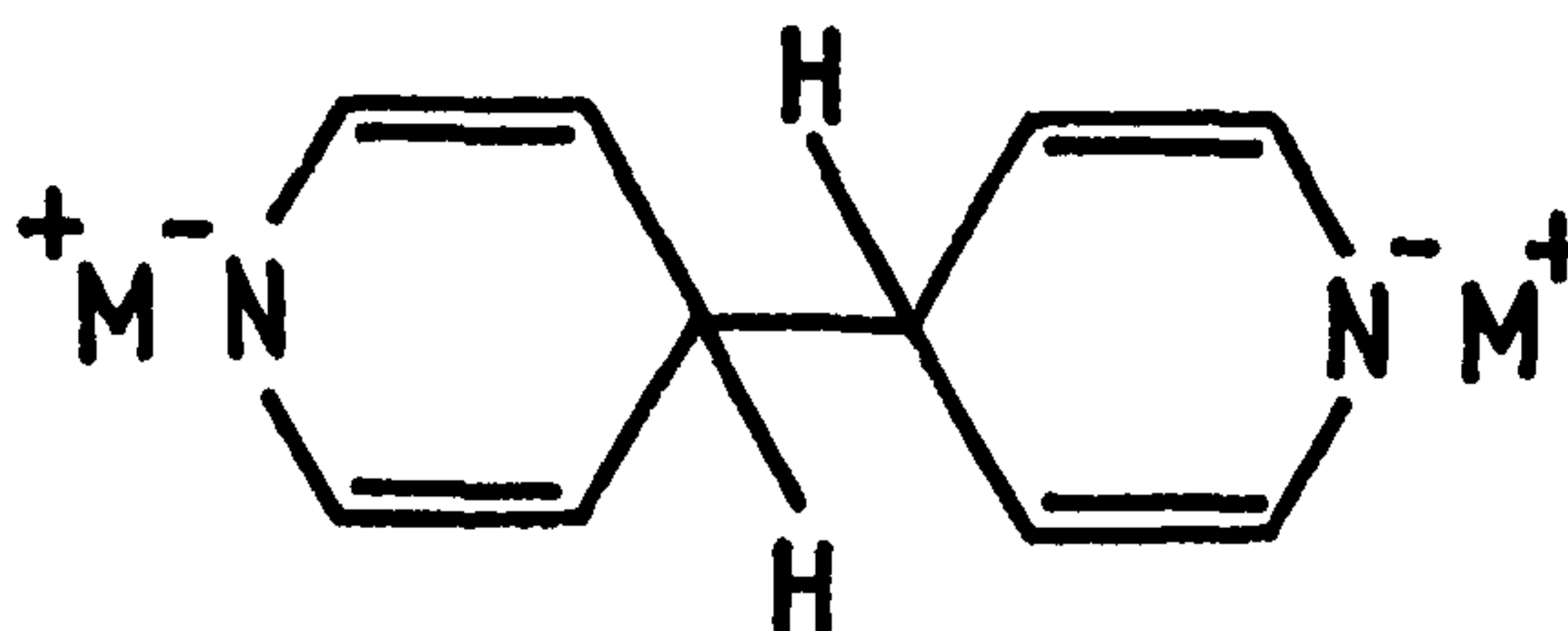
AND

RELATED COMPOUNDS

## INTRODUCTION

Intermediates in the reduction of pyridine by solutions of alkali metals have long evaded positive identification although the end-products of this reaction were known to be dipyridyls.<sup>51</sup> Pyridine, neat or dissolved in a variety of solvents, e.g. tetrahydrofuran (THF),<sup>52</sup> dimethoxyethane (DME),<sup>53</sup> or acetic anhydride,<sup>54,55</sup> and treated with alkali metals (or zinc for acetic anhydride) always yielded 4,4'-dipyridyl or (more rarely) 2,2'-dipyridyl<sup>56</sup> or a mixture of isomers. Water and oxygen were rigorously eliminated by some workers<sup>53</sup> to prevent decomposition of the intermediates but 4,4'-dipyridyl was still the first product characterised.

The initial step in the reaction of pyridine and an alkali metal solution was accepted as the transfer of an electron from the metal to pyridine to form the radical-anion ( $\text{py}^\cdot$ ) or, more probably in low-dielectric solvents, an ion pair  $\text{M}^+ \text{C}_6\text{H}_5\text{N}^\cdot$ . The pyridine radical was then assumed either to dimerise extremely rapidly,<sup>57</sup> which accounted for the failure to observe  $\text{py}^\cdot$ , or to react with a neutral pyridine molecule<sup>56</sup> to form a diamagnetic  $\sigma$ -complex of the form



The elimination of hydrogen with either oxygen or metal ions gives the

neutral dipyridyl which can take up a further electron to become dipyridyl<sup>•-</sup>.

Many pyridine radical-anions stabilised by substitution have been characterised by e.s.r.<sup>58-64</sup> but Kuwata<sup>65</sup> interpreted a singlet e.s.r. spectrum, obtained from a mixture of pyridine and sodium in THF, as py<sup>•-</sup>. The dissolution of potassium in pyridine/THF solution instead of sodium was claimed<sup>66</sup> to be responsible for the observation of an optical absorption peak at 330 nm which was ascribed to py<sup>•-</sup>, but a later attempt to confirm this by e.s.r. failed.<sup>67</sup> Confirmation was obtained, however, by several workers, of a band at about 330 nm which can be ascribed to py<sup>•-</sup> in pyridine solution,<sup>68</sup> liquid ammonia,<sup>69</sup> and a solid matrix of methyltetrahydrofuran (MTHF).<sup>70</sup>

More positive characterisation of the pyridine radical-anion would be desirable to prevent any further confusion from 'static' techniques which require a radical lifetime of at least several minutes. This has been achieved in the present work by the rapid-flow technique introduced in Chapter I and described in detail in the experimental section.

Since these results were obtained Talcott and Myers<sup>71</sup> have published similar results using an electrolysis apparatus and Kimmel and Strauss<sup>69</sup> have made use of this to correlate the optical band at 330 nm with the pyridine radical-anion.



## RESULTS AND DISCUSSION

The e.s.r. spectrum of the pyridine radical-anion was observed after a solution of pyridine in liquid ammonia was mixed in the cavity of the spectrometer with a solution of sodium in liquid ammonia using the rapid-flow apparatus described in the experimental section. The coupling constants and g-values of this and many substituted pyridines are given in Table III.

The best spectrum was obtained with very dilute solutions of ca.  $10^{-3}$  M;  $10^{-1}$  M solutions produced a very broad signal from which only the large coupling constants could be measured. Lower solute concentrations than  $10^{-3}$  M could not be used owing to the instability of the dilute solvated electron solution.

In an attempt to confirm other workers' observation of the 4,4'-dipyridyl, a dead volume was introduced between the point of mixing and the point of observation equivalent to a delay of approximately 1/3 sec and then 1 sec. At the shorter time only a very small pyridine radical-anion spectrum was seen and no spectrum at all at 1 sec. This confirms Henning's<sup>57</sup> suspicion that the decay of  $\text{py}^\cdot$  is fast and the difference between this half-life (less than 1 sec) and that determined by Talcott and Myers<sup>71</sup> (approx. 1 min) can be accounted for by the difference of the temperatures used (approx.  $-43^\circ\text{C}$  in this work,  $-70^\circ\text{C}$  in ref 71). After the disappearance of the pyridine spectrum the anticipated 4,4'-dipyridyl spectrum was not produced, which supports the suggestion<sup>51</sup> that oxygen is required before dimerisation can occur. It is a possibility that by using equal concentrations of  $\text{e}^-$  and of substrate that sufficient reducing solution was not present to remove hydride ions from the postulated sigma complex as sodium hydride.

A number of flow experiments were conducted to provide further information at the concentrations and delay times shown in Table I where it can be seen that with only one exception (a small and unidentifiable spectrum) either no spectrum, the  $e^-$  signal alone or the  $py^\cdot$  spectrum was obtained.

A semi-quantitative 'static' (as opposed to 'flow') system was developed to study the reduction reaction over a longer period of time. This comprised the mixing of pyridine with sodium in liquid ammonia in a glass tube placed in the cavity of the e.s.r. spectrometer, the required temperature being maintained by passing precooled nitrogen gas round the tube. Observation occurred within one minute of mixing and the spectrum of 4,4'-dipyridyl was produced which was stable for several hours;  $py^\cdot$  was not observed.

The three mono-methylpyridines, 2-, 3- and 4-methylpyridine gave the simple monomer radical-anions on the flow system - the spectrum of 3-methylpyridine is shown at the end of this chapter. The ammonia solutions were passed through the mixing-cell at very high flow rates and the reservoirs of reductant and substrate solutions (2 litres each) were soon exhausted, with the consequence that only short scan times were used to sweep the magnetic field range of interest. This disadvantage is seen in the 3-methylpyridine spectrum where the fast scan time (less than 5 mins) does not allow the recorder pen to keep pace with the number of hyperfine lines towards the centre.

Three dimethylpyridines, 2,6-, 3,5- and 3,4-dimethylpyridine were reduced to give the monomer radical-anions. 3,5-Dimethylpyridine has previously been characterised<sup>59</sup> and although 2,6-dimethylpyridine has produced a spectrum undoubtedly of the monomer<sup>71</sup> it was not analysed.

Both mono- and di-methylpyridines were mixed with sodium in liquid



TABLE I

Reaction of Sodium with Pyridine in Liquid Ammonia

<u>Position of mixer<sup>a</sup></u>	<u>Concentrations (M)</u>		<u>Comment</u>
	<u>[Na]</u>	<u>[Pyridine]</u>	
1. In cavity	(a) $5 \times 10^{-3}$	$5 \times 10^{-3}$	Good spectrum of $py^{\cdot-}$
	(b) $5 \times 10^{-3}$	$5 \times 10^{-2}$	Spectrum of $py^{\cdot-}$ but broader lines
2. $1\frac{1}{2}'$ from cavity	(a) $5 \times 10^{-3}$	$5 \times 10^{-3}$	Weak spectrum of $py^{\cdot-}$
	(b) $5 \times 10^{-3}$	$5 \times 10^{-2}$	No signal
	(c) $5 \times 10^{-2}$	$5 \times 10^{-3}$	Only $e^{\cdot-}$ signal
3. $6\frac{1}{2}'$ from cavity	(a) $10^{-1}$	$10^{-2}$	Only $e^{\cdot-}$ signal
	(b) $5 \times 10^{-3}$	$5 \times 10^{-2}$	Small signal, not large enough to identify. Not $py^{\cdot-}$ (major triplet split into 5 peaks)
	(c) Repeat of (b)		No signal
	(d) $5 \times 10^{-3}$	$5 \times 10^{-3}$	Very small signal - not identifiable
	(e) Repeat of (d)		No signal
	(f) $<< 5 \times 10^{-3}$	$5 \times 10^{-3}$	No signal

<sup>a</sup> Delay from mixing to observation

In cavity - nil (mixing within few milliseconds)

 $1\frac{1}{2}'$  from cavity - 0.3 seconds $6\frac{1}{2}'$  from cavity - 1.5 seconds

ammonia in the 'static' technique and all except 4-methylpyridine and 3,4-dimethylpyridine exhibited spectra showing that dimerisation had occurred; coupling constants for the dimers are shown in Table V. It appears that the blocking of the 4-position prevents dimerisation, and decay of the reduced monomer possibly proceeds via diamagnetic products; this has been noticed by other workers.<sup>72</sup>

The two trimethyl pyridines reduced were 2,4,6- and 2,3,6-collidine; the latter produced an expectedly complicated pattern of lines both from 'flow' and 'static' methods, and the symmetrical collidine produced a spectrum of 3,5-dimethylpyridine radical-anion even after repeated distillation. Two pure samples were therefore obtained, one commercially which was guaranteed to be free of 3,5-dimethylpyridine, and the other by formation of the pure picrate (which is separable from that of other methylpyridines by recrystallisation) and regeneration of the original collidine on an alumina column. Neither sample produced a spectrum from flow or static reduction.

A similar inseparable impurity effect was noticed for 4-methoxypyridine when the nitrobenzene radical-anion appeared, but no further work was done on this because of the small sample available.

2-Methoxy- and 2,6-dimethoxypyridine both behaved 'normally' giving monomer and dimer spectra on 'flow' and 'static'. The small coupling due to methoxy groups only appeared when very dilute solutions were used in the reduction.

Pyridine-N-oxide gave the anticipated spectrum by 'flow' but a curious sequence of reactions was observed by the 'static' method. The pyridine radical-anion spectrum itself was obtained and found to be stable for several minutes until dimerisation occurred yielding 2,2'-dipyridyl. This was



confirmed by comparison with the spectrum obtained by reduction of an authentic sample of 2,2'-dipyridyl. The formation of 2,2'-dipy<sup>•</sup> from pyridine-N-oxide has been noticed by other workers<sup>73</sup> while 4,4'-dipy<sup>•</sup> has also been obtained.<sup>74</sup>

Pyridine-d<sub>5</sub> gave extremely well-resolved monomer and dimer radical-anion spectra and the expected  $A_H : A_D$  ratio of approximately 6 : 1.

Pyridine-3- and -4-carboxylic acids produced the expected spectra but two different spectra were obtained from pyridine-2-carboxylic acid. After several runs a reproducible doublet of quartets was usually observed but irregularly a more complex spectrum would appear. The first spectrum was attributed to a radical similar to that produced by the other monocarboxylic acids, although the lines due to the 3- and 5- protons were not resolved, with consequent line width broadening (ca 1 Oe). The second was analysed in terms of one proton additional to the number expected. An extra proton was also apparent from the analysis of the spectra of five pyridinedicarboxylic acids. The fact that pyridine-2-carboxylic acid and not 3- or 4- mono-acids shows an extra proton might suggest hydrogen-bonding to the nitrogen but this is ruled out by the fact that pyridine-3,5-dicarboxylic acid exhibits an extra proton where hydrogen-bonding is not possible.

It is not unreasonable to assume that the extra proton is attached to the nitrogen atom and not, for example, at the 4- position, as the latter would probably give a recognisable 1 : 2 : 1 pattern superimposed upon the spectra of unsymmetrical molecules such as the 2,5-diacid. Melchior and Maki<sup>75</sup> have calculated that the ratio of hyperfine coupling constants of nitrogen to a proton bonded to that nitrogen should be 1 : 1.12 and their investigation of para-phenylenediamine radical-cation confirms this quite nicely by giving a ratio  $A_N : A_H$  of 1 : 0.90. A similar value for this ratio of 1.03 - 1.07

(depending on the temperature) has been obtained for the  $\text{N}_2\text{H}_4^+$  radical.<sup>76</sup> An inspection of coupling constants obtained for the pyridinedicarboxylic acids (Table III) reveals a similar ratio, hence strengthening the assumption that the nitrogen is protonated. Table II shows the ratios obtained. These ratios are in quite good agreement with the expected value of approximately 1.1.

Pyridine-2,6-dicarboxylic acid N-oxide was investigated in the hope that reduction would produce an unprotonated species. However, the spectrum of protonated pyridine-2,6-dicarboxylic acid only was seen, which presumably arises either by removal of N-oxygen by the reducing medium or from an impurity of the original acid.

The ionisation of  $\text{H}^+$  from the carboxylic acid group must be the source of protons in liquid ammonia solution and the sodium salt of the 2,6-dicarboxylic acid was investigated in order to eliminate surplus protons from the reduction process but was found to be insoluble. A similar attempt to remove protons was made by dissolving potassamide with the diacid in ammonia:  $\text{NH}_2^- + \text{H}^+ \rightarrow \text{NH}_3$ ; no spectrum was obtained.

In contrast to the previous experiments to prepare the parent acid radical, the preparation of protonated pyridine radical was attempted. Pyridine was dissolved in liquid ammonia ( $10^{-3}\text{M}$ ) and ethanol was added to make the solution  $1\text{M}$  in  $\text{H}^+$ ; this solution was then mixed with  $10^{-3}\text{M}$  sodium solution in the mixing-cell. A spectrum, analysed as arising from coupling with two pairs of equivalent protons, two inequivalent protons and a nitrogen atom was obtained (Table III) attributable to the neutral pyridine radical

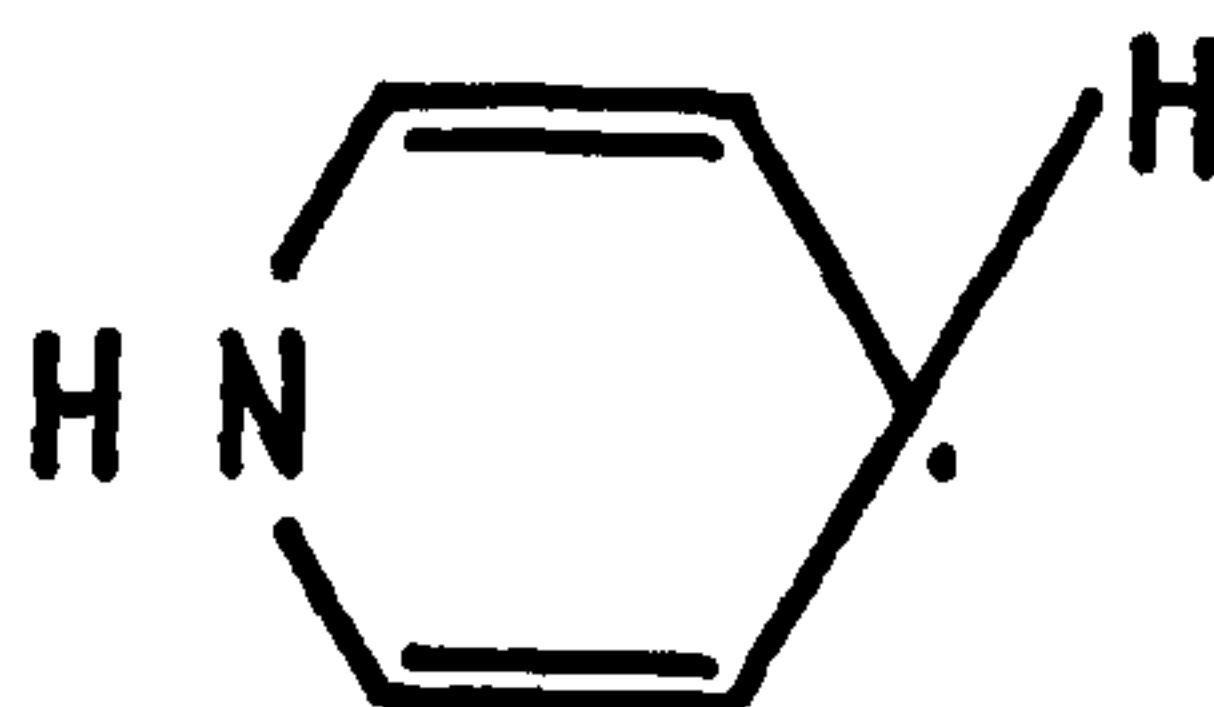




TABLE II

Ratios of Nitrogen and Attached Proton Coupling  
Constants for Pyridinecarboxylic acid Radicals

<u>Substrate</u>	<u>A<sub>N</sub></u>	<u>A<sub>H</sub></u>	<u>A<sub>N</sub>/A<sub>H</sub></u>
Pyridine-2,3-dicarboxylic acid	0.85	0.85	1.00
Pyridine-2,5-dicarboxylic acid	4.22	4.68	0.90
Pyridine-2,6-dicarboxylic acid	6.16	5.63	1.09
Pyridine-3,5-dicarboxylic acid	4.78	3.86	1.23
6-Methylpyridine-2,4-dicarboxylic acid	5.05	4.03	1.25
Pyridine-2-carboxylic acid	5.60	5.19	1.07

Similar coupling constants have been noticed by Chachaty<sup>77</sup> who obtained a much less well-resolved spectrum by  $\gamma$ -radiolysis of frozen solutions of pyridine in ethanol at 77° K. Only the particular concentrations of pyridine/ethanol and sodium mentioned above gave the protonated pyridine radical spectrum; all other concentrations attempted gave either  $\text{py}^\cdot$  or no spectrum.

The sequence of reactions to produce  $\text{pyH}^\cdot$  are as follows:



accompanied by the following reaction competing for  $\text{e}^-_{\text{solv}}$ <sup>50</sup> as discussed in the introduction;



The presence of a competing reaction probably accounts for the critical concentration found to be necessary since too high a concentration of ethanol would use all available solvated electron at the expense of pyridine radical-anion reduction and too low a concentration of ethanol would not provide a sufficient quantity of protons for reduction. For all the substituted pyridine compounds investigated the critical concentration for ethanol/substrate mixtures could not be found and no spectra were obtained. In order to obtain a better spectrum of protonated pyridine and to obtain a series of protonated substituted pyridines a two-stage mixing device was developed. Pyridine and solvated electron were mixed at stage I to produce  $\text{py}^\cdot$  which, a few milliseconds later, was mixed with ethanol solution at stage II. It was hoped that this device would minimise the effect of the competing reaction, but either no spectrum at all was obtained or by decreasing the ethanol concentration only the substrate monomer spectrum was obtained.

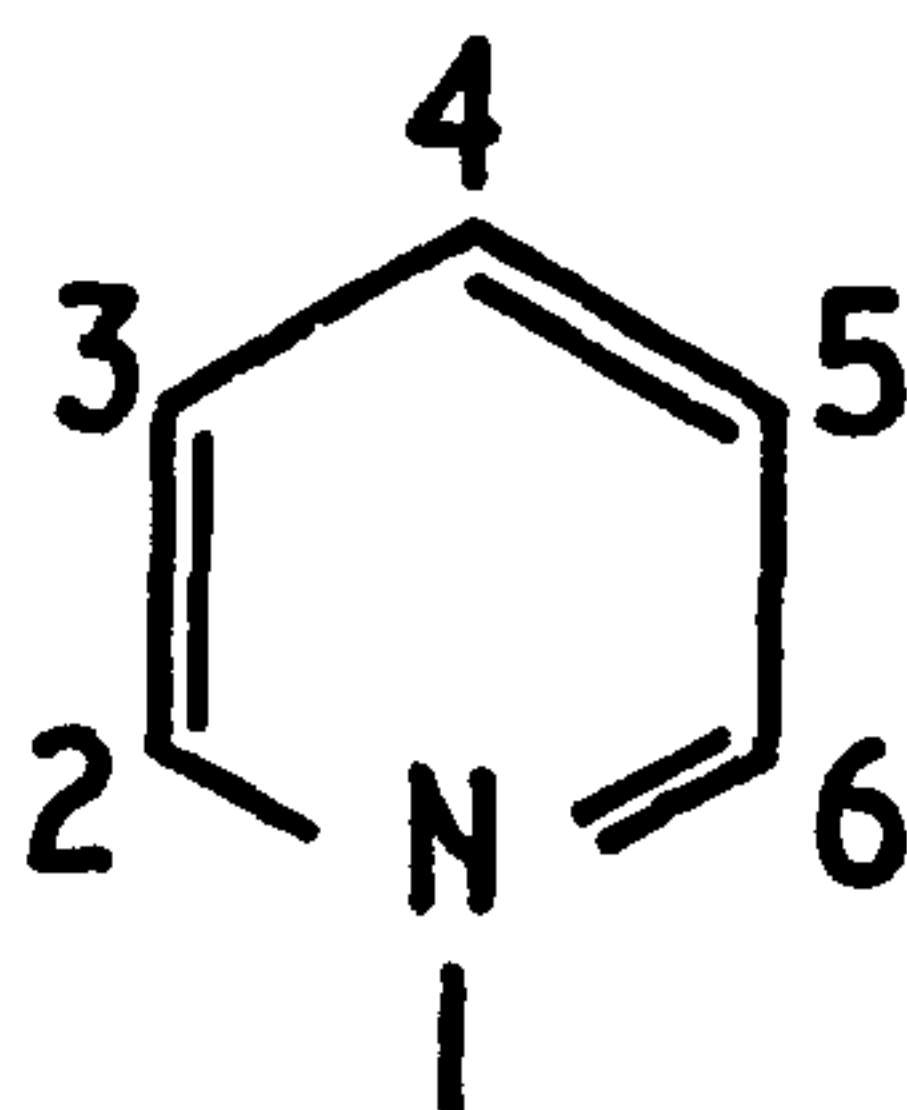


## MOLECULAR ORBITAL CALCULATIONS

A computer program (see experimental chapter) was used to calculate the Hückel and McLachlan theoretical spin densities for substituted pyridines shown in the Tables. No attempt was made at a detailed theoretical investigation, the only aim of evaluating approximate spin densities being to assist in assigning experimental coupling constants. In order to calculate spin densities the following parameters are required:

- h the Coulomb integral for each atom, representing the energy of an electron in a  $\pi$  atomic orbital,
- k the resonance integral for each bond representing the energy of an electron when it is between two atoms,
- $\lambda$  the approximate configuration interaction constant used by McLachlan.<sup>78</sup>

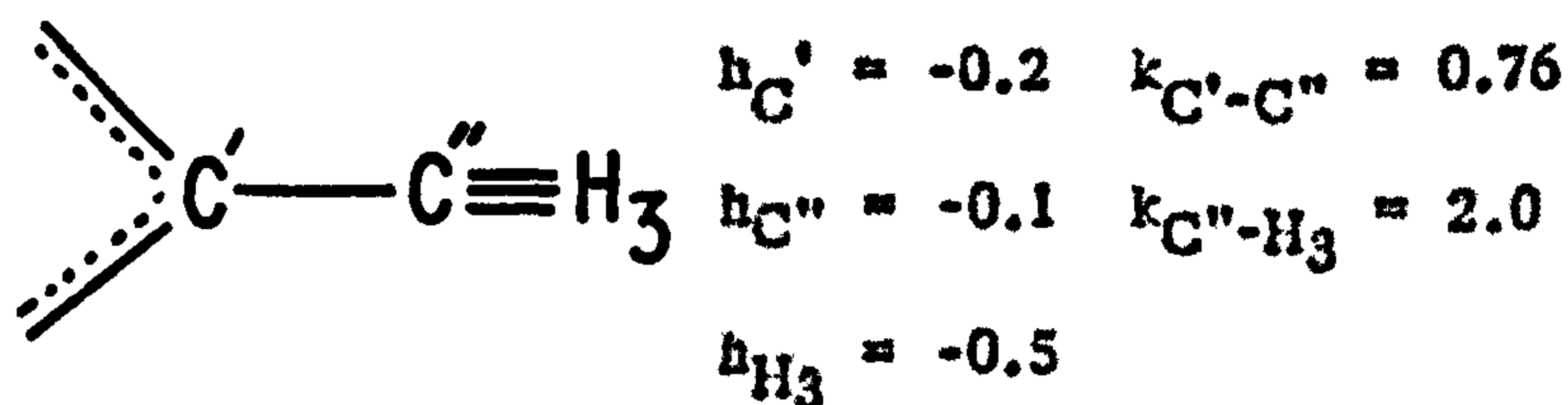
The approximate spin densities for pyridine were obtained from a knowledge of the values for substituted pyridines, e.g. 3,5-dimethylpyridine,<sup>59</sup> and more exact figures from the computer program by intelligent adjustment of the parameters. Spin densities for the substituted pyridines were then obtained by retaining the previously determined values of h, k and  $\lambda$  for the pyridine nucleus and inserting appropriate values for the substituent. Carbon atom Coulomb integrals are usually taken as zero;  $\lambda$ , following ref. 71, was given the value 0.75 and the other variables were set as follows:



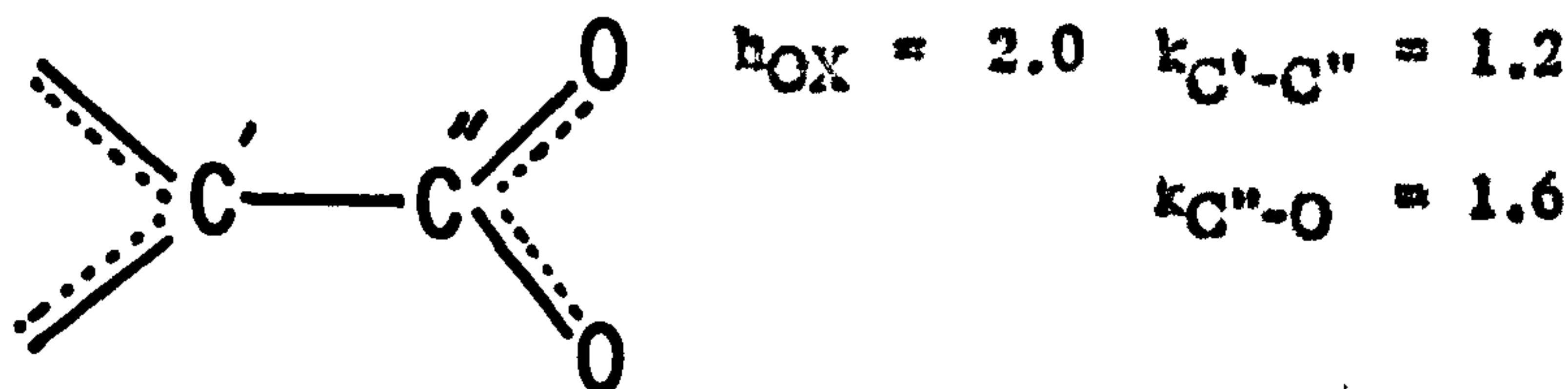
$$h_N = 0.8 \quad k_{C-N} = 1.1$$

$$k_{C-C} = 1.0$$

For methyl groups a combination of the inductive and hyperconjugative<sup>78</sup> models was used;



The Coulomb and resonance integrals for -COOH were obtained from a study of benzoic acid and its derivatives (see Chapter IV)



The McConnell relationship<sup>79</sup> provides a link between experimentally observed coupling constants ( $A$ ) and spin densities ( $\rho$ ),

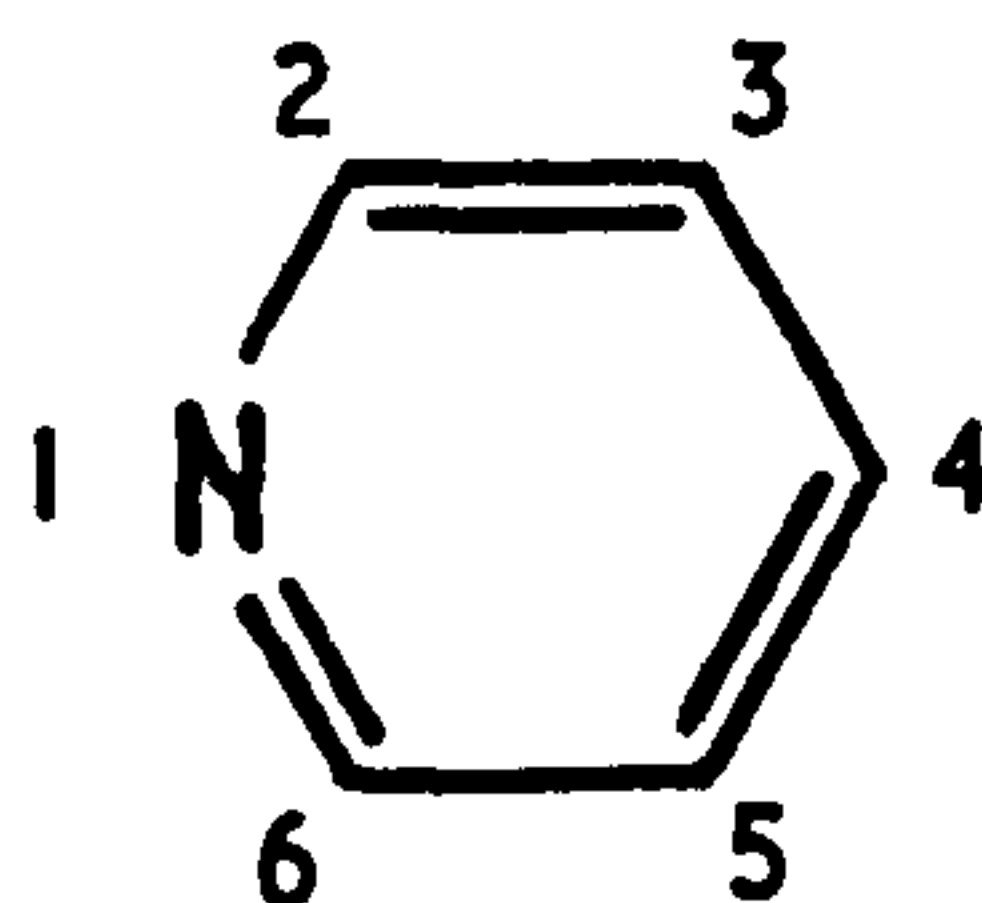
$$A = \rho Q$$

$Q$  is a constant and for pyridines  $Q_{\text{CH}}^{\text{H}}$  was found to be 23.6.

TABLE III

Coupling Constants and Theoretical Spin Densities  
for Pyridine Radical-anions

Ring positions are numbered as in the following diagram;



Substrate	Position	Experimental		Calculated	
		Coupling constants (G)	Spin densities	Hückel	McLachlan
Pyridine	1	6.31	0.226	0.256	0.273
	2	3.55	0.150	0.143	0.148
	3	0.79	0.033	0.059	0.011
	4	9.63	0.403	0.338	0.403
Pentadeuterio-pyridine	1	6.33			
	2	0.50			
	3	0.13			
	4	1.49			
2-Methylpyridine	1	5.64	0.202	0.239	0.252
	2	2.34	0.033	0.039	0.079
	3	1.56	0.066	0.106	0.074
	4	9.53	0.403	0.333	0.401
	5	< .1	< 0.004	0.028	-0.029
	6	4.39	0.186	0.189	0.212
3-Methylpyridine	1	6.34	0.227	0.259	0.274
	2	4.07	0.172	0.185	0.203
	3	0.45	0.016	0.039	-0.012
	4	9.61	0.407	0.322	0.390
	5	1.35	0.057	0.079	0.040
	6	2.68	0.113	0.109	0.105

....continued



TABLE III (continued)

Substrate	Position	Experimental		Calculated	
		Coupling Constants (Oe)	Spin densities	Spin densities	
				Hückel	McLachlan
4-Methylpyridine	1	5.67	0.204	0.246	0.260
	2	3.63	0.155	0.144	0.155
	3	0.053	0.024	0.014	-0.004
	4	11.31	0.403	0.320	0.383
2,3-Dimethylpyridine	1	5.78	0.206	0.243	0.258
	2	2.89	0.103	0.132	0.132
	3	0.46	0.016	0.078	0.039
	4	8.66	0.366	0.320	0.388
	5	0.82	0.034	0.044	-0.004
	6	2.89	0.122	0.147	0.159
2,6-Dimethylpyridine	1	4.86	0.174	0.224	0.235
	2	3.16	0.112	0.130	0.133
	3	0.71	0.030	0.055	0.023
	4	9.29	0.393	0.341	0.413
3,4-Dimethylpyridine	1	5.77	0.208	0.247	0.261
	2	4.98	0.211	0.189	0.213
	3	< 0.2	< 0.007	0.026	-0.027
	4	11.48	0.410	0.308	0.369
	5	2.34	0.099	0.065	0.025
	6	1.51	0.064	0.108	0.107
3,5-Dimethylpyridine	1	6.40	0.229	0.264	0.281
	2	3.18	0.134	0.149	0.153
	3	1.06	0.037	0.036	0.012
	4	8.85	0.375	0.306	0.373
2-Methoxypyridine	1	8.86		0.232	0.243
	2	0.23	0.007	0.006	0.001
	3	1.09	0.046	0.130	0.105
	4	7.14	0.302	0.331	0.397
	5	0.46	0.019	0.018	-0.043
	6	4.29	0.181	0.212	0.241

....continued

TABLE III (continued)

Substrate	Position	Experimental		Calculated	
		Coupling constants (G)	Spin densities	Spin densities	
				Hückel	McLachlan
2,6-Dimethoxypyridine	1	4.41		0.217	0.227
	2	0.15	0.005	0.010	0.006
	3	0.83	0.035	0.073	0.030
	4	10.16	0.430	0.361	0.437
Pyridine-N-oxide	1	11.00		0.270	0.293
	2	3.03	0.128	0.116	0.118
	3	0.43	0.018	0.058	0.020
	4	8.52	0.361	0.303	0.368
Pyridine-2-carboxylic acid	1	4.1		0.132	0.206
	2			0.208	0.227
	3			0.062	0.045
	4	5.5	0.230	0.099	0.088
	5			0.183	0.211
	6	4.1	0.173	0.005	-0.037
Pyridine-2-carboxylic acid (protonated)	1	5.60	0.224	0.146	0.143
	2			0.240	0.286
	3	0.96	0.041	0.021	-0.030
	4	9.39	0.398	0.192	0.224
	5	1.66	0.070	0.091	0.067
	6	3.08	0.131	0.103	0.105
	N-H	5.19			
Pyridine-3-carboxylic acid	1	1.64	0.064	0.050	0.019
	2	1.09	0.046	0.055	0.050
	3			0.157	0.152
	4	7.28	0.308	0.216	0.259
	5	0.47	0.019	0.009	-0.049
	6	8.83	0.374	0.278	0.339
Pyridine-4-carboxylic acid	1	5.51	0.190	0.192	0.215
	2	1.96	0.083	0.071	0.051
	3	1.96	0.083	0.115	0.116
	4			0.201	0.218

....continued



TABLE III (continued)

Substrate	Position	Experimental		Calculated	
		Coupling constants (Oe)	Spin densities	Spin densities	
				Hückel	McLachlan
Pyridine-ethanol	1	5.79	0.241	0.164	0.150
	2	5.79	0.245	0.226	0.266
	3	0.74	0.031	0.028	-0.043
	4	11.62	0.492	0.328	0.404
	N-H	4.21			
Pyridine-2,3-dicarboxylic acid	1	0.85		0.125	0.124
	2			0.304	0.369
	3			0.049	0.013
	4	3.41	0.144	0.094	0.099
	5	3.41	0.144	0.104	0.098
	6	0.85	0.036	0.040	0.019
	N-H	0.85			
Pyridine-2,5-dicarboxylic acid	1	4.22		0.102	0.097
	2			0.265	0.320
	3	1.59	0.067	0.031	-0.019
	4	8.51	0.360	0.216	0.256
	5			0.095	0.079
	6	0.91	0.038	0.022	0.002
	N-H	4.68			
Pyridine-2,6-dicarboxylic acid	1	6.16		0.176	0.176
	2			0.183	0.212
	3	0.83	0.035	0.003	-0.048
	4	0.07	0.384	0.195	0.238
	N-H	5.63			
Pyridine-2,6-dicarboxylic acid diethyl ester	1	3.08			
	2	0.60			
	3	1.19			
	4	9.93			
Pyridine-3,5-dicarboxylic acid	1	4.78	0.225	0.121	0.106
	2	5.52	0.233	0.160	0.187
	3			0.030	-0.029
	4	12.31	0.521	0.431	0.543
	N-H	3.86			

....continued

TABLE III (continued)

Substrate	Position	Experimental		Calculated	
		Coupling constants (G)	Spin densities	Spin densities	
6-Methylpyridine-2,4-dicarboxylic acid	1	5.05		0.131	0.133
	2			0.175	0.202
	3	1.35	0.058	0.000	-0.044
	4			0.175	0.193
	5	3.36	0.142	0.157	0.163
	6	2.70	0.096	0.103	0.101
	N-H	4.03			

TABLE IV

Calculated g-Values for Pyridine Radical-anions

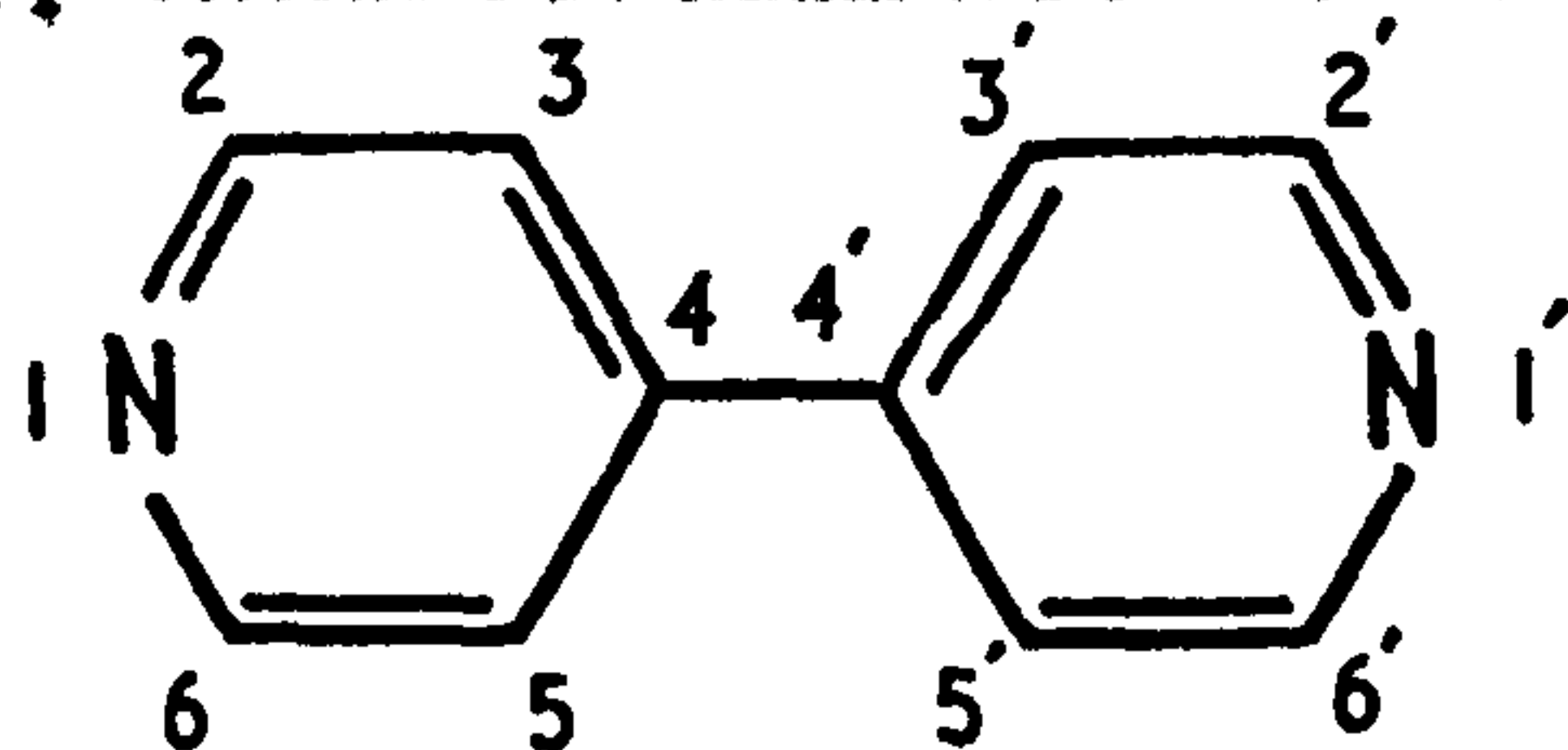
<u>Substrate</u>	<u>g-Value</u>
Pyridine	2.0034
Pentadeuteropyridine	2.0035
Pyridine-N-oxide	2.0035
2-Methylpyridine	2.0034
3-Methylpyridine	2.0036
4-Methylpyridine	2.0033
2,3-Dimethylpyridine	2.0034
2,6-Dimethylpyridine	2.0033
3,4-Dimethylpyridine	2.0033
3,5-Dimethylpyridine	2.0034
2-Methoxypyridine	2.0032
2,6-Dimethoxypyridine	2.0032
Pyridine-ethanol	2.0038
Pyridine-2-carboxylic acid	2.0036
Pyridine-3-carboxylic acid	2.0034
Pyridine-4-carboxylic acid	2.0037
Pyridine-2,3-dicarboxylic acid	2.0038
Pyridine-2,5-dicarboxylic acid	2.0036
Pyridine-2,6-dicarboxylic acid	2.0035
Pyridine-2,6-dicarboxylic acid diethyl ester	2.0037
Pyridine-3,5-dicarboxylic acid	2.0033
6-Methylpyridine-2,4-dicarboxylic acid	2.0035



TABLE V

Coupling Constants and Theoretical Spin Densities  
of Pyridine Dimer (1, 4'-dipyridyl) Radical-anions  
obtained from the Static Reduction Technique

Ring positions are numbered as in the following diagram:



Radical-anion	Position	Experimental		Calculated	
		Coupling constants (G)	Spin densities	Spin densities	
				Hückel	McLachlan
Pyridine dimer	1	4.03	0.143	0.126	0.140
	2	0.56	0.023	0.046	0.033
	3	2.70	0.114	0.076	0.077
	4			0.130	0.140
Pentadeuterio-pyridine dimer	1	3.59			
	2	0.07			
	3	0.36			
2-Methylpyridine dimer	1	2.75	0.097	0.117	0.130
	2	0.60	0.021	0.033	0.023
	3	2.75	0.116	0.074	0.101
	4			0.131	0.142
	5	1.82	0.077	0.054	0.062
	6	0.18	0.007	0.050	0.039
3-Methylpyridine dimer	1	3.57	0.129	0.127	0.142
	2	2.03	0.088	0.065	0.058
	3	1.93	0.063	0.052	0.059
	4			0.120	0.129
	5	2.39	0.101	0.033	0.038
	6	0.45	0.019	0.004	0.018

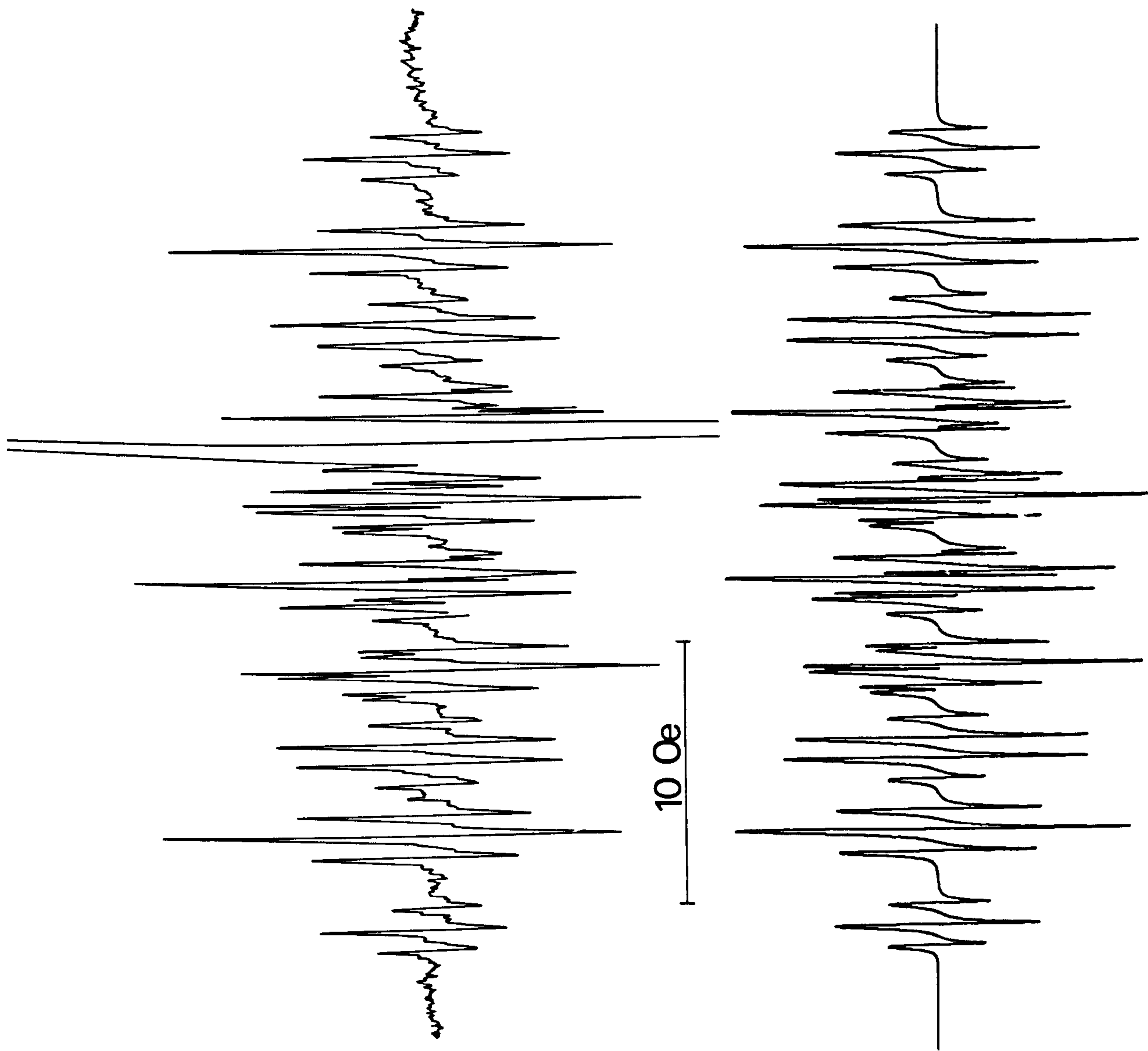
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TABLE V (continued)

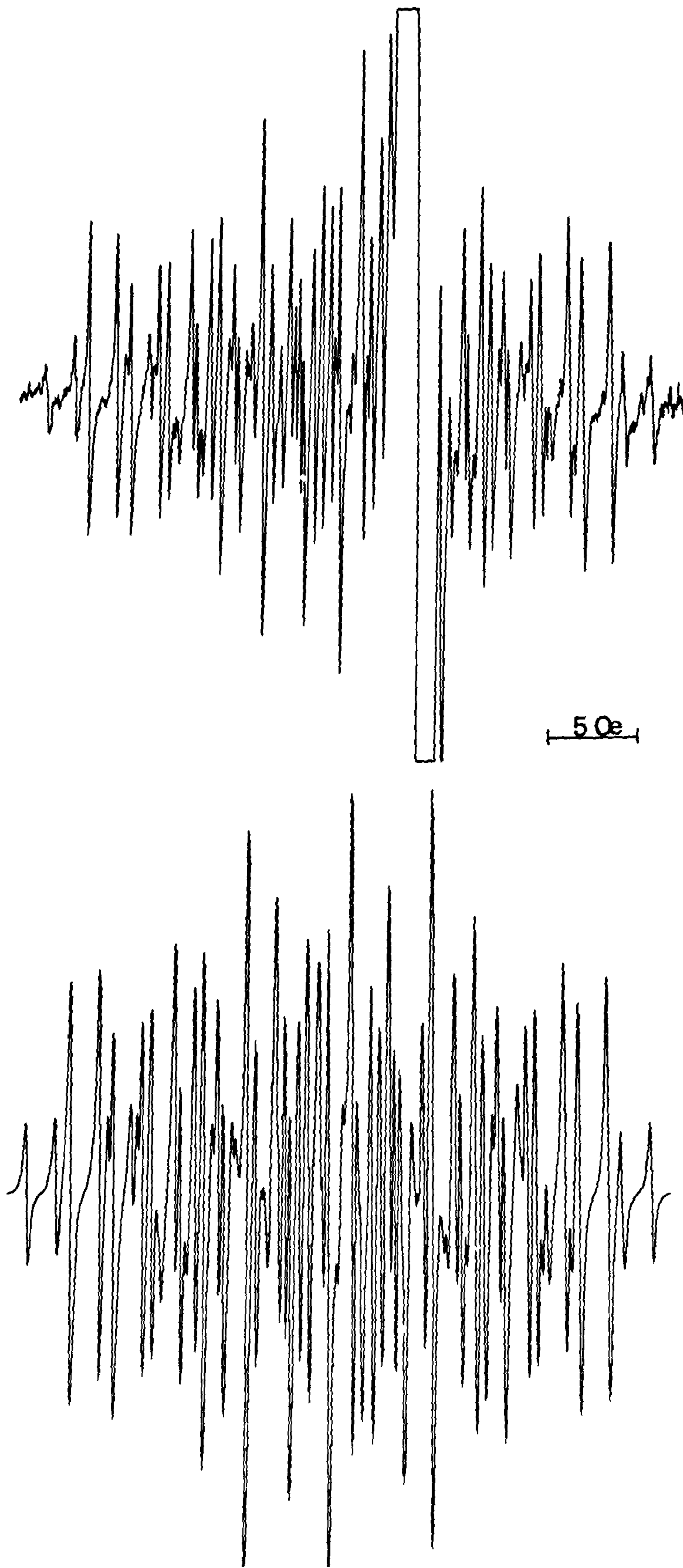
Radical-anion	Position	Experimental		Calculated	
		Coupling constants (G)	Spin densities	Spin densities	
				Hückel	McLachlan
2,6-Dimethylpyridine dimer	1	2.84	0.100	0.103	0.120
	2	0.28	0.010	0.042	0.029
	3	2.84	0.120	0.082	0.085
	4			0.133	0.144
3,5-Dimethylpyridine dimer	1	3.71	0.130	0.129	0.145
	2	0.58	0.024	0.051	0.042
	3	1.85	0.066	0.069	0.069
	4			0.110	0.118
2,6-Dimethoxypyridine dimer	1	2.68		0.105	0.116
	2	0.14	0.004	0.004	0.001
	3	2.56	0.108	0.084	0.089

**Spectrum of the pyridine radical-anion (upper)  
and the computer simulation (lower).**



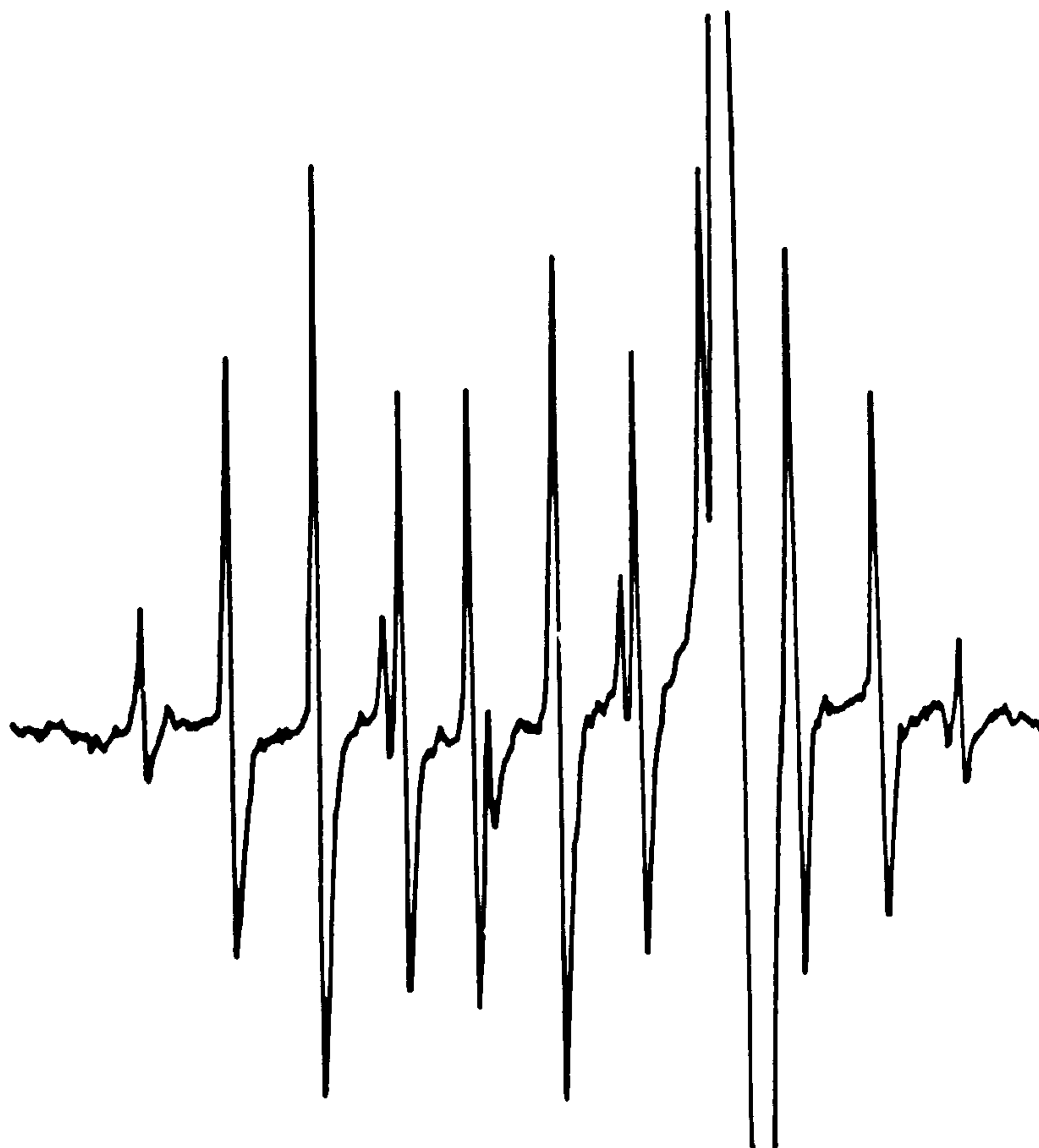


Spectrum of the 2-methylpyridine radical-anion (upper)  
and the computer simulation (lower).

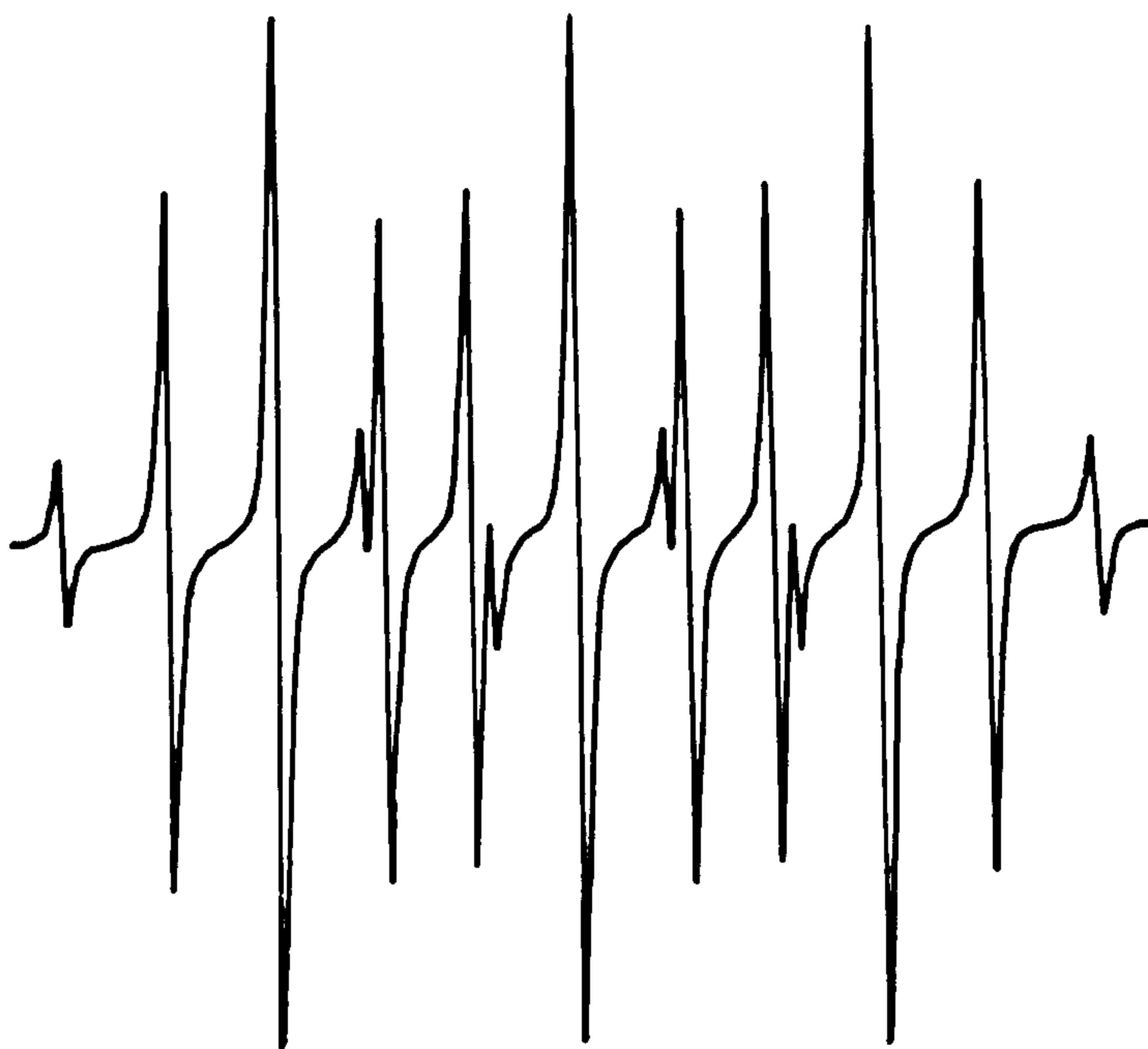




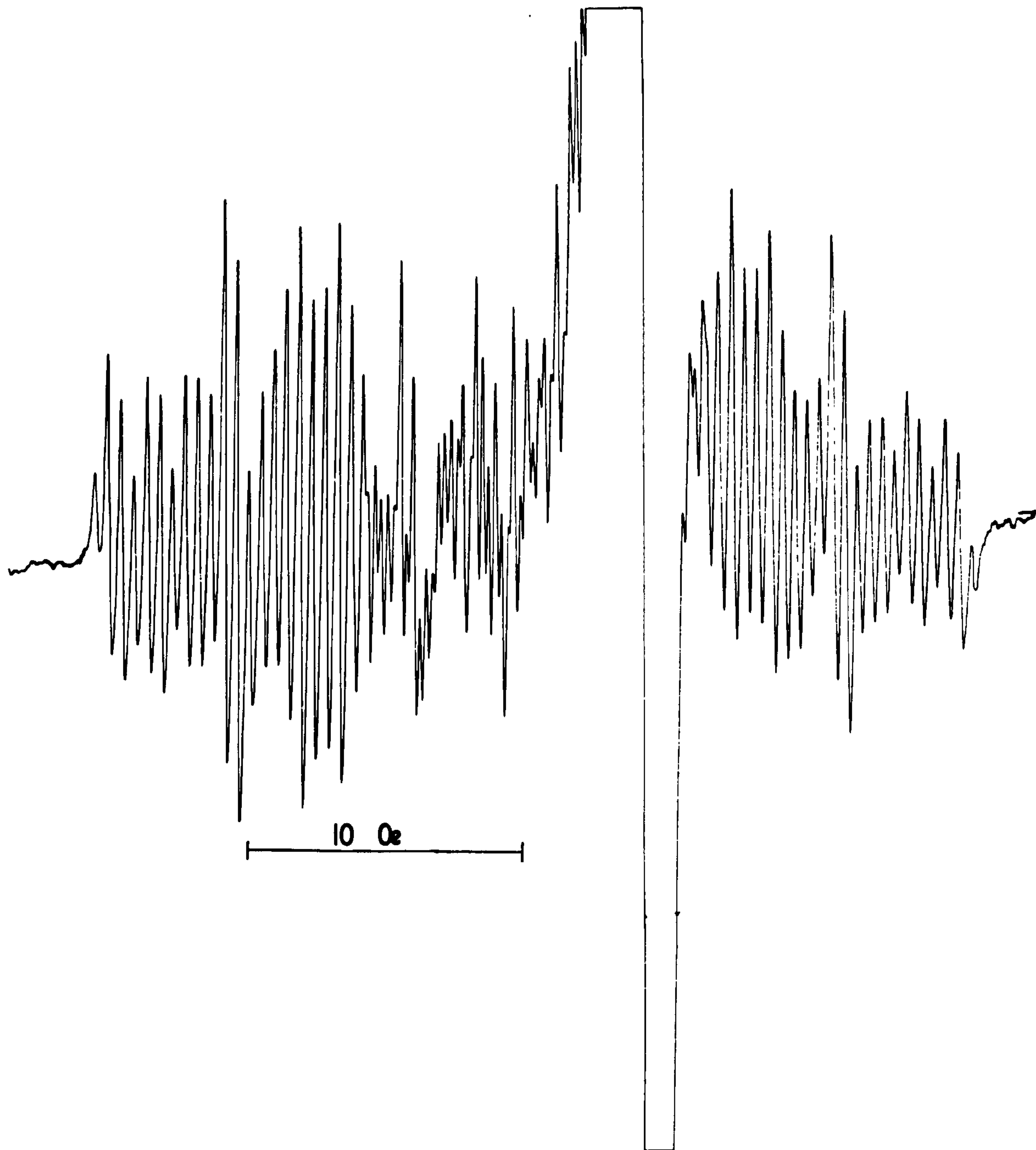
**Spectrum of the radical-anion of pyridine-4-carboxylic acid (upper) and the computer simulation (lower).**



10 Oe

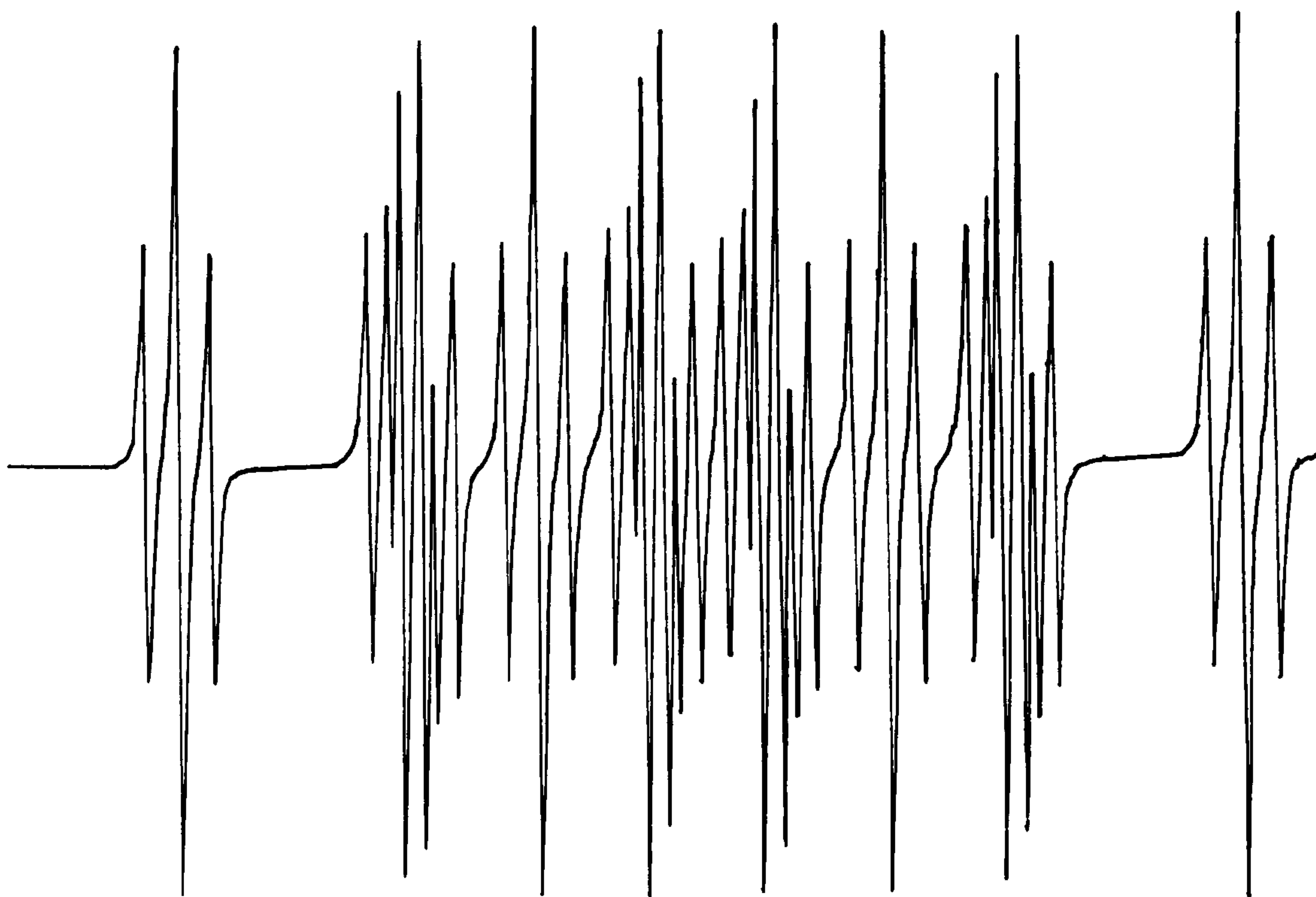
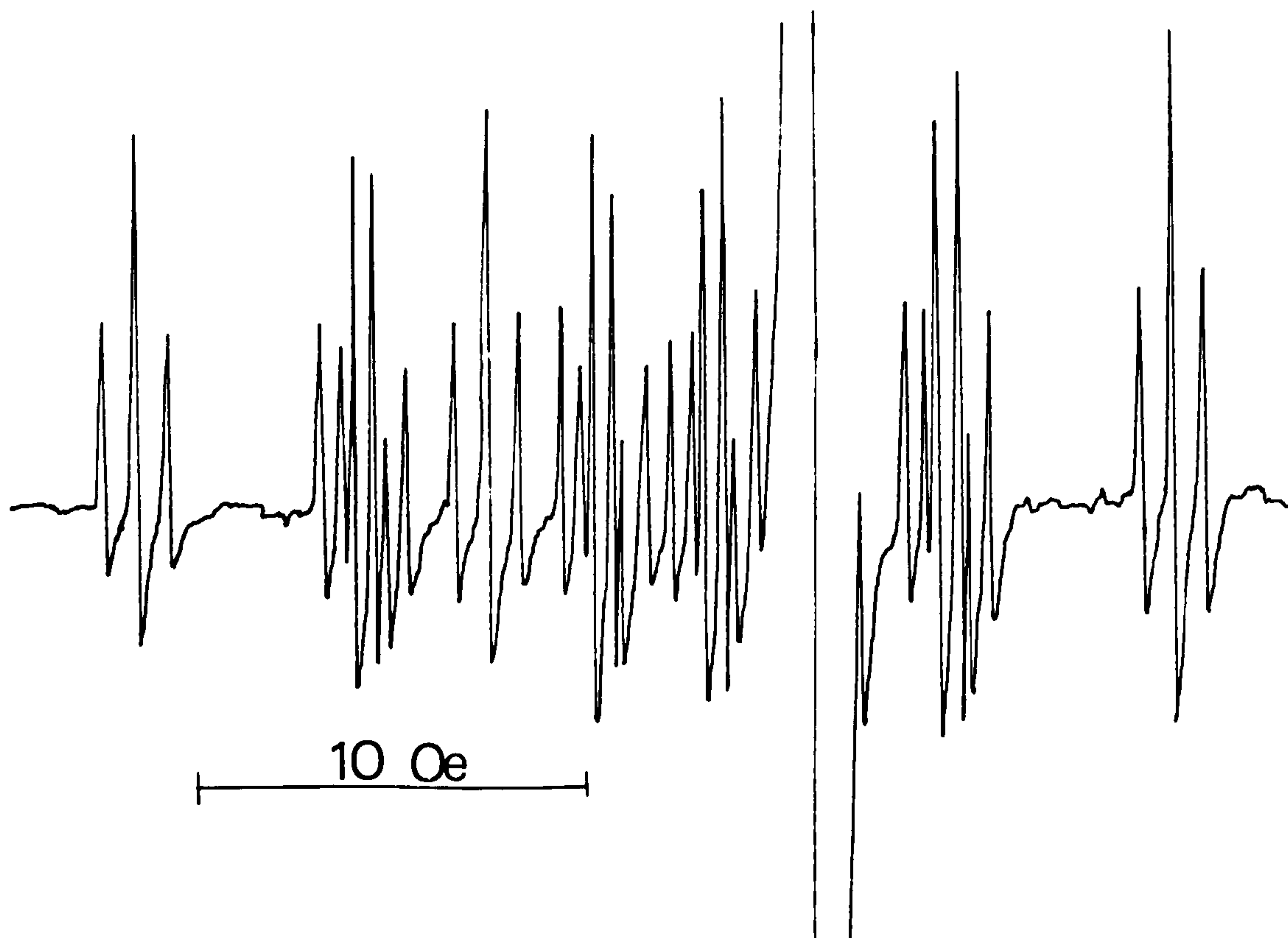


**Spectrum of the radical-anion of 3-methylpyridine.**

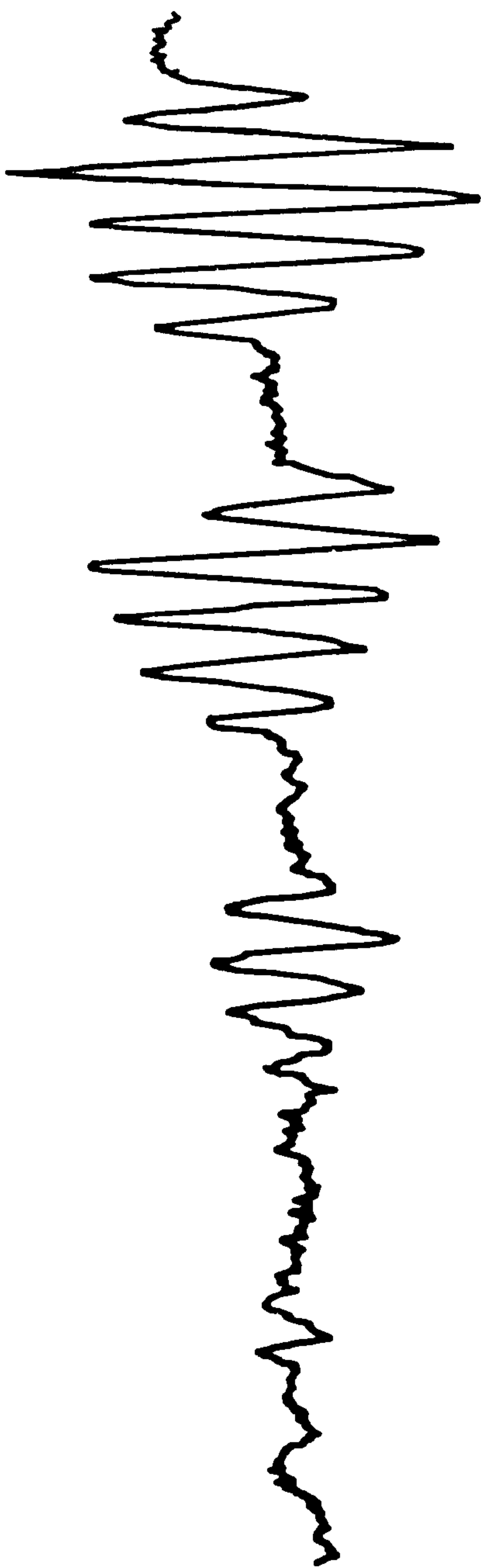




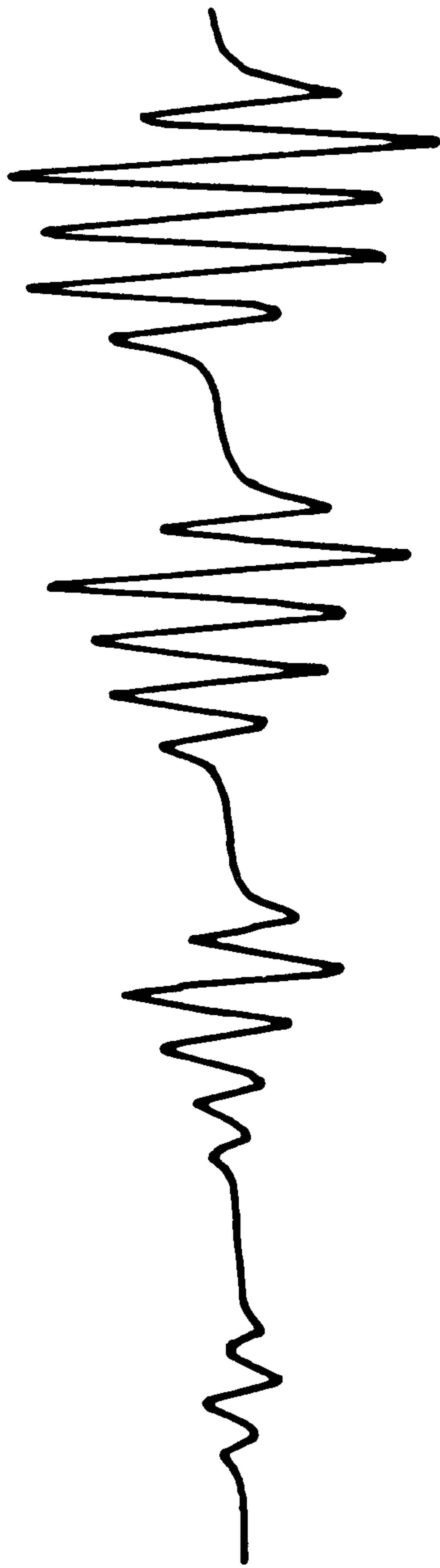
**Spectrum obtained from reduction of pyridine-2,6-dicarboxylic acid and the computer simulation.**



Half-spectrum of the protonated pyridine radical (upper)  
and the computer simulation (lower).

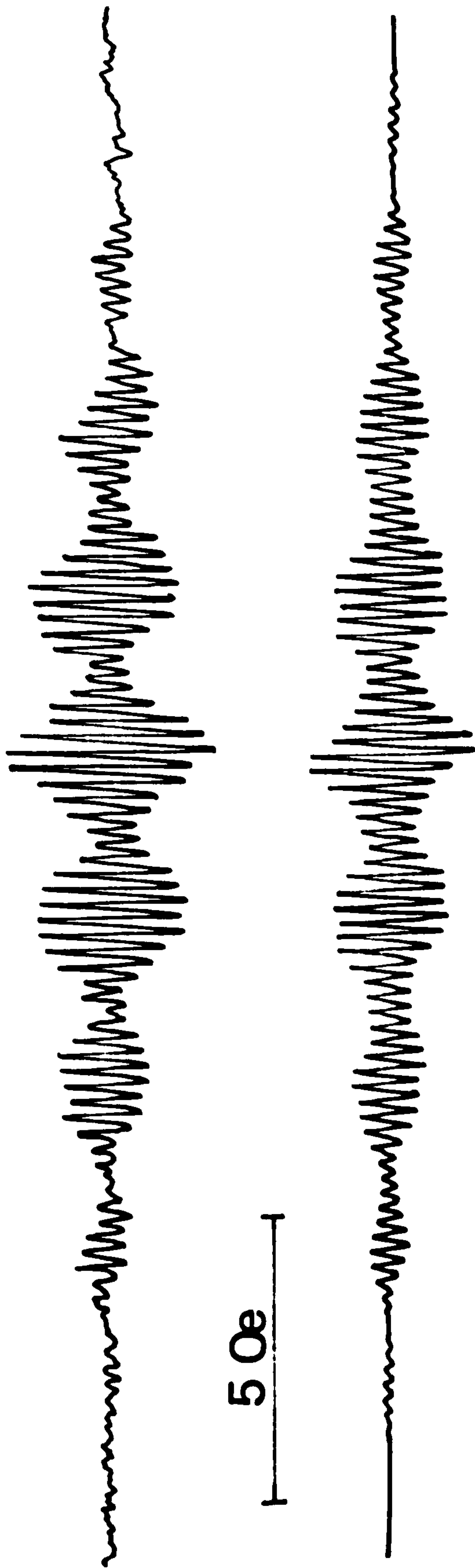


10 Oe

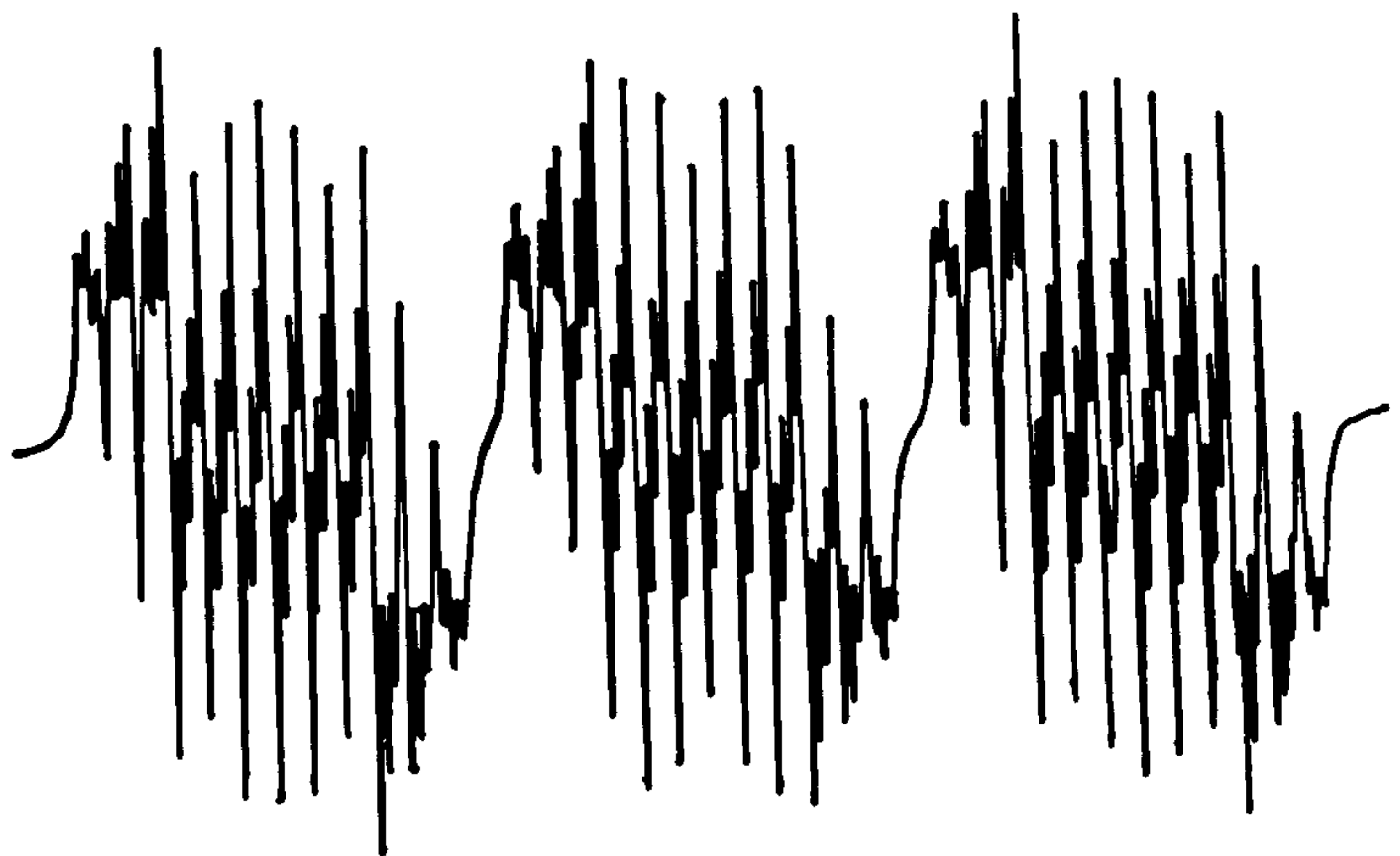
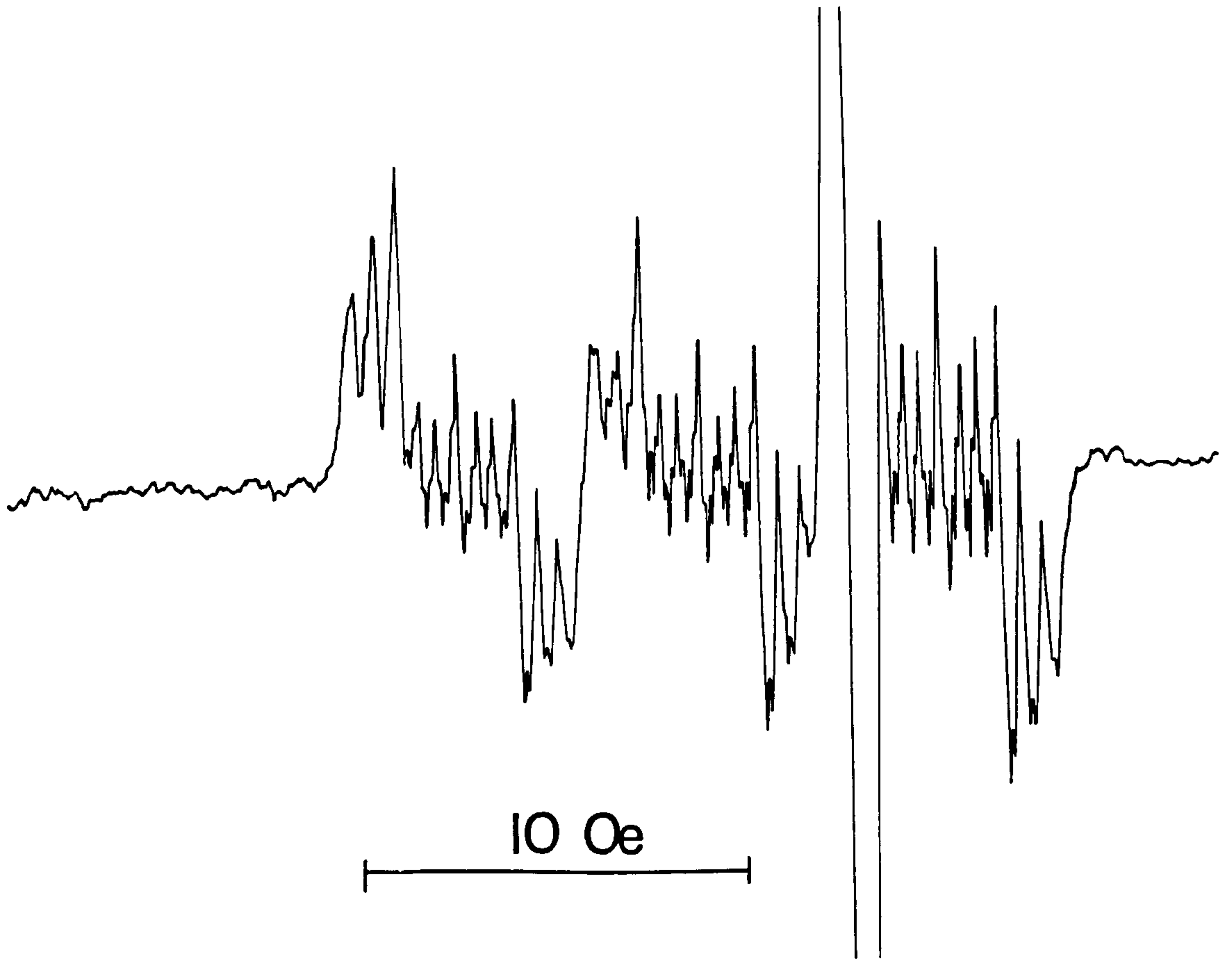




Spectrum obtained from static reduction of 2,6-dimethylpyridine (upper) and the computer simulation (lower).



Spectrum of the radical-anion of pyridine- $d_5$  (upper)  
and the computer simulation (lower).





## REDUCTION OF ARYL HALIDES

## INTRODUCTION

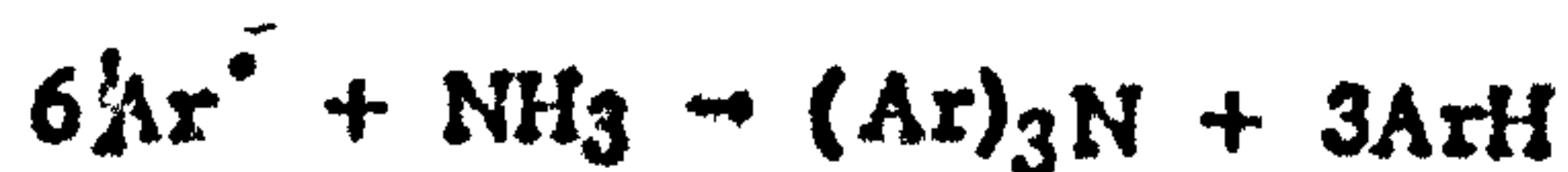
During reduction of aryl halides the carbon-halogen bond is frequently cleaved and advantage has been taken of this both in organic preparative work, for example the synthesis of polyphenyls from iodobenzene in benzene,<sup>80</sup> and in analytical techniques where cleaved halide is estimated volumetrically or gravimetrically.<sup>81,82</sup>

E.s.r. investigations of aryl halides have been unevenly distributed in favour of substituted nitrobenzenes,<sup>83-86</sup> although halo-benzenes, -toluenes and -styrenes<sup>87</sup> have been studied using product analysis. The order of ease of loss of halogen appears to be in the sequence  $I > Br > Cl \gg F$ .<sup>86,88</sup> In the potassium/THF reduction of halodiphenyls, Allred and Bush<sup>89</sup> concluded that the large carbon-fluorine bond energy was responsible for the relatively high stability of fluoro-compounds while the easy transfer of an electron to vacant d-orbitals of the other halogens facilitated the formation of  $K^+$ . For steric reasons, ortho-halogen substituted nitrobenzenes lose halogen more easily than para-substituted and the stability of meta-substituted is often greater than either of these.

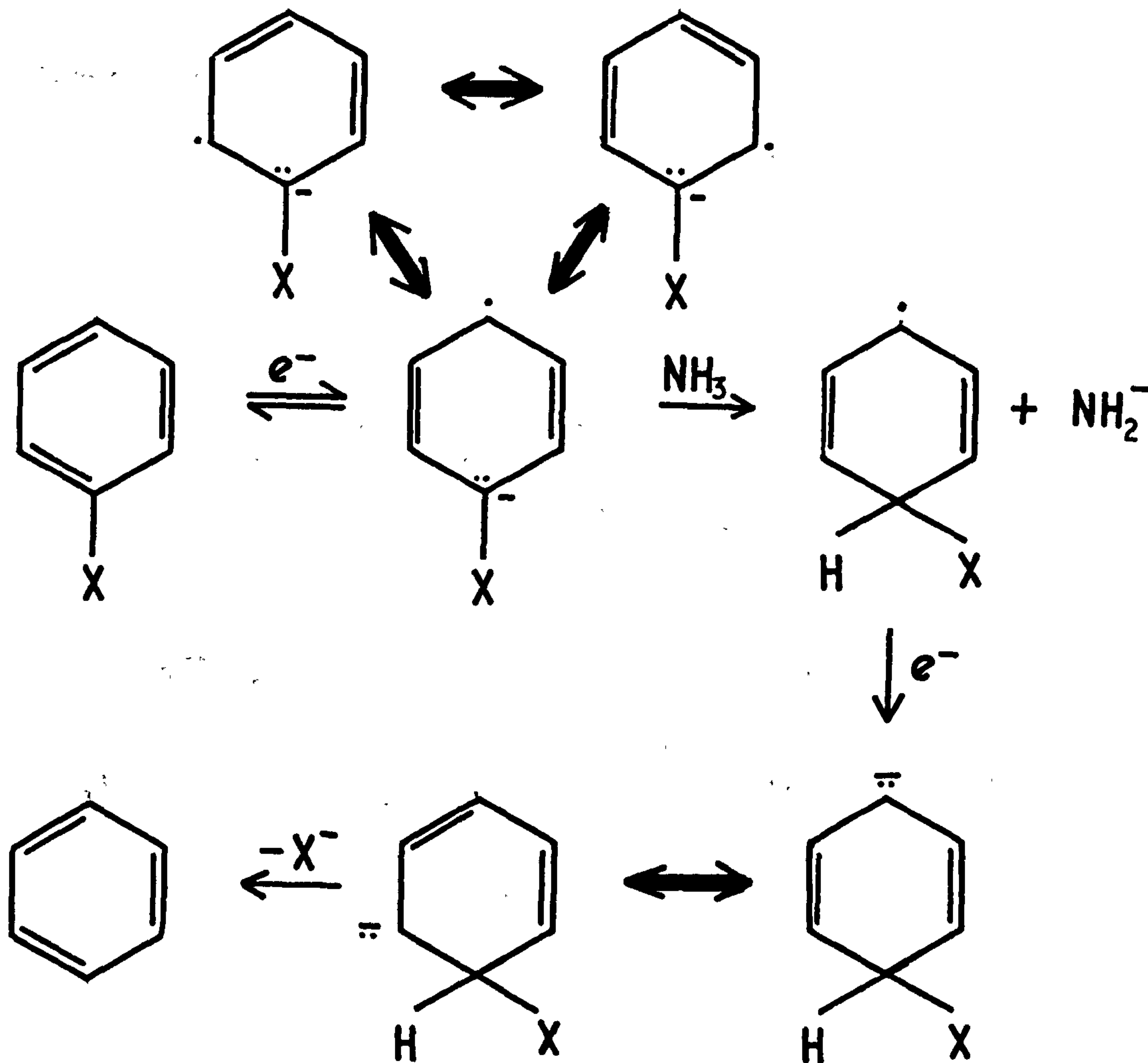
From an e.s.r. study of fluoronitrobenzenes, Carrington<sup>90</sup> came to the conclusions that replacement of hydrogen by fluorine has little effect on the distribution of spin density and that fluorine coupling is about twice the proton coupling (in the absence of stereochemical influence due to greater size). A result of the large coupling is that little difficulty is experienced in characterising fluorine when halogen retention occurs after reduction, in contrast to aryl chlorides where either no chlorine coupling or very small coupling is observed commensurate with its small nuclear magnetic moment (for example 2-chloro-5-nitropyridine<sup>64</sup>).

Kitagawa,<sup>86</sup> from a combination of polarographic and e.s.r. measurements in dimethylformamide states that an initial addition of  $2e^-$  to iodonitrobenzene cleaves the carbon-iodine bond and is followed by a further electron addition to form the aryl radical-anion. Bennett<sup>91,92</sup> provides evidence in favour of a one electron addition causing aryl-halogen cleavage.

The e.s.r. observation of aryl halide reduction in liquid ammonia appears not to have been attempted but Kraus and White<sup>93,94</sup> after a product analysis investigation have proposed the mechanism of reduction to follow the equations



Hudson<sup>87</sup> rejects this mechanism after quantitative analysis of amine production in the reaction of metal/ammonia with halobenzenes and halo-styrenes. His results indicated an initial addition of an electron to form  $\text{RX}^\cdot$  followed by slow uptake of a proton from  $\text{NH}_3$ .



Amines are then formed by further benzyne-type reactions of anilide ion.

In more recent work by Jacobus<sup>95</sup> two reaction paths are considered to give an overall scheme of



similar to that of Hudson, and a rate of reduction of approximately  $10^9 - 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$  determined by product analysis after introduction

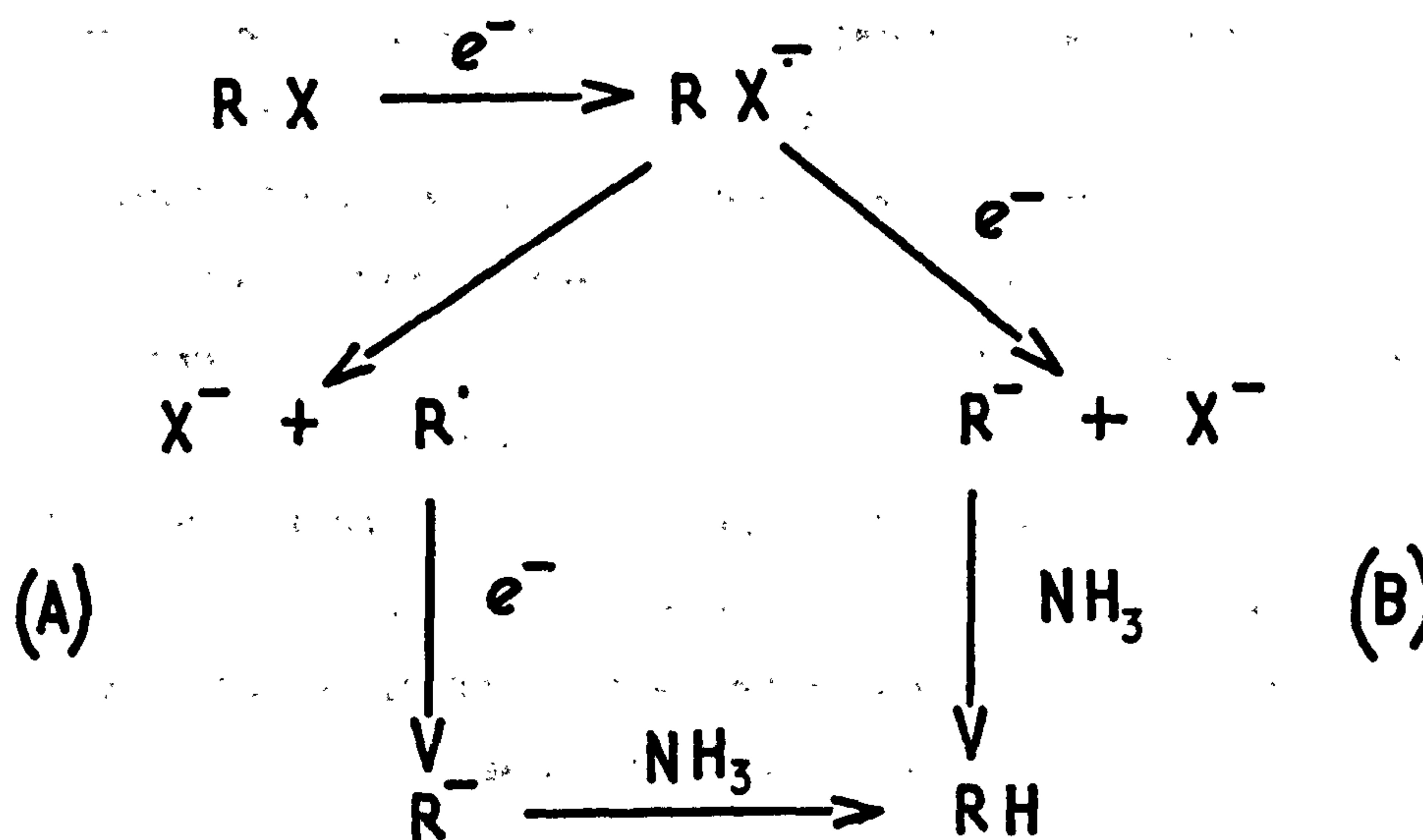


of the competing reaction



which is known to have a rate constant of approximately  $10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ . 50

The two paths are



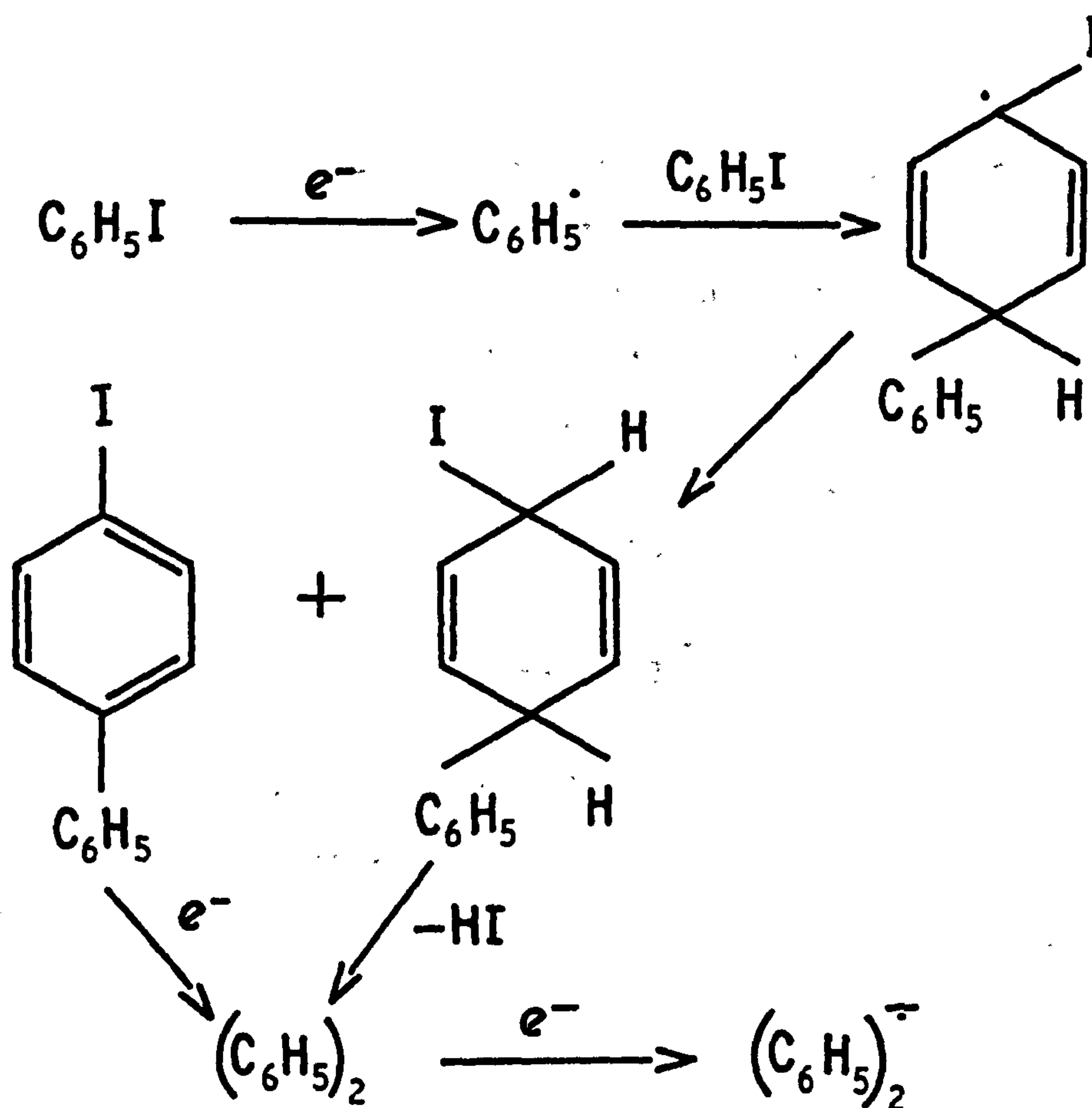
Path (B) is somewhat similar to Hudson's mechanism while path (A) may be rejected from the stereochemical behaviour of  $\text{R}^\cdot$ ,<sup>96,97</sup>

Since the rate of halogen loss from an aryl halide is postulated to occur after a very short period of time then it was thought that the aryl halide radical-anion itself might well be observable by e.s.r. using a rapid-flow technique where observation is possible only a few milliseconds after reduction.

## RESULTS AND DISCUSSION

Chloro-, bromo- and iodo- substituted compounds all lost halogen before the e.s.r. spectrum of an aryl halide radical-anion could be observed. The halo-pyridines (except fluoropyridine), -pyrimidines and -naphthalene produced well-resolved spectra of the parent radical-anions with coupling constants in good agreement with those obtained in the present work and by Talcott and Myers<sup>71</sup> and are shown in Table II. Although these results give weight to the predicted rate of dehalogenation they provide little information concerning the mechanism of reduction.

Reduction of redistilled commercial iodobenzene gave a very well-resolved spectrum analysing as two pairs of equivalent protons, a single proton and a nitrogen with similar coupling constants to nitrobenzene radical-anion. G.L.C. analysis of a sample of the iodobenzene gave a peak with exactly the same retention time as an authentic sample of nitrobenzene and comparison of peak areas put an upper limit of nitrobenzene impurity at 0.5%. A pure sample of iodobenzene was therefore prepared (see experimental) to ensure complete absence of nitro-compounds and run in the flow system. The spectrum obtained was not the halide or parent hydrocarbon but a dimeric product with coupling constants characteristic of the well-known diphenyl radical-anion.<sup>98</sup> Addition of an electron to  $C_6H_5I$  has been shown to give<sup>92,99</sup>  $C_6H_5^{\cdot}$  and Walling<sup>100</sup> has postulated further attack on the parent halide rather than immediate dimerisation of the phenyl radicals. Hudson<sup>87</sup> has identified small yields of diphenyl during reduction of iodobenzene in liquid ammonia.



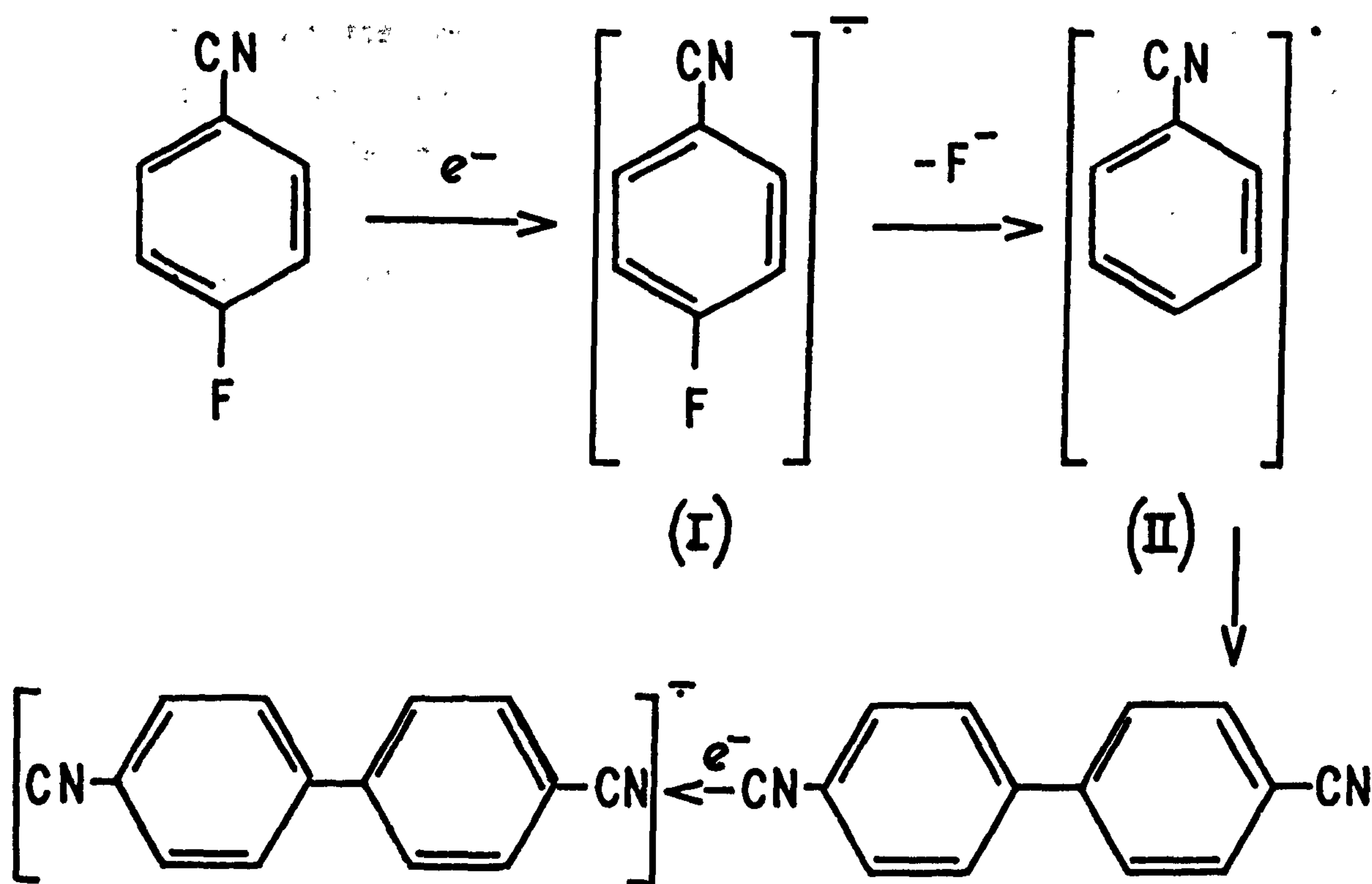
Para-di-iodobenzene behaved in a similar manner and gave the spectrum of diphenyl radical-anion.

Bush,<sup>101</sup> attempting the e.s.r. observation of halosubstituted diphenyls by potassium/tetrahydrofuran reduction, was able to assign spectra from chloro- and bromo- diphenyls to the parent hydrocarbon radical while halogen retention was found for 3,3'- and 4,4'-difluoro- and 4-fluorodiphenyls. 2,2'-Difluorodiphenyl however did not retain fluorine and it is interesting that on the liquid ammonia flow system a mixed spectrum was obtained with the dominant species analysable as 2,2'-difluorodiphenyl. The smaller spectrum was undoubtedly the parent radical which was enhanced to the complete exclusion of halogenated radical using either a twenty-fold excess of sodium or a dead space of

about one second imposed between the points of observation and mixing.

Ring substitution by electronegative groups greatly modifies the ease with which aryl halides shed halogen on reduction and was discussed briefly in the introduction. The presence of a cyano- group on fluoro-benzene labilises the carbon-fluorine bond and the reduction of 4-fluorobenzonitrile produces the radical-anion of 4,4'-dicyanodiphenyl.<sup>84</sup>

Rieger suggested the following mechanism;



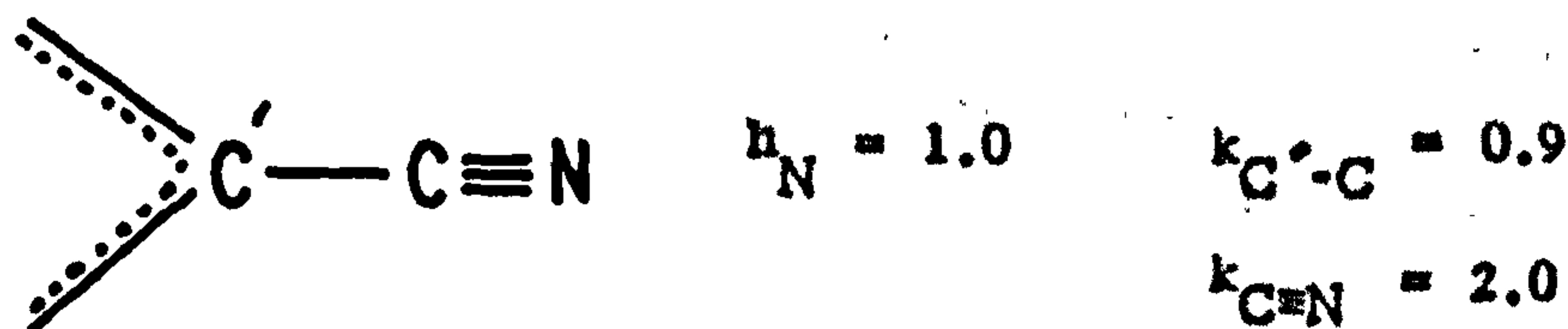
Using the rapid mixing technique three fluorobenzonitriles were reduced in liquid ammonia with interesting results. 4-Fluorobenzonitrile gave a complex spectrum analysable as a mixture of unsubstituted benzonitrile and fluorobenzonitrile radical-anions in almost equal amounts. By imposing a dead space of about one second as before, benzonitrile radical



was seen to the exclusion of  $\text{F-C}_6\text{H}_4\text{CN}^\cdot$ . 2-Fluorobenzonitrile produced a pure spectrum of halobenzonitrile radical-anion when mixing occurred in the cavity and the benzonitrile radical after a one second delay, implying that in this case the production of the former radical is slower. 3-Fluorobenzonitrile, however, only produced the fluorosubstituted spectrum, no halogen loss being observed at any stage of reduction. 2-Chlorobenzonitrile was reduced but even in the cavity only the unsubstituted benzonitrile radical was detected. It is clear that for all three fluoro-compounds the first stage of reduction is formation of a radical-anion such as (I). The 2- and 4- substituted compounds then give the aryl radical (II) which abstracts hydrogen from the ammonia and receives an electron to form the benzonitrile radical-anion before dimerising. Coupling constants for the fluorobenzonitrile radical-anions are shown in Table I.

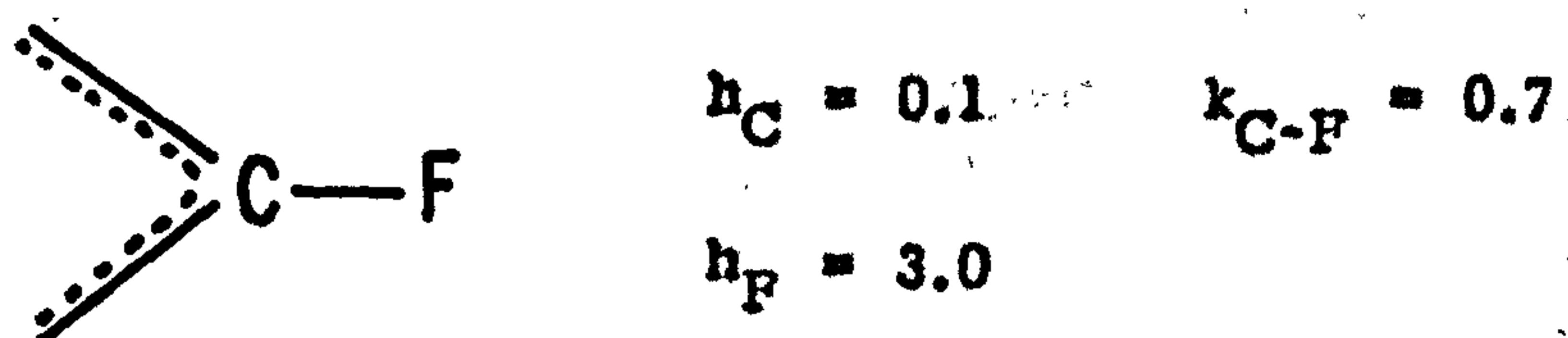
## MOLECULAR ORBITAL CALCULATIONS

Theoretical spin densities were obtained in a similar way to those in the previous chapter. Coulomb ( $h$ ) and resonance ( $k$ ) integral parameters used for benzonitrile were from Rieger and Fraenkel<sup>102</sup> i.e.



A  $Q_{CH}^H$  value of 23.6 Oe was used to correlate proton coupling constants with spin densities.

The most suitable parameters for fluorine were found to be



Experimental fluorine spin density was calculated using a McConnell  $Q_F$  value of 50 and compared with the Hückel and McLachlan spin density on the contiguous carbon atom.

TABLE I

Coupling Constants and Theoretical Spin Densitiesfor Halobenzonitrile Radical-anions

Substrate	Position	Experimental		Calculated	
		Coupling constants (G)	Spin densities	Hückel	McLachlan
2-Fluoro-Benzonitrile	N	2.17		0.116	0.120
	F	5.54	0.111	0.104	0.103
	3	0.47	0.020	0.043	-0.007
	4	0.14	0.387	0.252	0.333
	5	1.11	0.047	0.037	-0.024
	6	3.41	0.144	0.119	0.127
3-Fluoro-benzonitrile	N	2.26		0.117	0.121
	F	2.51	0.005	0.039	-0.021
	2	4.74	0.201	0.118	0.125
	3	7.87	0.333	0.249	0.329
	5	0.57	0.024	0.044	-0.013
	6	2.94	0.125	0.107	0.108
4-Fluoro-benzonitrile	N	2.08		0.117	0.121
	F	22.96	0.459	0.249	0.326
	2,6	4.38	0.186	0.116	0.113
	3,5	0.84	0.036	0.039	-0.019
Benzonitrile	N	2.19		0.117	0.121
	2,6	3.82	0.162	0.112	0.115
	3,5	0.32	0.001	0.042	-0.017
	4	8.52	0.361	0.232	0.332
Benzonitrile <sup>a</sup>	N	2.15			
	2,6	3.63			
	3,5	0.30			
	4	8.42			

....continued

TABLE I (continued)

Substrate	Position	Experimental		Calculated	
		Coupling constants (Oe)	Spin densities	Spin densities	
				Hückel	McLachlan
2-Chloro-benzonitrile	N	2.16			
	2,6	3.83			
	3,5	0.31			
	4	8.50			
4-Chloro-benzonitrile	N	2.13			
	2,6	3.80			
	3,5	0.34			
	4	8.44			

<sup>a</sup> Values from refs. 180, 181.

- - - - -

Calculated g-Values for Fluorobenzonitrile

Radical-anions

<u>Substrate</u>	<u>g-Value</u>
2-Fluorobenzonitrile	2.0029
3-Fluorobenzonitrile	2.0028
4-Fluorobenzonitrile	2.0031
Benzonitrile	2.0028



TABLE II

Coupling Constants for Radical-anionsProduced from Aryl Halides

Substrate	Radical-anion	Coupling constants (oersted)					
		$a_N$	$a_2$	$a_6$	$a_3$	$a_5$	$a_4$
2-Fluoro-pyridine	2-Fluoro-pyridine	4.82	7.12, <sup>a</sup>	4.62	3.67,	1.67 <sup>b</sup>	8.31
2-Bromo-pyridine	Pyridine	6.26	3.54	0.82	9.54		
2-Chloro-pyridine		6.5	3.7	0.8	9.9		
3-Chloro-pyridine		6.30	3.35	0.81	9.63		
3-Iodopyridine		6.33	3.55	0.81	9.66		
2,3-Dichloro-pyridine		6.3	3.4	0.8	9.6		
2,6-Dichloro-pyridine		6.30	3.54	0.83	9.72		
3,5-Dichloro-pyridine		6.18	3.49	0.78	9.58		
2,6-Dibromo-pyridine		6.23	3.50	0.78	9.54		
Pyridine	Pyridine <sup>c</sup>	6.28	3.55	0.82	9.70		
2,4-Dichloro-pyrimidine	Pyrimidine	3.3	0.7 <sup>d</sup>	1.3 <sup>e</sup>	9.9 <sup>f</sup>		
4,6-Dichloro-pyrimidine	Pyrimidine	3.27	0.75 <sup>d</sup>	1.33 <sup>e</sup>	9.82 <sup>f</sup>		
Pyrimidine	Pyrimidine <sup>c</sup>	3.26	0.72 <sup>d</sup>	1.31 <sup>e</sup>	9.78 <sup>f</sup>		

....continued

TABLE II (continued)

Substrate	Radical-anion	Coupling constants (Oersted)					
		$a_N$	$a_2$	$a_6$	$a_3$	$a_5$	$a_4$
Iodobenzene	Diphenyl		2.72		0.40		5.44
p-Di-iodobenzene			2.70		0.40		5.41
2-Iodobiphenyl			2.70		0.38		5.40
Diphenyl	Diphenyl <sup>g</sup>		2.73		0.43		5.46
2,2'-Difluoro-diphenyl	2,2'-Difluoro-diphenyl		3.78, <sup>a</sup>	3.25	0.35, <sup>d</sup>	0.73	5.84
1-Iodonaphthalene	Naphthalene		5.02, <sup>h</sup>	1.85 <sup>i</sup>			
Naphthalene	Naphthalene <sup>j</sup>		5.01, <sup>h</sup>	1.79 <sup>i</sup>			

<sup>a</sup> Probably  $a_p$ .

<sup>b</sup> An assignment between the two alternative positions has not been made.

<sup>c</sup> Values from ref. 71.

<sup>d</sup>  $a_2$ .

<sup>e</sup>  $a_5$ .

<sup>f</sup>  $a_4, a_6$ .

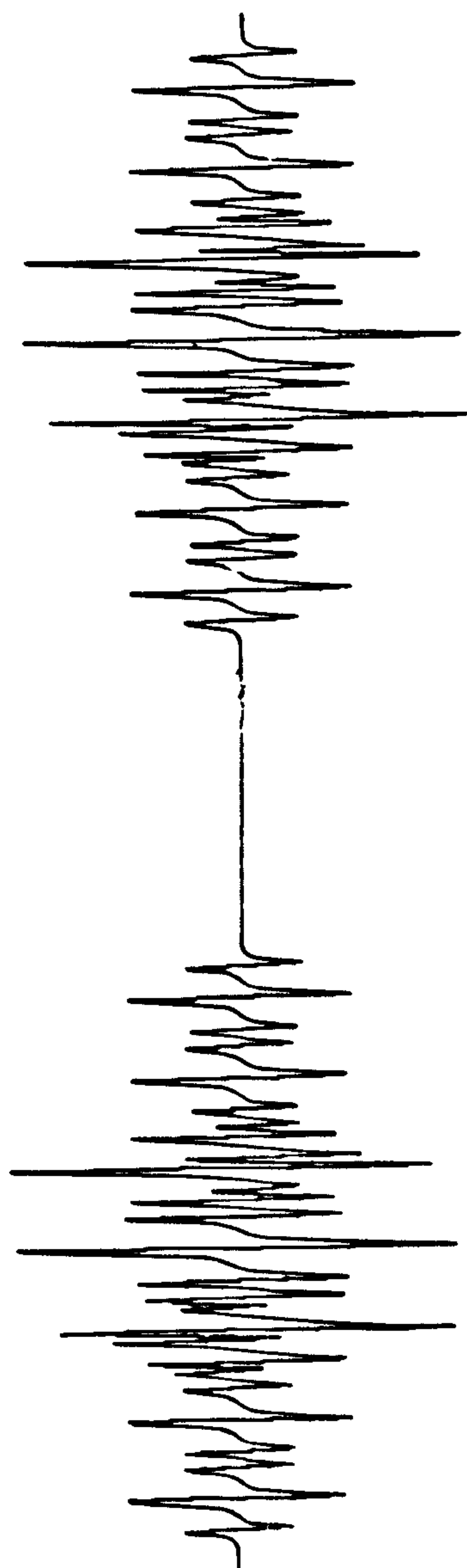
<sup>g</sup> In THF or DME; values from ref. 67.

<sup>h</sup>  $a_2, a_3, a_6, a_7$ .

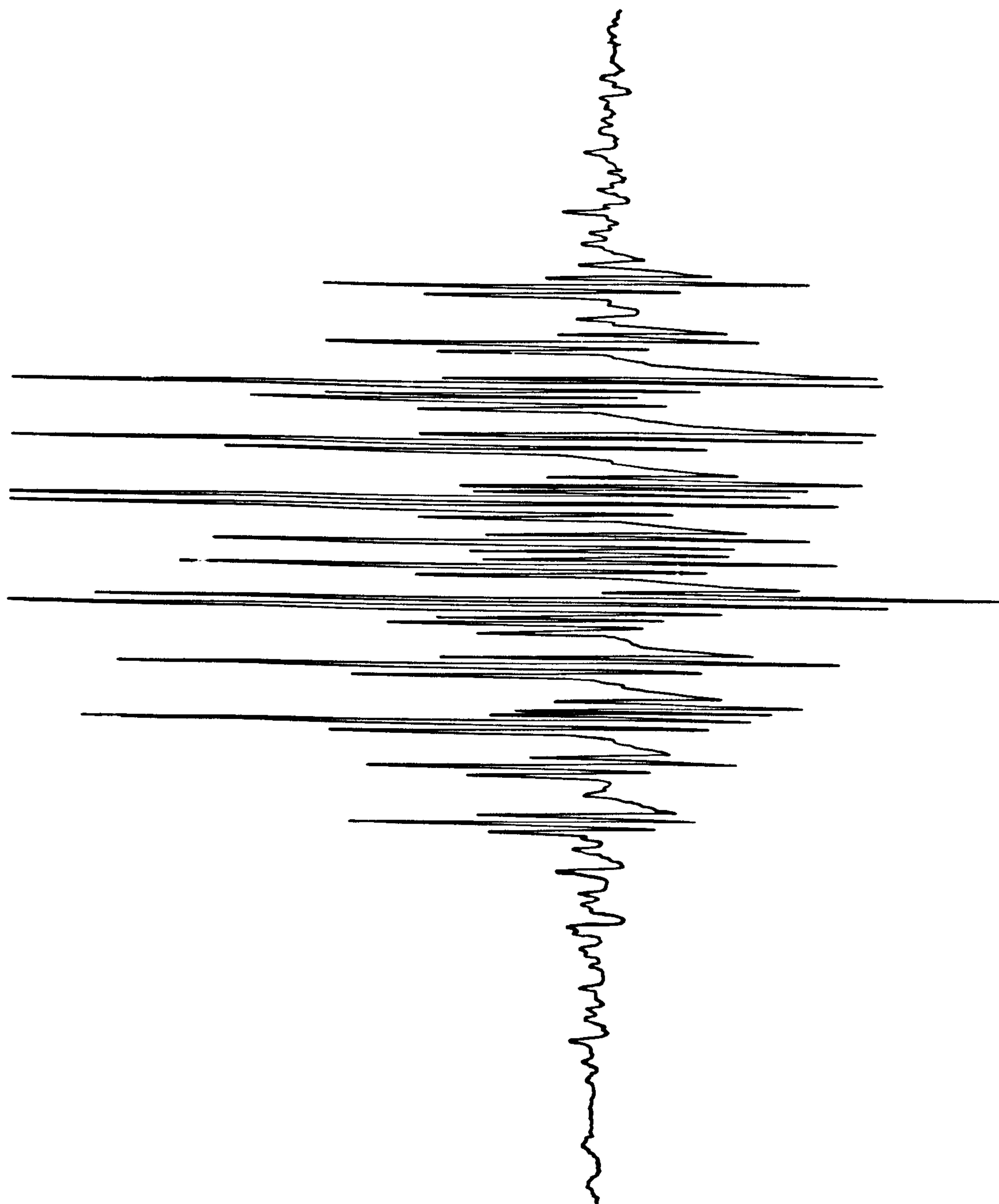
<sup>i</sup>  $a_1, a_4, a_5, a_8$ .

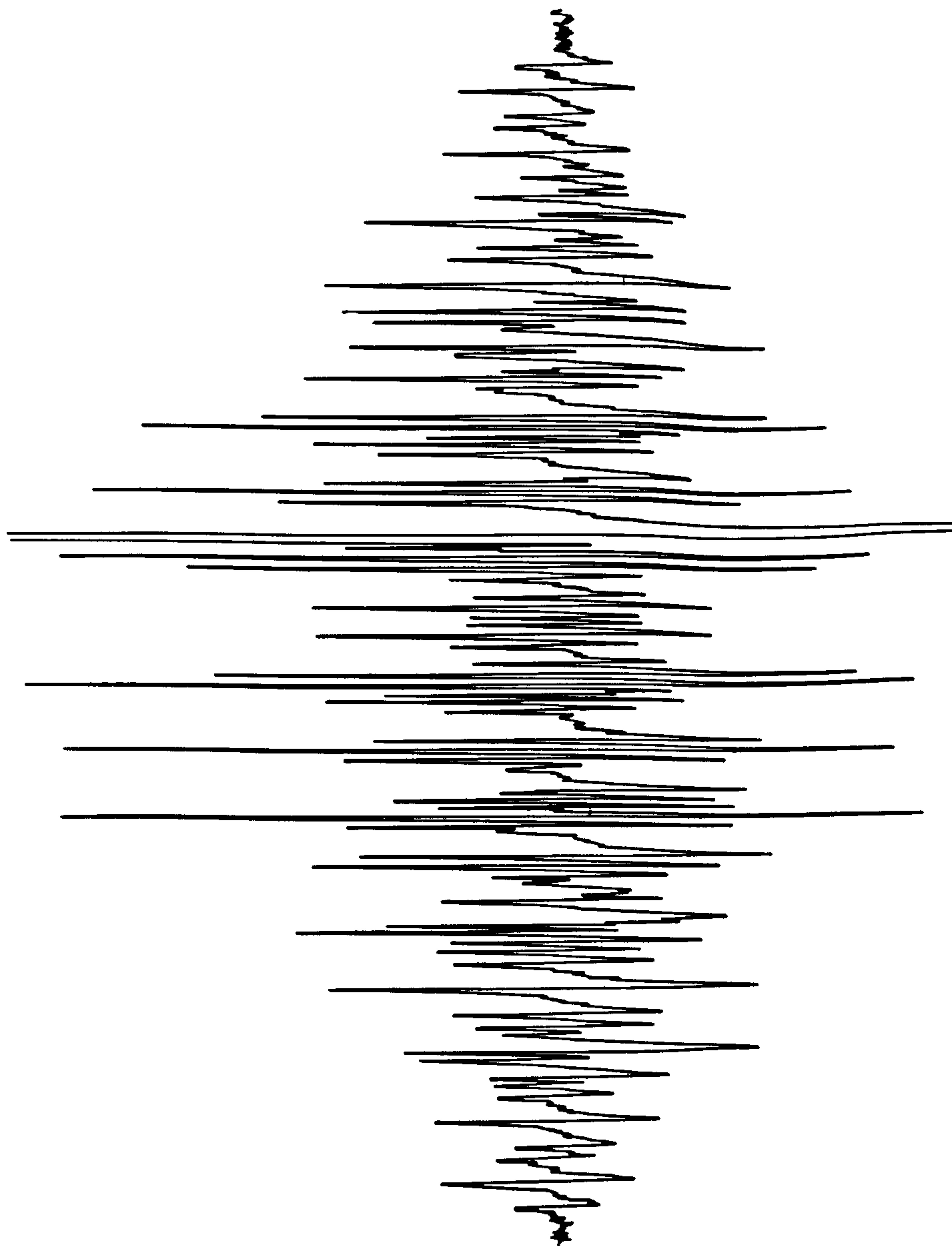
<sup>j</sup> In THF or DME; values from ref. 179.

4-Fluorobenzonitrile 'in cavity' mixed spectrum with a first overlay of the 'out of cavity' benzonitrile radical-anion spectrum and a second overlay of a computer simulation of the 4-fluorobenzonitrile radical-anion spectrum.

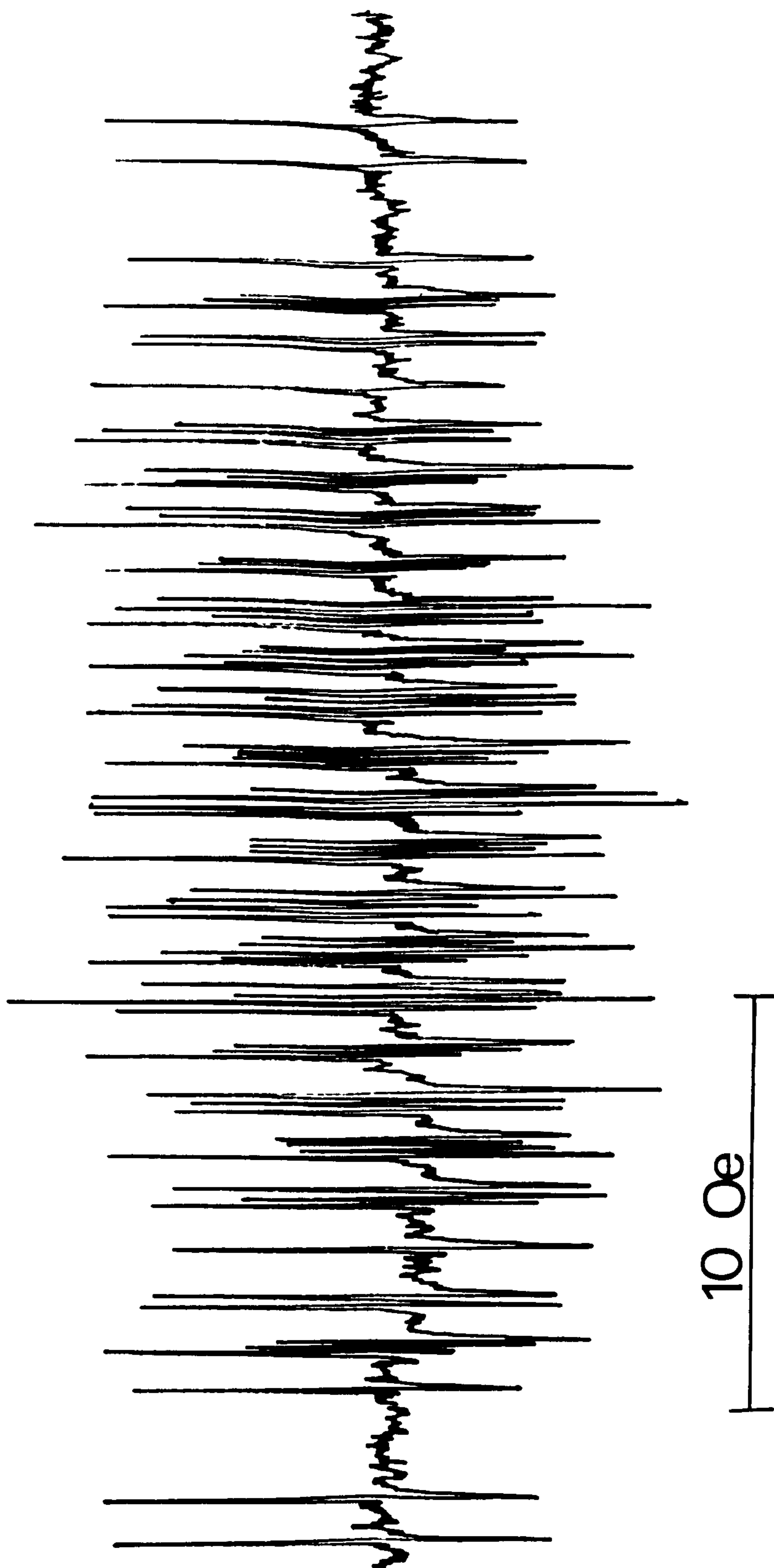






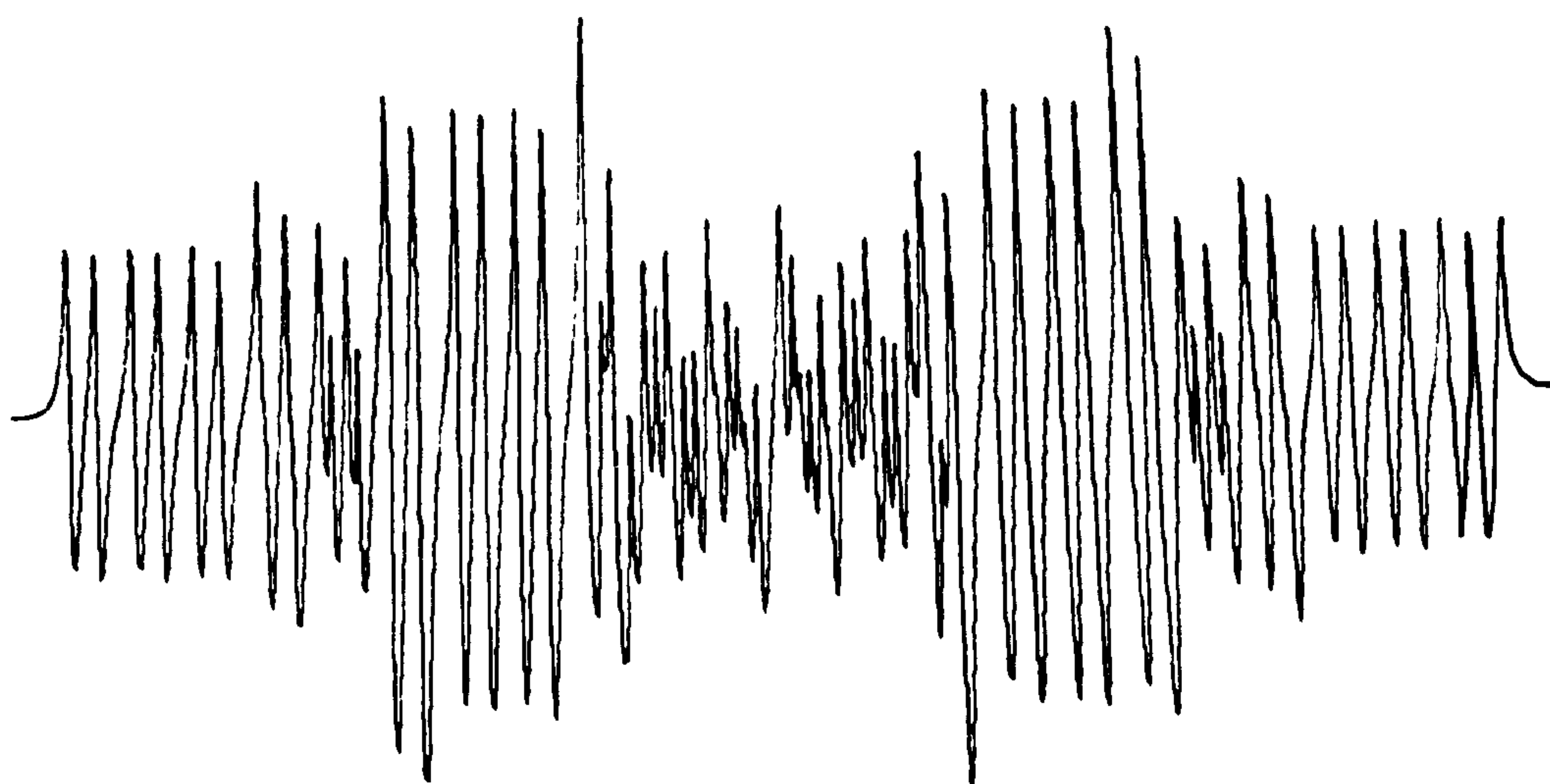
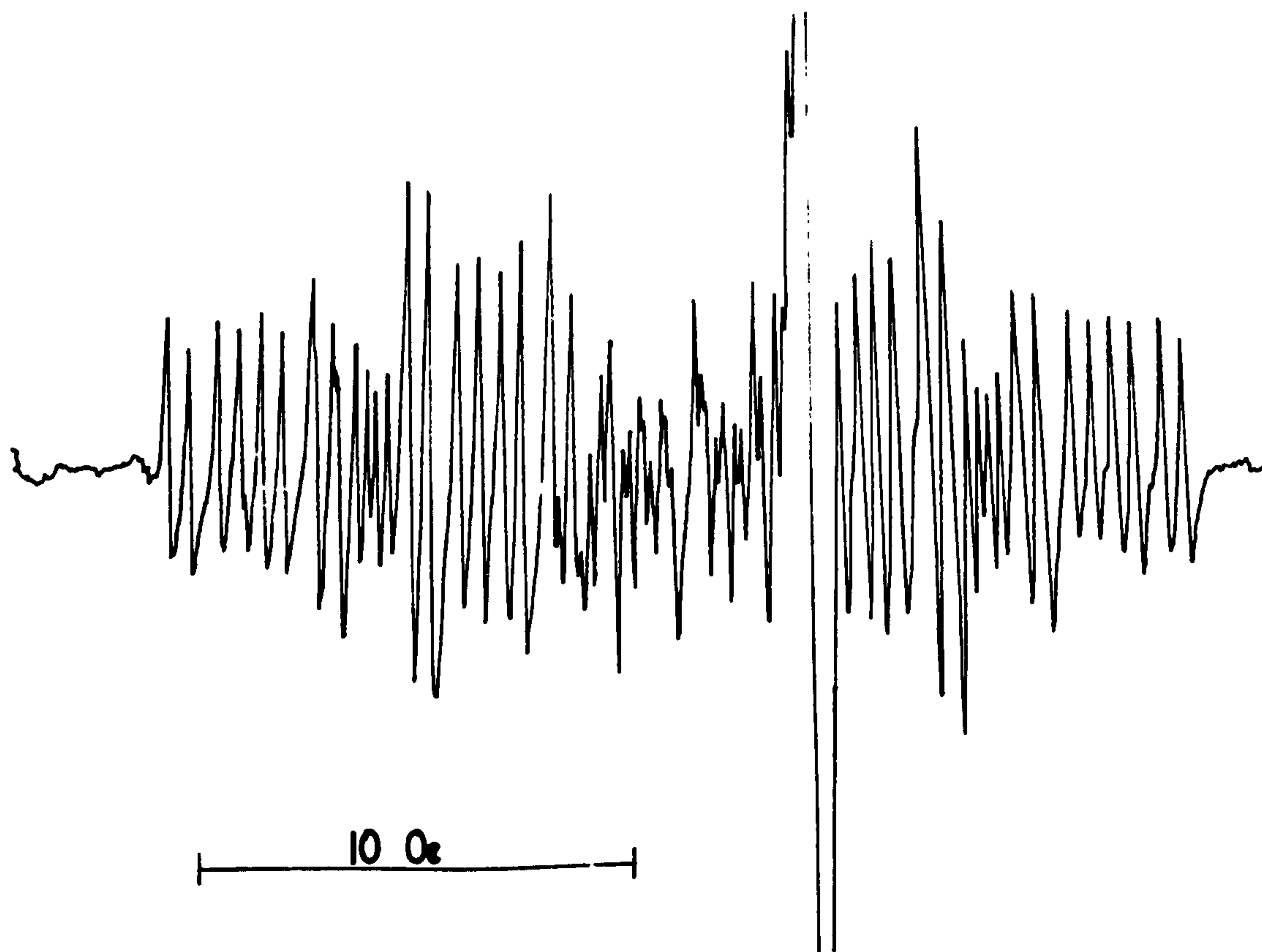


Spectrum of the radical-anion of 2-fluoropyridine.

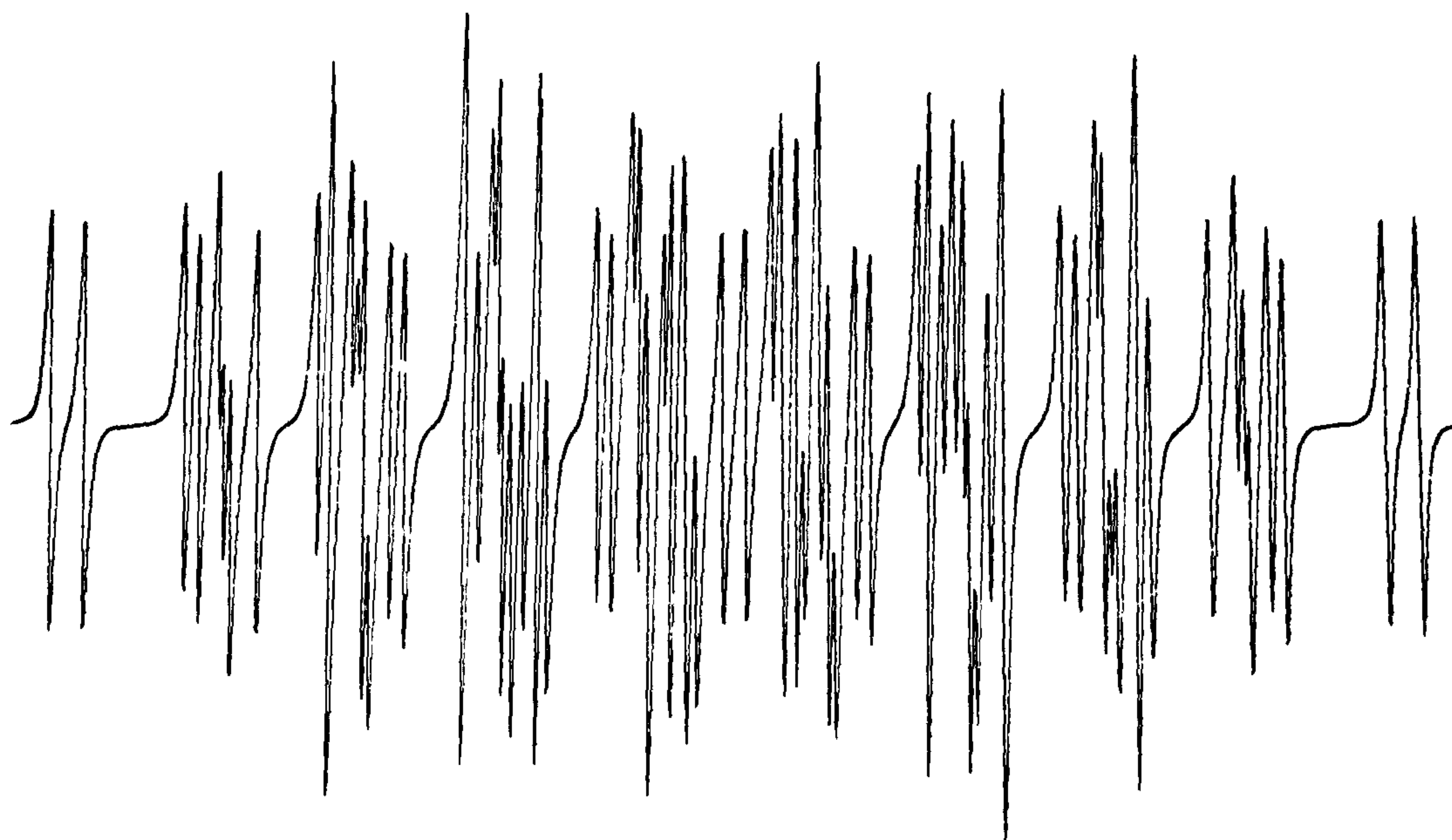
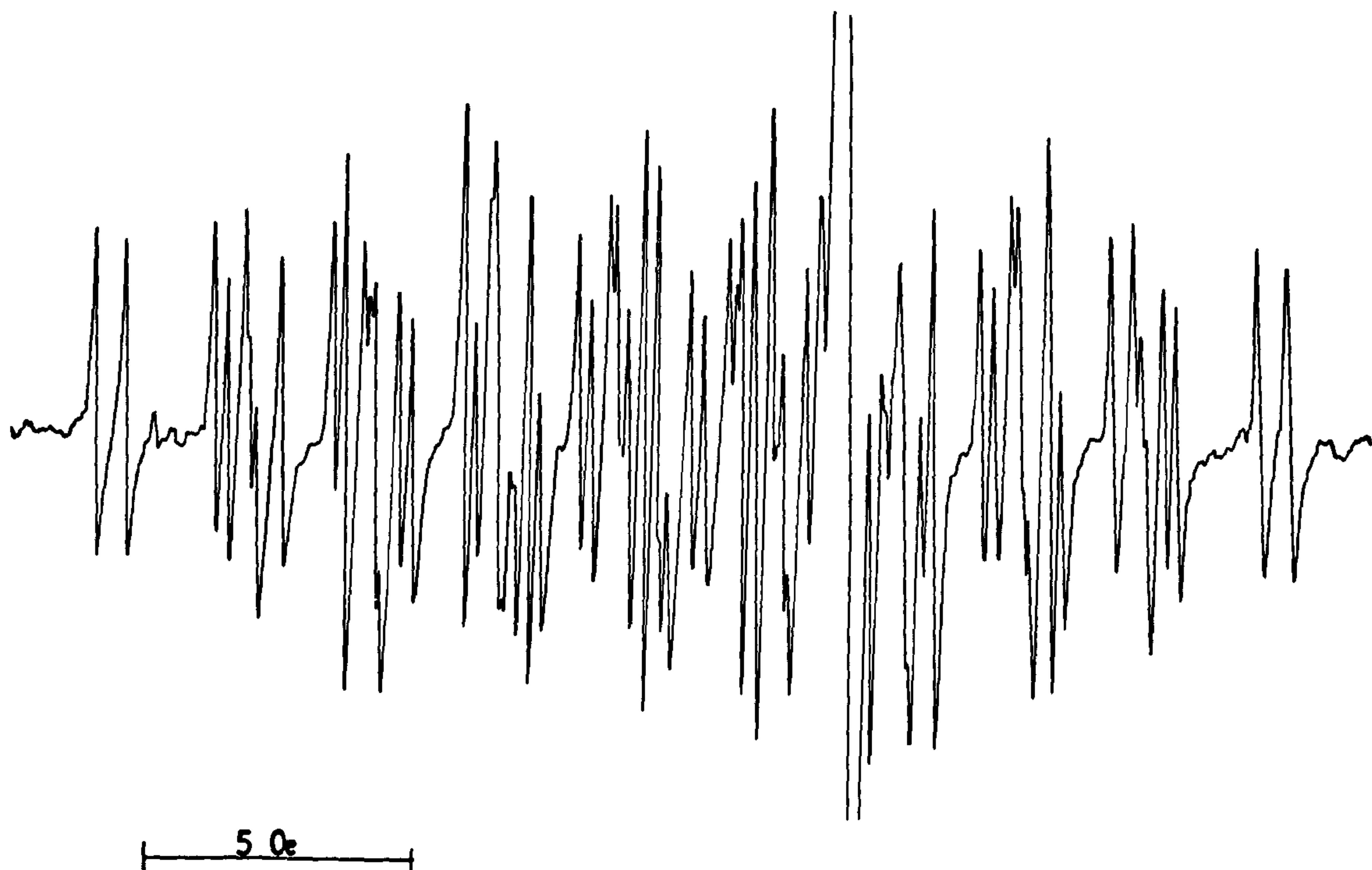




Spectrum of the radical-anion of ortho-fluorobenzonitrile (upper)  
and the computer simulation (lower).

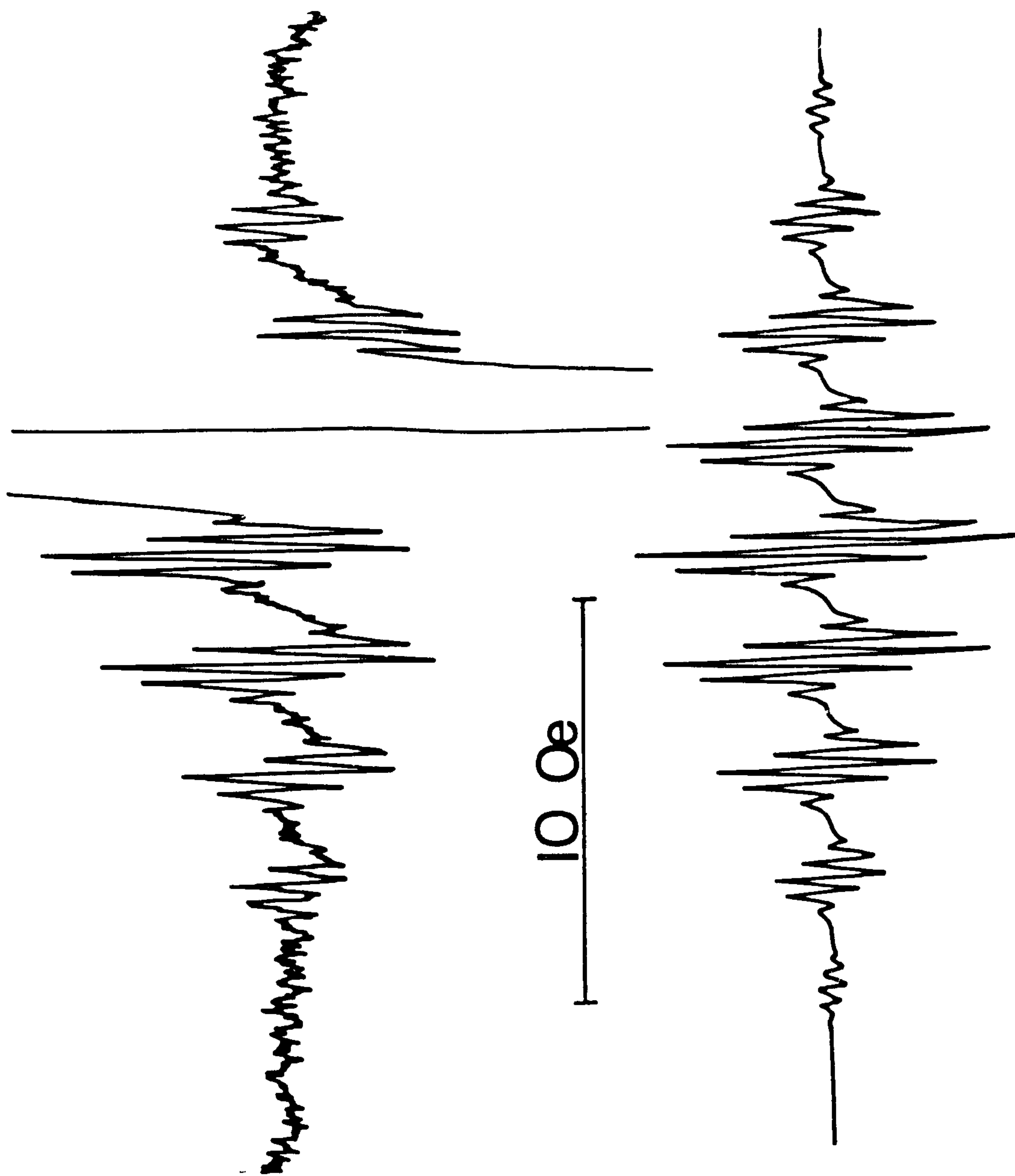


**Spectrum of the radical-anion of 3-fluorobenzonitrile (upper)  
and the computer simulation (lower).**



**Spectrum of the diphenyl radical-anion (and the computer simulation) obtained from reduction of iodobenzene.**

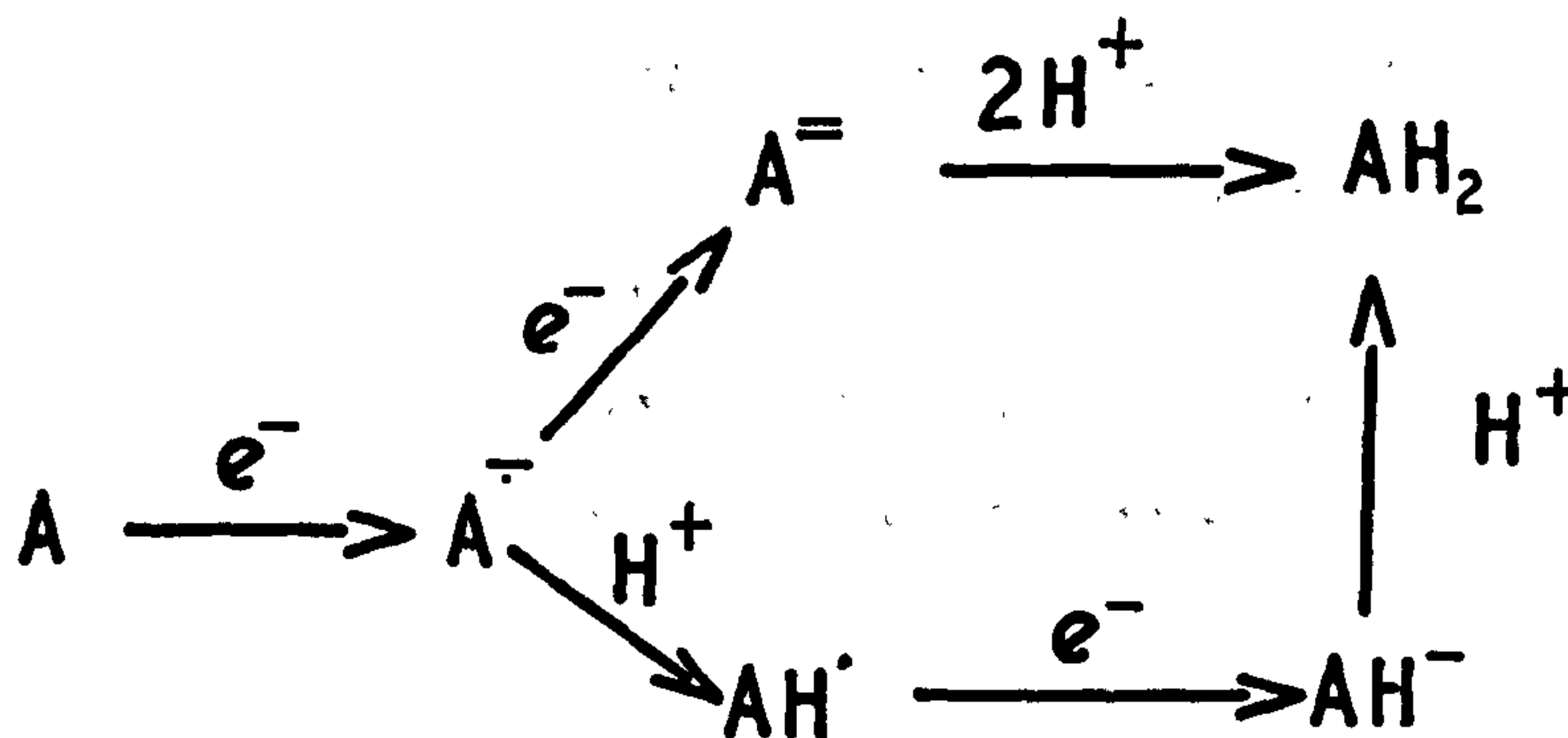




**REDUCTION OF**  
**AROMATIC CARBOXYLIC ACIDS**

## INTRODUCTION

Reduction of aromatic carboxylic acids by a solution of sodium in liquid ammonia has yielded hydro-derivatives; 1,4-dihydro-acids are obtained from benzoic,<sup>103</sup> ortho-toluic<sup>104</sup> and ortho-anisic acids<sup>105</sup> in the presence of methanol or ethanol while tetrahydro-acids are obtained from para-toluic<sup>104</sup> and meta-anisic acids.<sup>103, 106</sup> Kuehne<sup>103</sup> has suggested the following mechanism for sodium/liquid ammonia reduction of acids,



postulating the first step as an electron attachment to form the radical-anion. Second-order rate constants for reduction by hydrated electron of many substituted aromatic acids have been determined<sup>107-109</sup> and the process  $A_{\text{acid}} + e^-$  is very fast, of the order of  $10^9 \text{ M}^{-1} \text{ sec}^{-1}$ .

Compounds of the general formula  $[X-C_6H_4COOH]^{\cdot-}$  have been observed by e.s.r. where the radical-anion is stabilised as, for example, when X is electronegative ( $X = -CN$ ,<sup>84</sup>  $NO_2$ <sup>110, 111</sup>) or the acid group has been esterified.<sup>112</sup> The rotating cryostat technique of Bennett<sup>113</sup> produced an e.s.r. spectrum of the benzoic acid radical-anion and although poorly-

resolved, a 1 : 3 : 3 : 1 pattern of intensity ratios was observed and assigned to equivalent ortho and para protons; the hydroxyl proton was known, from a series of deuterated compounds, not to give sufficient coupling with the unpaired electron to be resolved in a solid matrix.

In the electrolytic generation of radicals from naphthalic acid derivatives at high potentials,<sup>114</sup> protonated species are observed by e.s.r. and the extra proton is assumed to be accommodated at the 4-position for 1,8-naphthalic anhydride. Other electrolytic reduction products of aromatic acids are given by Swan.<sup>115</sup>

It is apparent from the literature that radical-anions of benzoic acid and other simple aromatic carboxylic acids have very short lifetimes in solution, too short to allow production of a sufficiently high steady state concentration of radicals to be observed by presently available e.s.r. techniques; the liquid ammonia flow system was employed to gather more information concerning fast reduction reactions of aromatic carboxylic acids.



## RESULTS AND DISCUSSION

Several methylbenzoic acids gave well-resolved spectra which were relatively simple to interpret. Benzoic acid itself was analysable as

$A_{\text{para H}} = 2A_{\text{ortho H}} - A_{\text{meta H}}$  from the line positions but an exact match of intensities was only obtainable from computer simulation after slight trial and error alterations of the difference between  $A_{\text{ortho H}}$  and  $A_{\text{para H}}$ ; these and other coupling constants are shown in Table I.

4-Methoxy- and 4-ethoxybenzoic acids produced the expected spectra showing small coupling constants for the methoxy and ethoxy substituents. Aromatic ring coupling constants similar to those shown by 4-alkoxybenzoic acids were found for the 4-hydroxy acid with an additional large coupling from the -OH proton; 4-hydroxybenzonitrile also gave a large -OH coupling. 4-Hydroxynitrobenzene did not show -OH coupling and gave a spectrum agreeing closely with that obtained by Levy and Myers.<sup>116</sup> Hydroxylic coupling constants for  $[\text{OH-C}_6\text{H}_4\text{COO}]^{2-}$ , shown in Table I, and for  $[\text{OH-C}_6\text{H}_4\text{CN}]^-$  ( $A_{\text{OH}}^{\text{H}} = 3.5 \text{ Oe}$ ) indicate a McConnell  $Q_{\text{OH}}^{\text{H}}$  value of ca. 60 Oe, which is large by comparison with literature values.<sup>117-119</sup> The wide range of values for  $Q_{\text{OH}}^{\text{H}}$  reflects sensitivity to electronic and chemical environment as well as different approaches to theoretical treatment.

In Chapter III aryl halides (except fluorides) were observed to lose halogen on reduction and chloro-, bromo- and iodo-benzoic acids are no exception, giving poorly-resolved spectra in most cases but analysable by comparison as benzoic acid with similar coupling constants. 4-Fluorobenzoic acid gave a mixed spectrum indicating carbon-halogen bond cleavage similar to that shown by 4-fluorobenzonitrile (Chapter III) and pentafluorobenzoic acid.<sup>120</sup> 4-Chlorobenzoic acid gave a spectrum identical to that obtained from 4-nitrobenzoic acid and it seems that electron-transfer is taking place from the dominant radical-anion to a trace impurity. This

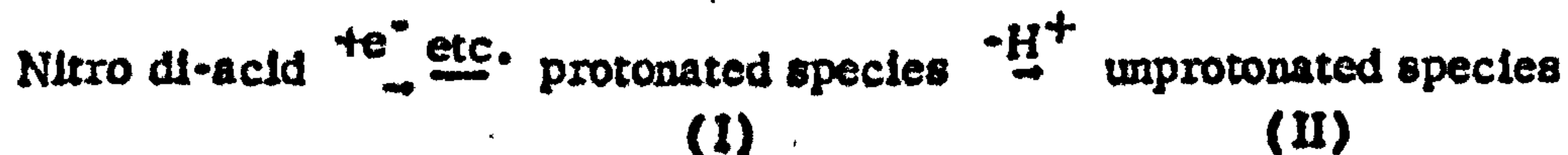


may be compared with the production of the nitrobenzene radical-anion on flowing a commercial sample of iodobenzene (Chapter III).

Two thio-acids, thiobenzic and thioterephthalic, were investigated; the former gave a spectrum with coupling constants of a similar order to benzoic acid and a higher  $g$ -value; the latter produced a weak spectrum consisting of five main broad lines of ca. 3 Oe separation, each showing considerable hyperfine structure, but apart from assuming the main lines to be due to equivalent ring protons no further analysis was possible.

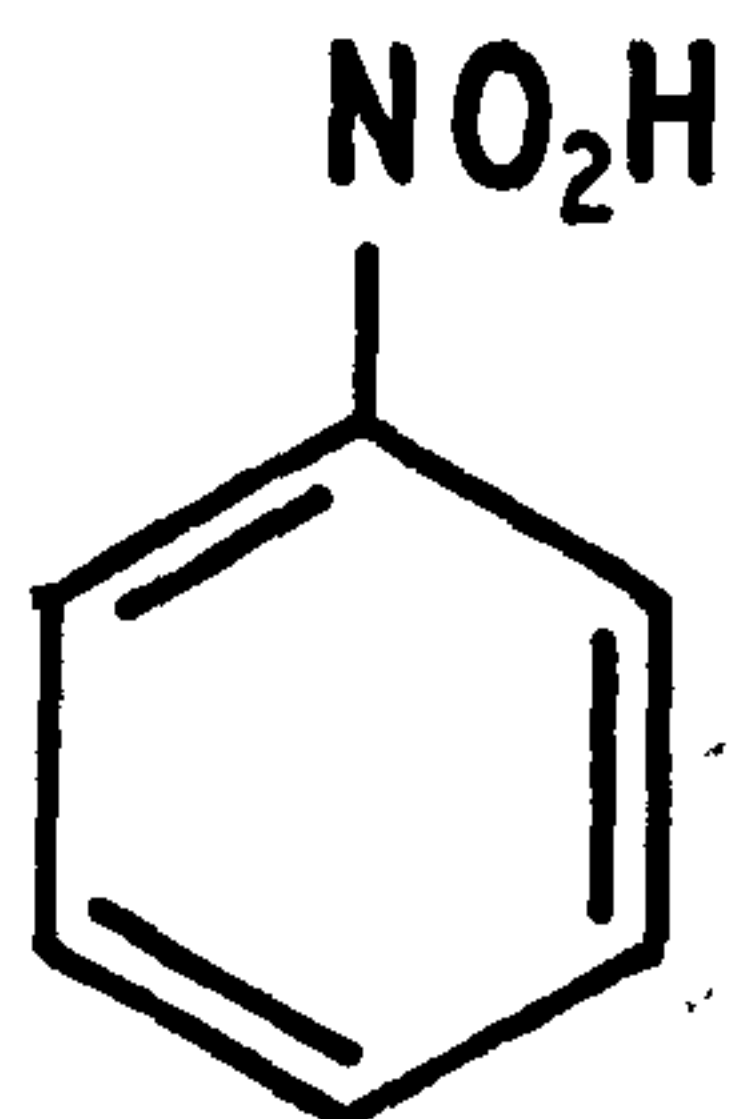
Inequivalent ring proton coupling constants were obtained from 4-aldehydobenzoic acid and are almost certainly due to slow rotation of the aldehyde group as in benzaldehyde<sup>121</sup> and terephthaldehyde.<sup>122, 123</sup>

Of the several phthalic acids investigated on the flow system isophthalic and terephthalic acids gave an expected pattern of coupling constants, one (3-nitrophthalic acid) was insoluble in liquid ammonia and two nitro di-acids produced unusual results. Nitroterephthalic acid and 5-nitro-isophthalic acid each gave two spectra, one (or a mixed spectrum) appearing during a flow reduction, the other after static reduction. The coupling constants are shown in Table III and it is apparent that the first species formed contains one more than the expected number of protons for the parent acid. Flow and static spectra from 4-nitrobenzoic acid are identical and agree with the published spectrum for the radical-anion.<sup>110</sup> The probable reaction scheme is therefore

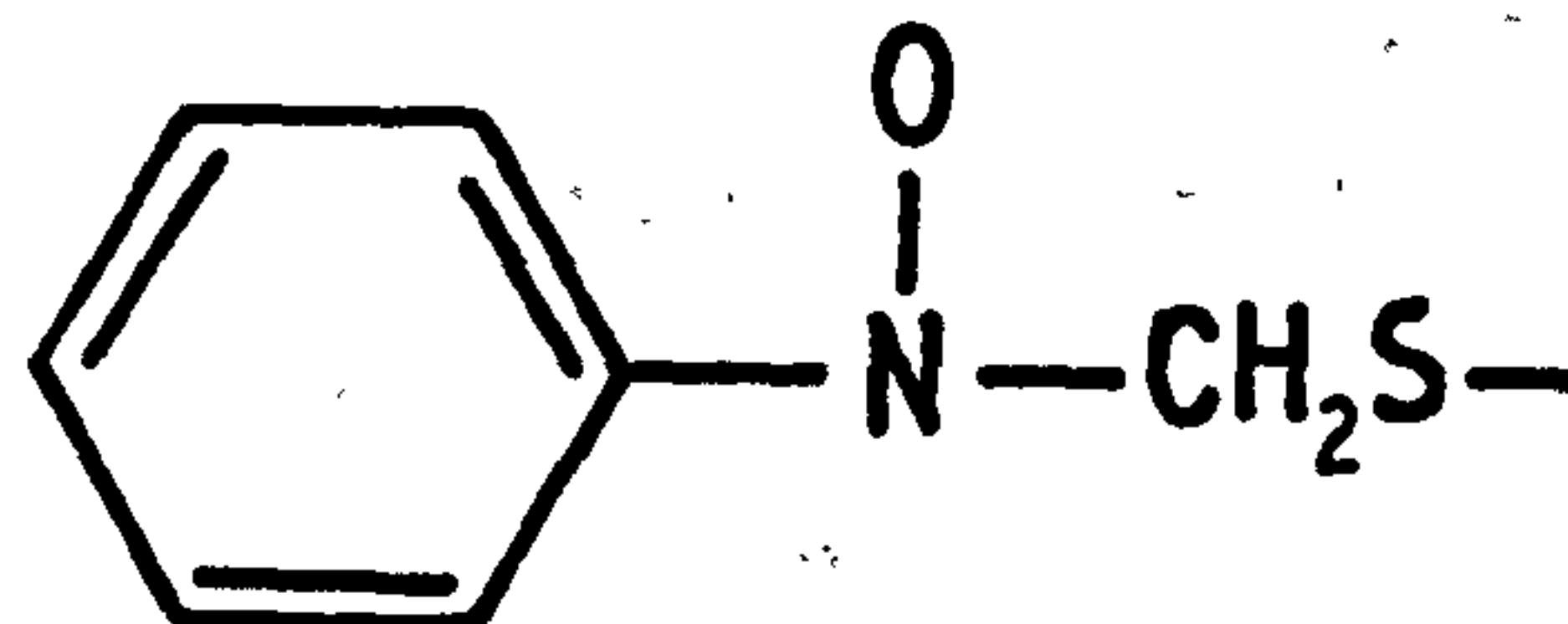


Comparison of the coupling constants obtained for (I) and those of the cyclohexadienyl radical<sup>124a</sup> shows that the extra proton is not in the aromatic ring.

Structures such as



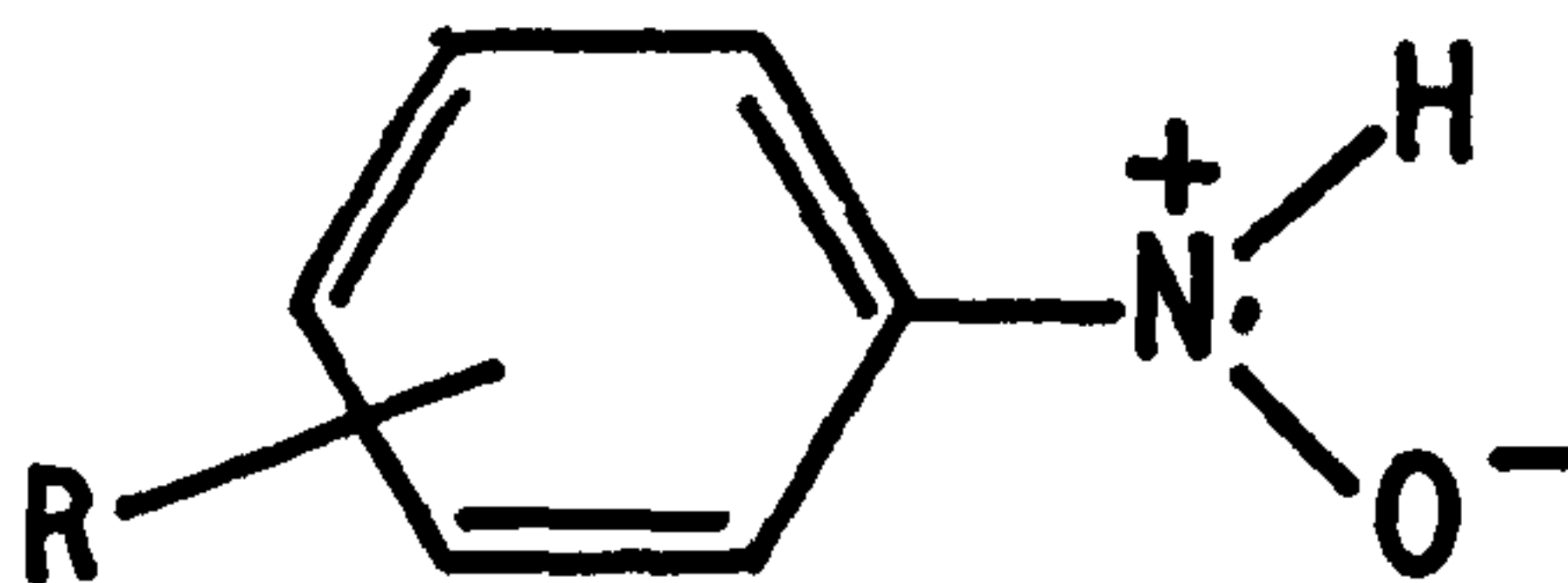
(III)



(IV)

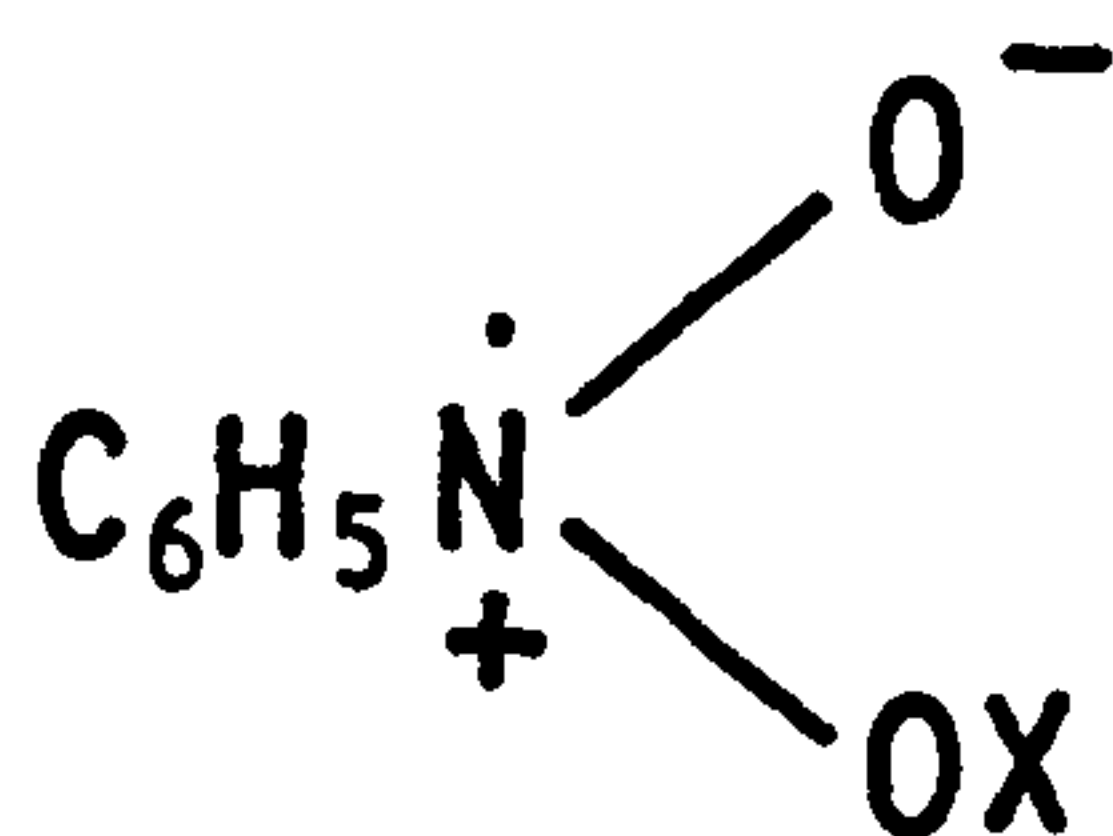
where  $-\text{CH}_2\text{S}-$  is a solvent or other substrate fragment, are eliminated since  $A_{\text{H}}/A_{\text{N}}$  for (III) is small<sup>124b</sup> ( $A_{\text{H}}$  is often 0.2 - 0.4 G) and for (IV)  $A_{\text{H}}/A_{\text{N}}$  is approximately 0.7.<sup>124c</sup> Coupling constants for protons attached directly to nitrogen are known to be large and have a ratio of proton to nitrogen coupling constants approximately 0.9 - 1.3 (e.g. pyridines Chapter II and refs. 21, 125); in particular, for two protonated nitro-carboxylic acids  $A_{\text{H}}/A_{\text{N}} = 1.31$ <sup>125c</sup> and 1.38.<sup>125d</sup> Consideration of  $A_{\text{H}}/A_{\text{N}}$  for (I) for each acid gives 1.30 and 1.32 and therefore the extra proton is assigned to an N-H bond.

A likely structure for (I) is a nitroxide of the form

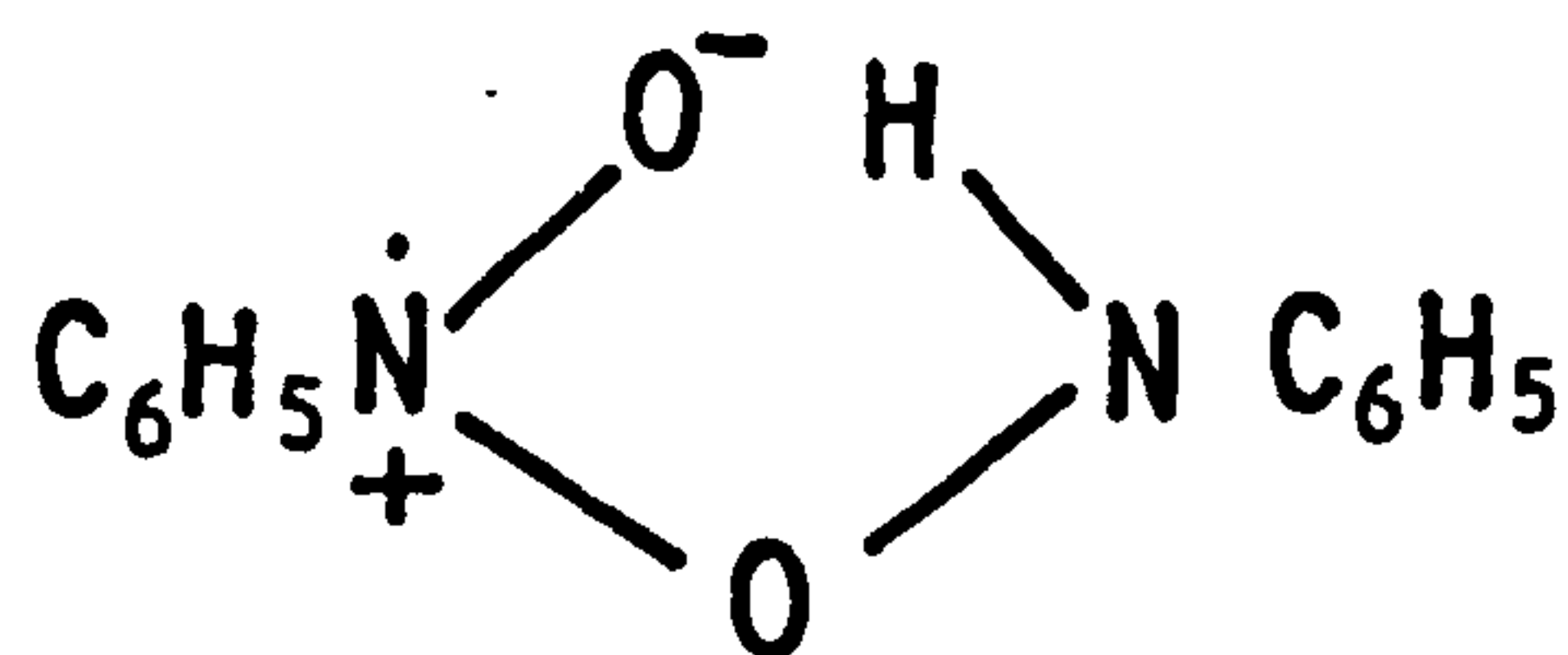


and although many workers have quoted positions ortho to nitrogen to be equal in a symmetrical aromatic nitroxide,<sup>126,127</sup> Wajer<sup>128</sup> has shown that positions 2- and 4- are equivalent, ortho positions being affected by restricted rotation of the nitroxide group.

The stable species (II) is unlikely to be the radical-anion of the original nitro di-acid although coupling constants would agree with this assignment. A nitrosobenzene structure is also possible from the observed spin density distribution; Levy and Myers<sup>116</sup> have shown that slow rotation of the  $C_6H_5 - NO$  bond causes inequivalent ortho coupling constants in the nitrosobenzene radical-anion in liquid ammonia although in a different solvent ortho protons have been found equivalent.<sup>126</sup> Nitrosobenzene, however, is unlikely to appear after a nitroxide in the normal sequence of aromatic nitro group reduction. The most likely structure for radical (II) is that possibly formed from a nitroxide, as suggested by Russell,<sup>129</sup> i.e.



where a specific possibility is



in which all observations can be adequately accommodated.

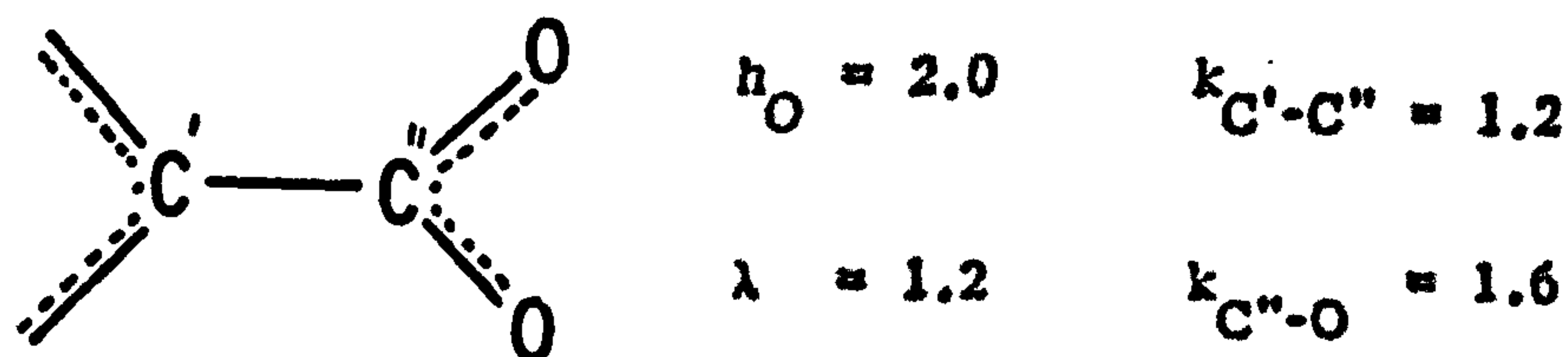
Further information might be forthcoming from the investigation of



more nitro di-acids but solubility difficulties precluded such investigations. Although 5-nitrophthalic acid (and benzene-1,3,5-tricarboxylic acid) was soluble in liquid ammonia with 10% v/v tetrahydrofuran co-solvent, no spectrum was obtained on reduction.

## MOLECULAR ORBITAL CALCULATIONS

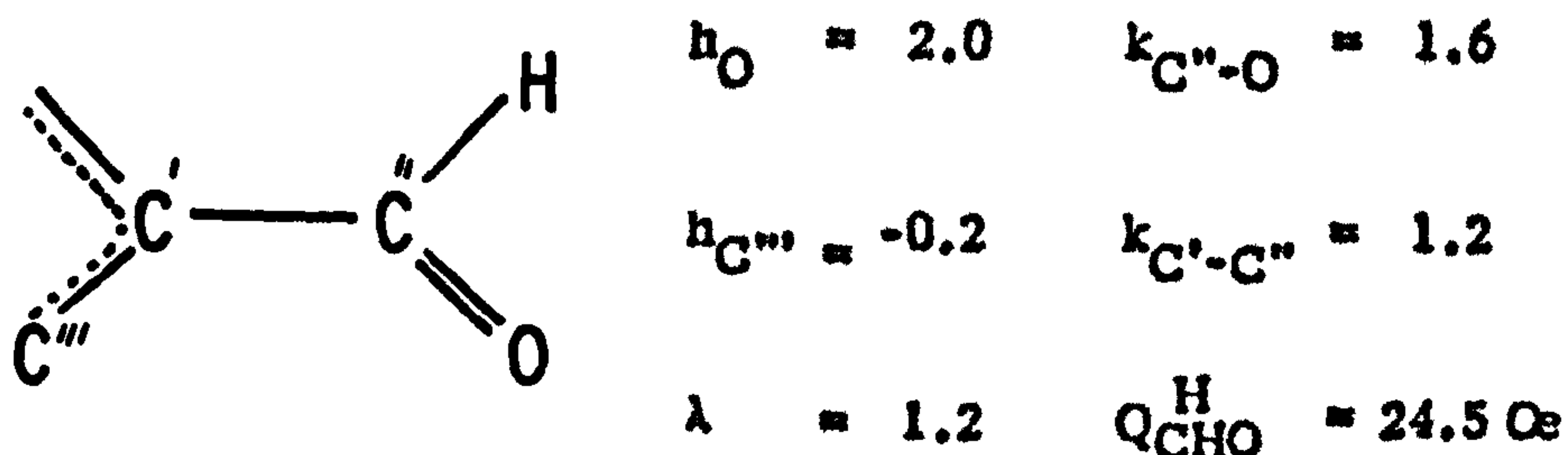
The carboxyl group of the acids in liquid ammonia is assumed to be completely ionised giving equivalent C-O bonds. Variation of Coulomb ( $h$ ) and resonance ( $k$ ) integrals and the McLachlan configuration-interaction parameter ( $\lambda$ ) eventually produced an ortho/para ratio of spin densities (0.549) agreeing with an experimental coupling constant ortho/para ratio (0.545) and were



A McConnell  $Q_{CH}^H$  value of 24.5 Oe was used to correlate experimental and theoretical data.

Parameter values for  $-CH_3$  and  $-F$  groups have been given in previous chapters.  $Q_{OR}^H$ , where  $R = CH_3$  or  $C_2H_5$ , was taken as 30 Oe after Forbes and Sullivan.<sup>130</sup>

For aldehydobenzoic acid the following values,



where  $h_{C'''}$  is an auxiliary inductive parameter to produce inequivalent



ring spin densities, were used and are fairly close to those used by Steinberger and Fraenkel.<sup>131</sup>

For nitro groups

$$h_N = 2.0 \quad k_{C-N} = 1.2$$

$$h_O = 2.0 \quad k_{N-O} = 1.67$$

gave a reasonable fit with experiment.

TABLE I

**Coupling Constants and Theoretical Spin Densities**  
**for Radical-anions of Aromatic Carboxylic Acids**

Substrate	Position	Experimental		Calculated	
		Coupling constants (Oe)	Spin densities	Hückel	McLachlan
Benzoic acid	1			0.169	0.167
	2,6	4.24	0.173	0.140	0.174
	3,5	0.81	0.033	0.026	-0.046
	4	7.78	0.318	0.232	0.317
Isophthalic acid	1,3			0.098	0.069
	2	1.21	0.049	0.0	-0.031
	4,6	6.87	0.280	0.269	0.378
	5	3.03	0.124	0.0	-0.101
Terephthalic acid	1,4			0.169	0.198
	2,6	1.69	0.069	0.079	0.066
	3,5	1.69	0.069	0.079	0.066
2-Methyl-benzoic acid	1			0.154	0.150
	2	4.32 <sup>a</sup>	0.154	0.110	0.126
	3	0.73	0.030	0.049	-0.011
	4	8.90	0.363	0.234	0.320
	5	1.02	0.042	0.013	-0.066
	6	4.65	0.190	0.165	0.216
3-Methyl-benzoic acid	1			0.169	0.168
	2	4.42	0.180	0.160	0.204
	3	0.93 <sup>a</sup>	0.033	0.020	-0.050
	4	7.47	0.305	0.221	0.304
	5	0.72	0.029	0.030	-0.038
	6	4.02	0.164	0.125	0.153

....continued

TABLE I (continued)

Substrate	Position	Experimental		Calculated	
		Coupling constants (Oe)	Spin densities	Spin densities	
				Hückel	McLachlan
4-Methyl-benzoic acid	1			0.156	0.150
	2,6	4.96	0.202	0.144	0.185
	3,5	1.16	0.047	0.015	-0.058
	4	9.18 <sup>a</sup>	0.328	0.219	0.297
3,4-Dimethyl-benzoic acid	1			0.156	0.151
	2	5.18	0.211	0.160	0.211
	3	0.97 <sup>a</sup>	0.035	0.012	-0.060
	4	9.07 <sup>a</sup>	0.324	0.212	0.288
	5	0.89	0.036	0.019	-0.051
	6	4.86	0.198	0.131	0.167
3,5-Dimethyl-benzoic acid	1			0.170	0.170
	2,6	4.13	0.169	0.144	0.183
	3,5	0.80 <sup>a</sup>	0.029	0.024	-0.042
	4	7.12	0.291	0.210	0.290
4-Methoxy-benzoic acid	1			0.155	0.148
	2,6	4.84	0.198	0.149	0.195
	3,5	1.29	0.053	0.013	-0.053
	0	0.32 <sup>b</sup>	0.011	0.019 <sup>c</sup>	0.017
4-Ethoxy-benzoic acid	1			0.156	0.149
	2,6	4.77	0.194	0.149	0.193
	3,5	1.24	0.050	0.013	-0.062
	0	0.22 <sup>b</sup>	0.007	0.016 <sup>c</sup>	0.015
4-Hydroxy-benzoic acid	1			0.145	0.138
	2,6	4.99	0.204	0.152	0.202
	3,5	1.42	0.059	0.007	-0.068
	0	2.05 <sup>d</sup>		0.043 <sup>e</sup>	0.036

....continued

TABLE I (continued)

Substrate	Position	Experimental		Calculated	
		Coupling constants	Spin densities	Spin densities	
		(Oe)		Hückel	McLachlan
4-Aldehyde-benzoic acid	1			0.154	0.193
	2	0.99	0.040	0.053	0.018
	3	3.17	0.129	0.109	0.129
	4 <sup>f</sup>	8.25	0.336	0.260	0.304
	5	4.21	0.171	0.122	0.155
	6	0.41	0.016	0.025	-0.023
3-Fluoro-benzoic acid	1			0.169	0.167
	2	4.63	0.189	0.146	0.185
	3	3.22 <sup>g</sup>	0.064	0.024	-0.045
	4	7.26	0.296	0.223	0.315
	5	0.27	0.011	0.027	-0.043
	6	3.22	0.131	0.135	0.168
4-Fluoro-benzoic acid	1			0.163	0.161
	2,6	4.68	0.191	0.140	0.176
	3,5	1.19	0.049	0.022	-0.048
	4	17.45 <sup>g</sup>	0.349	0.226	0.304
Thiobenzoic acid	2,6	4.02			
	3,5	1.14			
	4	5.53			

<sup>a</sup> Methyl proton coupling.<sup>b</sup> Alkoxy proton coupling.<sup>c</sup> Spin density at alkoxy oxygen.<sup>d</sup> Hydroxy proton coupling.<sup>e</sup> Spin density at hydroxy oxygen.<sup>f</sup> Aldehydic carbon atom.<sup>g</sup> Fluorine coupling.

TABLE II

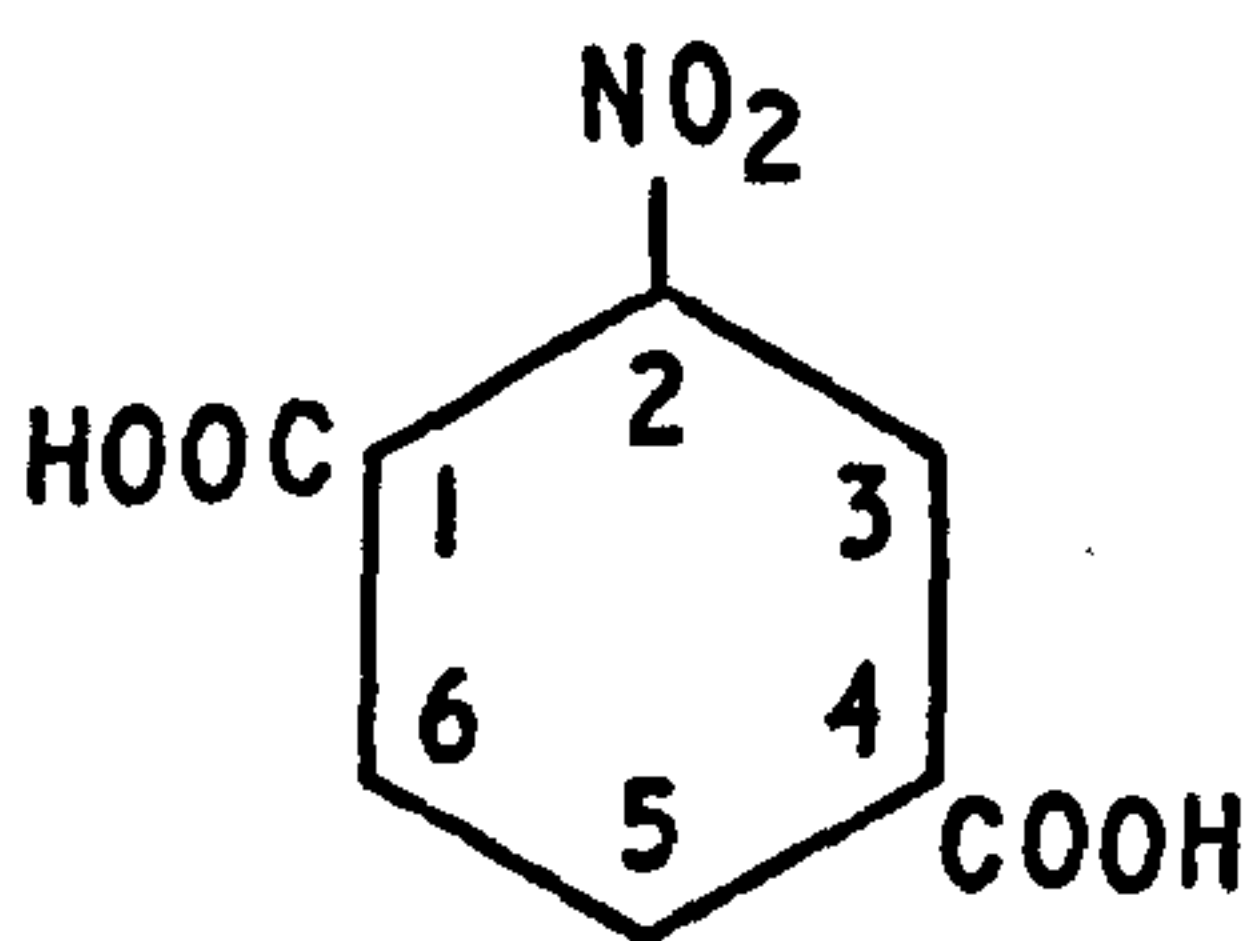
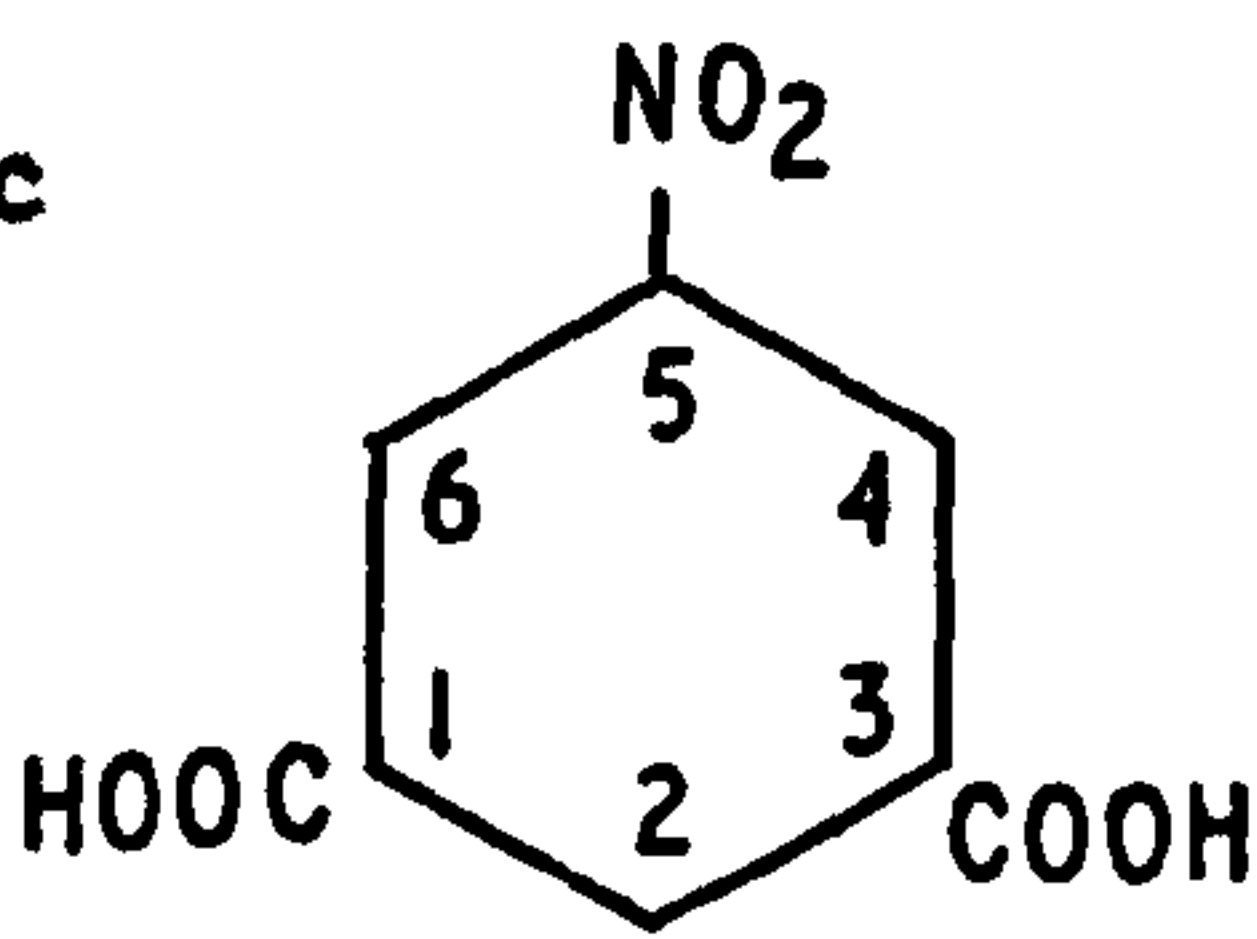
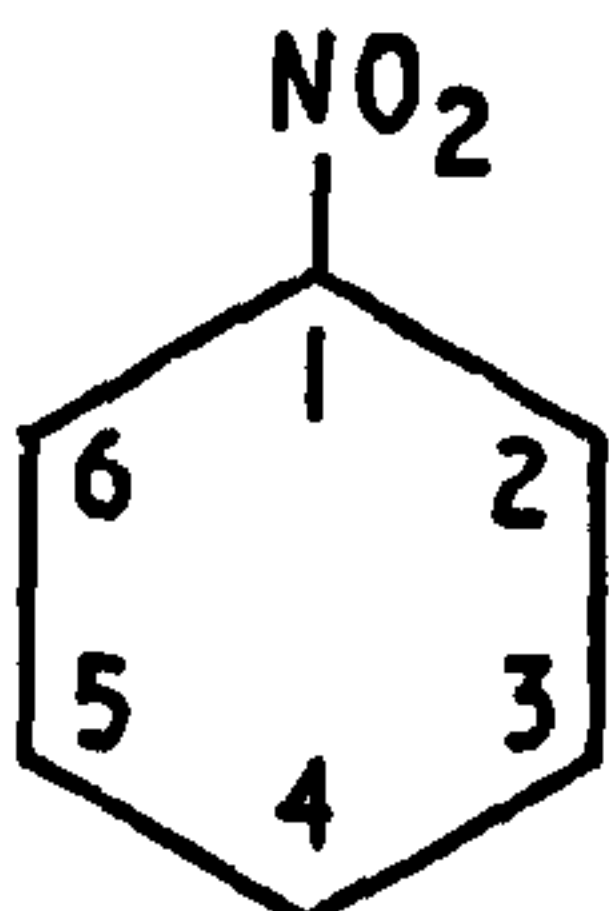
Calculated g-Values for Radical-anions of  
Aromatic Carboxylic Acids

<u>Substrate</u>	<u>g-Value</u>
Benzoic acid	2.0034
Isophthalic acid	2.0034
Terephthalic acid	2.0039
2-Methylbenzoic acid	2.0031
3-Methylbenzoic acid	2.0034
4-Methylbenzoic acid	2.0037
3,4-Dimethylbenzoic acid	2.0022
3,5-Dimethylbenzoic acid	2.0034
4-Methoxybenzoic acid	2.0029
4-Ethoxybenzoic acid	2.0038
4-Hydroxybenzoic acid	2.0039
4-Aldehydobenzoic acid	2.0042
3-Fluorobenzoic acid	2.0032
4-Fluorobenzoic acid	2.0037
Thiobenzoic acid	2.0046

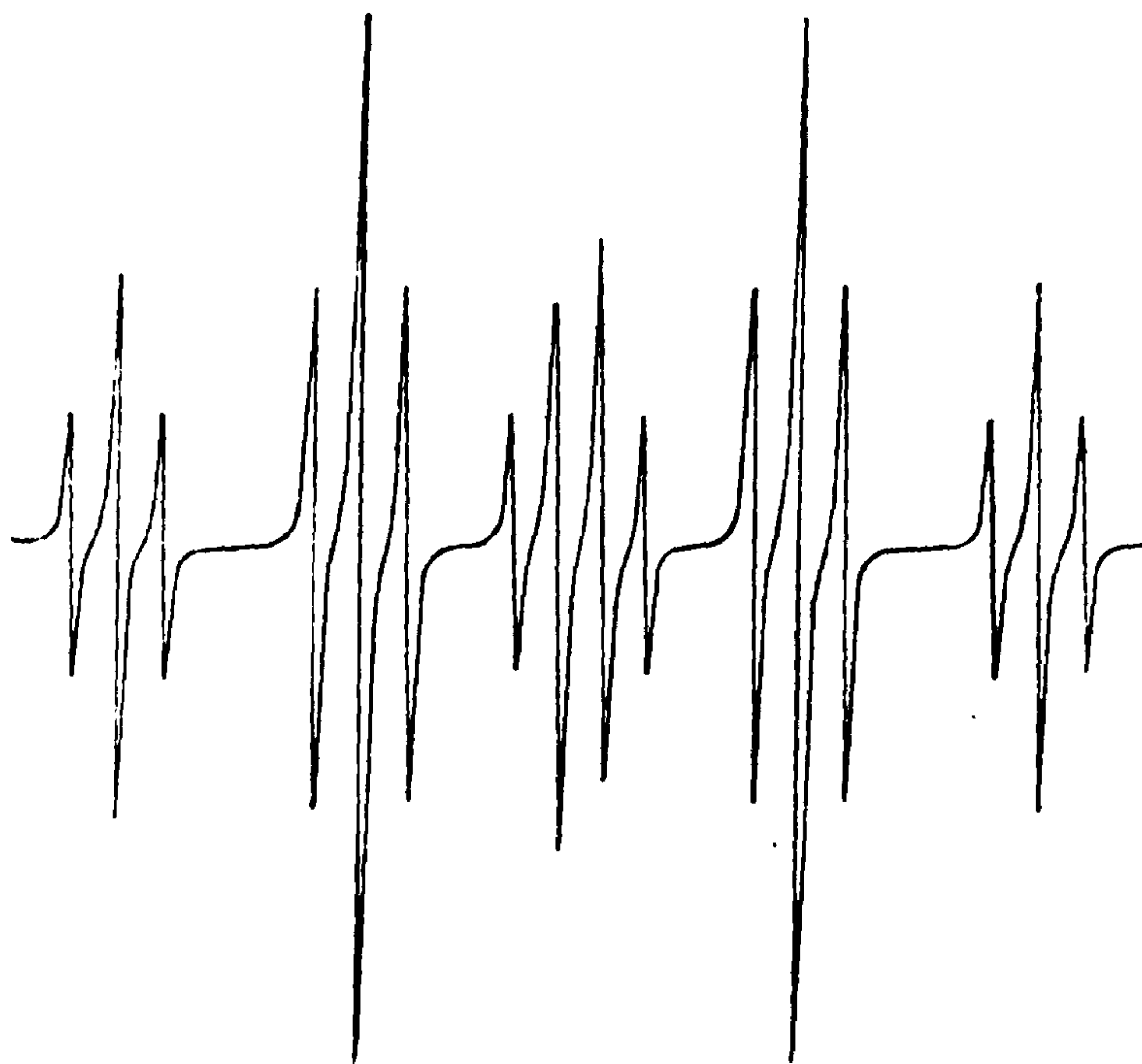
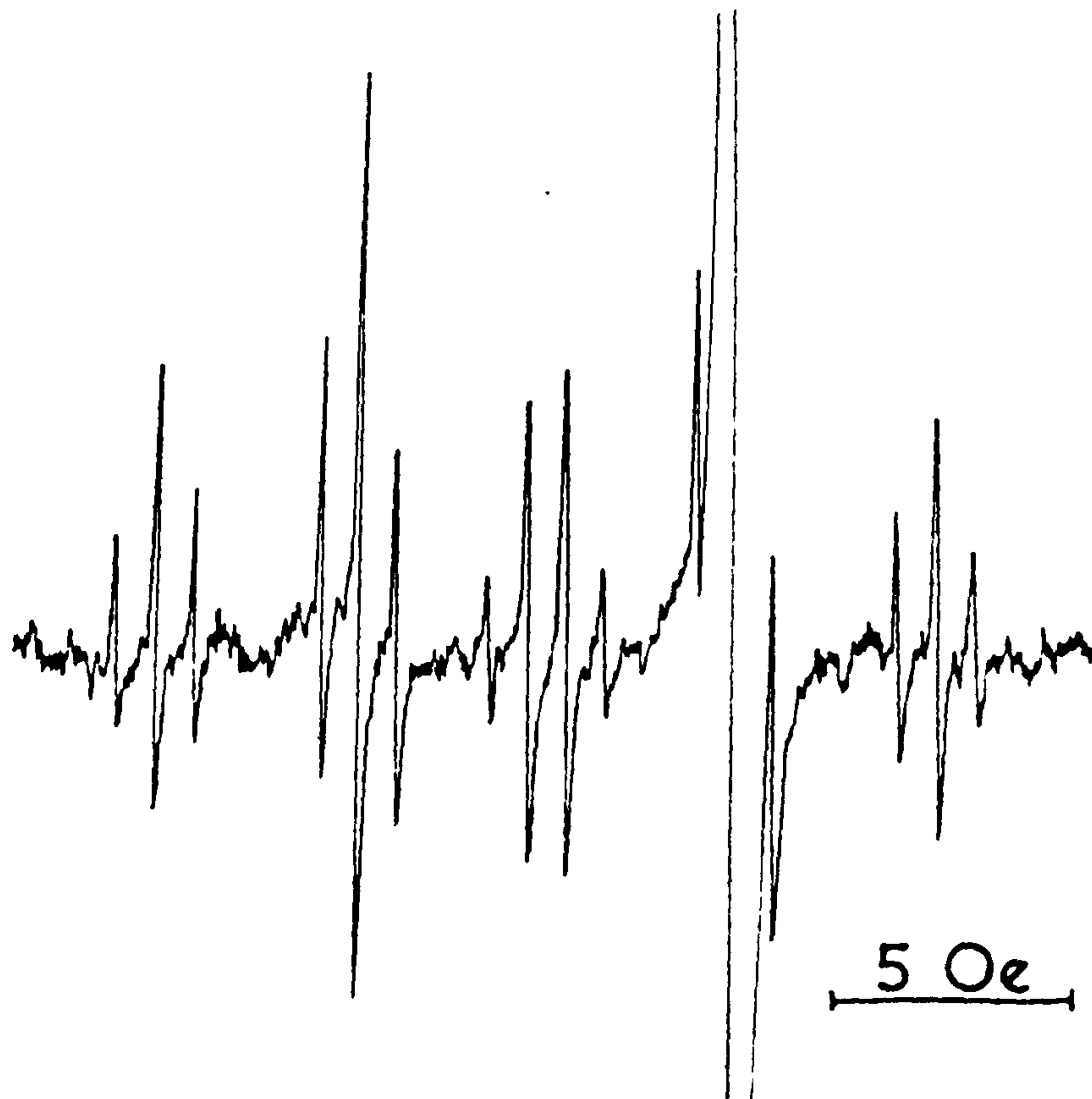


TABLE III

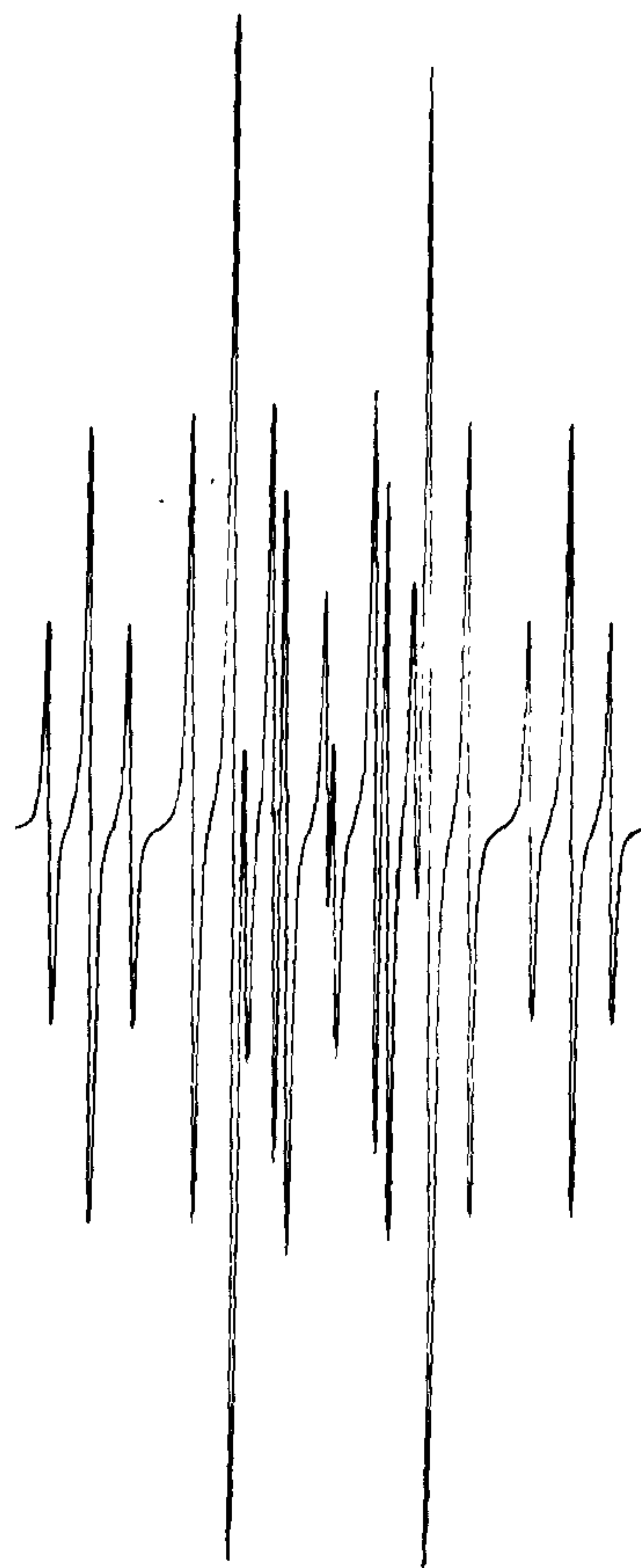
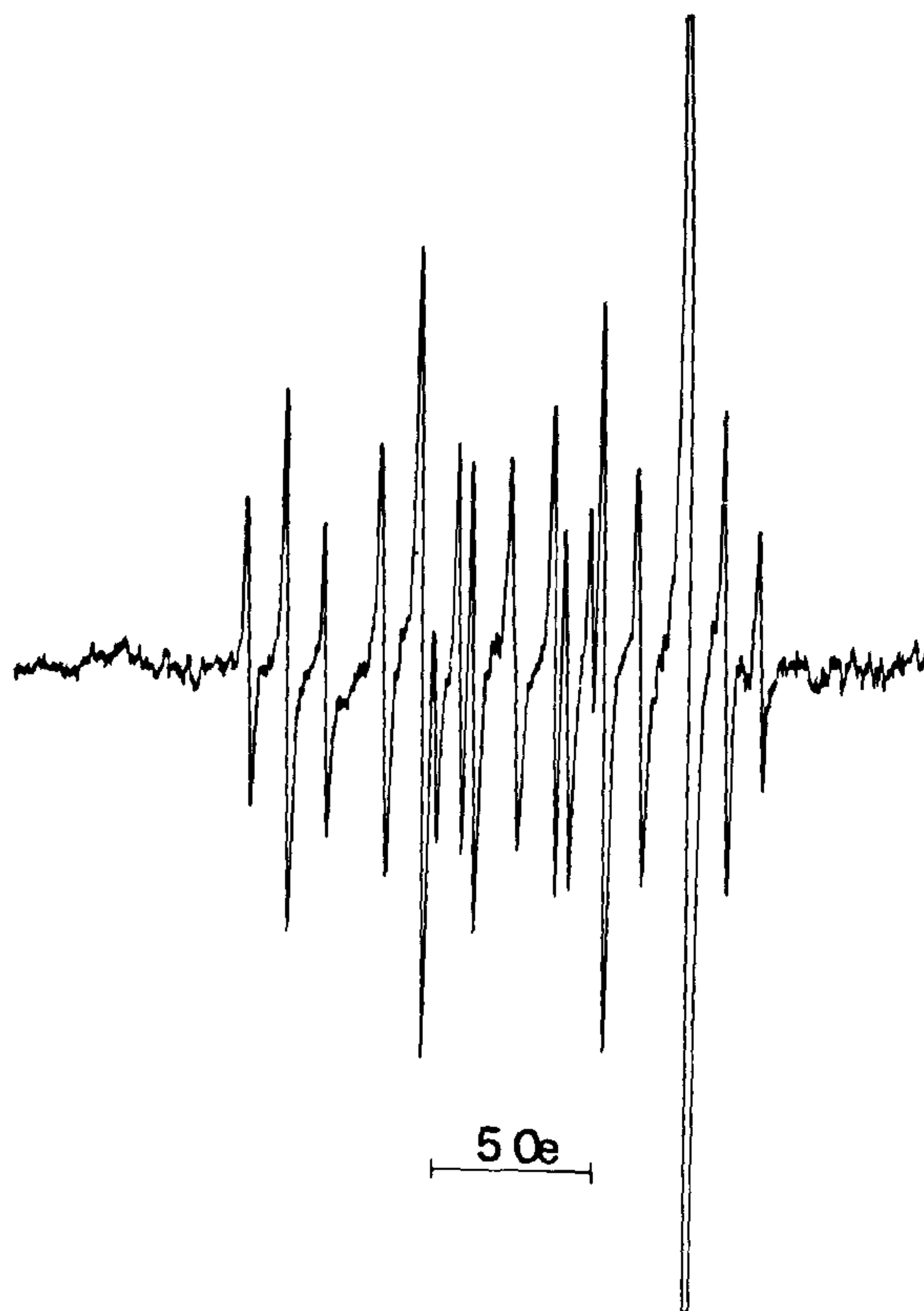
Coupling Constants for Radicals of  
Nitrophthalic Acids

Substrate	Position	Coupling constants (G)	
		Flow	Static
Nitroterephthalic acid 	N	9.21	8.12
	3	3.26	3.77
	5	3.26	3.92
	6	0.98	1.01
	N-H	12.19	
5-Nitroisophthalic acid 	N	9.23	12.05
	2	3.34	3.41
	4	3.34	3.41
	6	2.90	3.75
	N-H	12.05	
4-Nitrobenzoic acid 	N	10.78	
	2,6	1.11	
	3,5	3.33	

**Spectrum of the radical-anion of benzoic acid (upper)  
and the computer simulation (lower).**

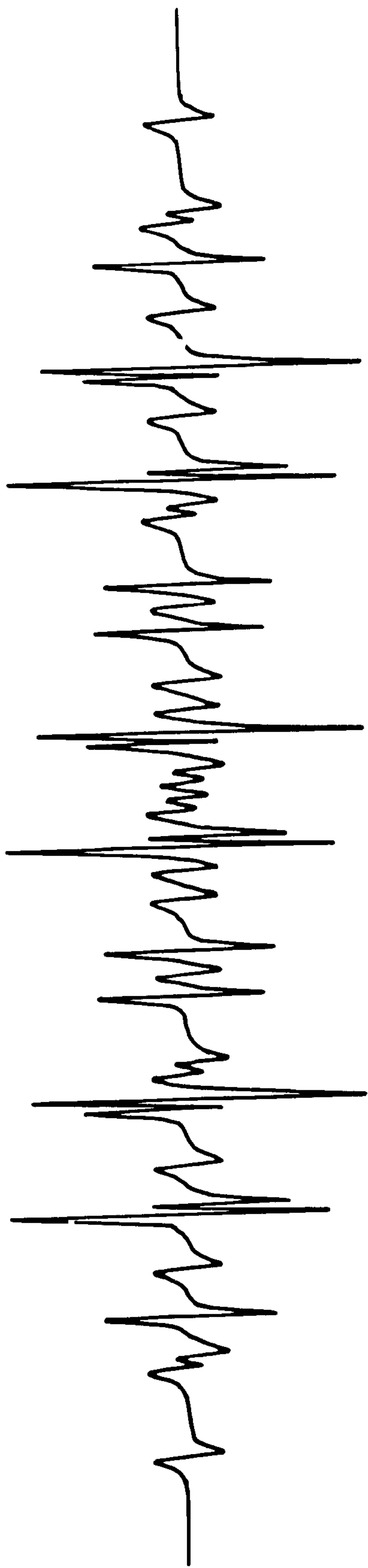


**Spectrum of the radical-anion of thiobenzoic acid (upper)  
and the computer simulation (lower).**

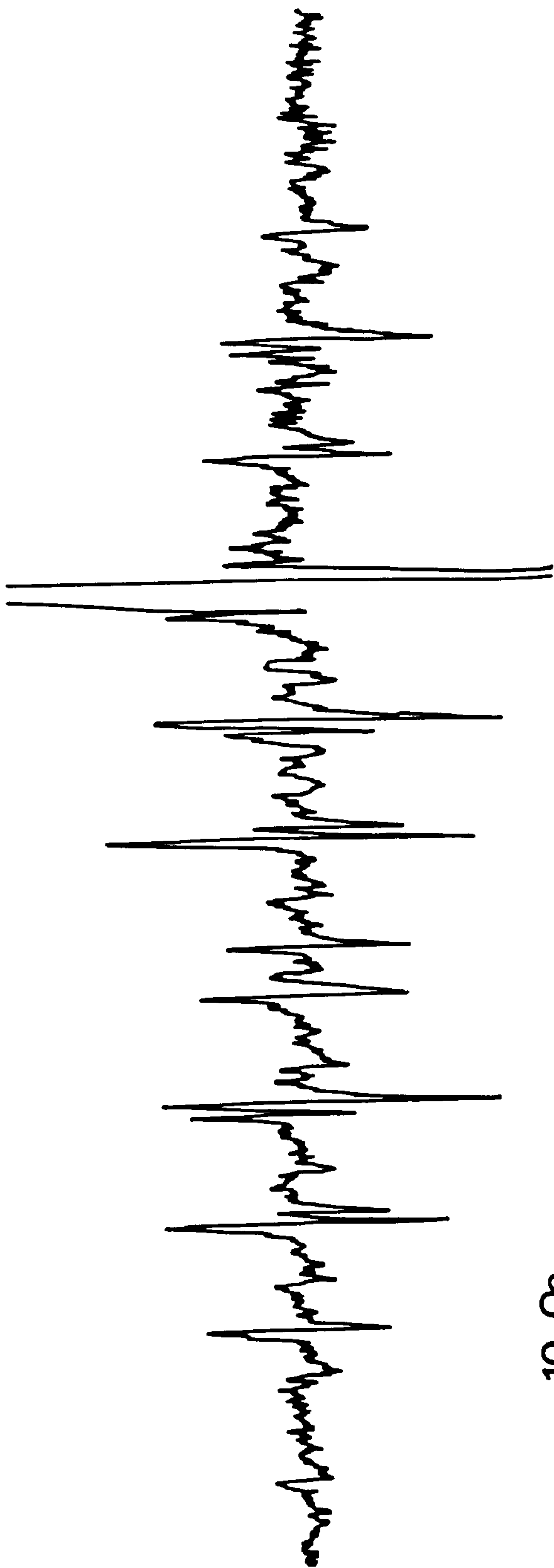


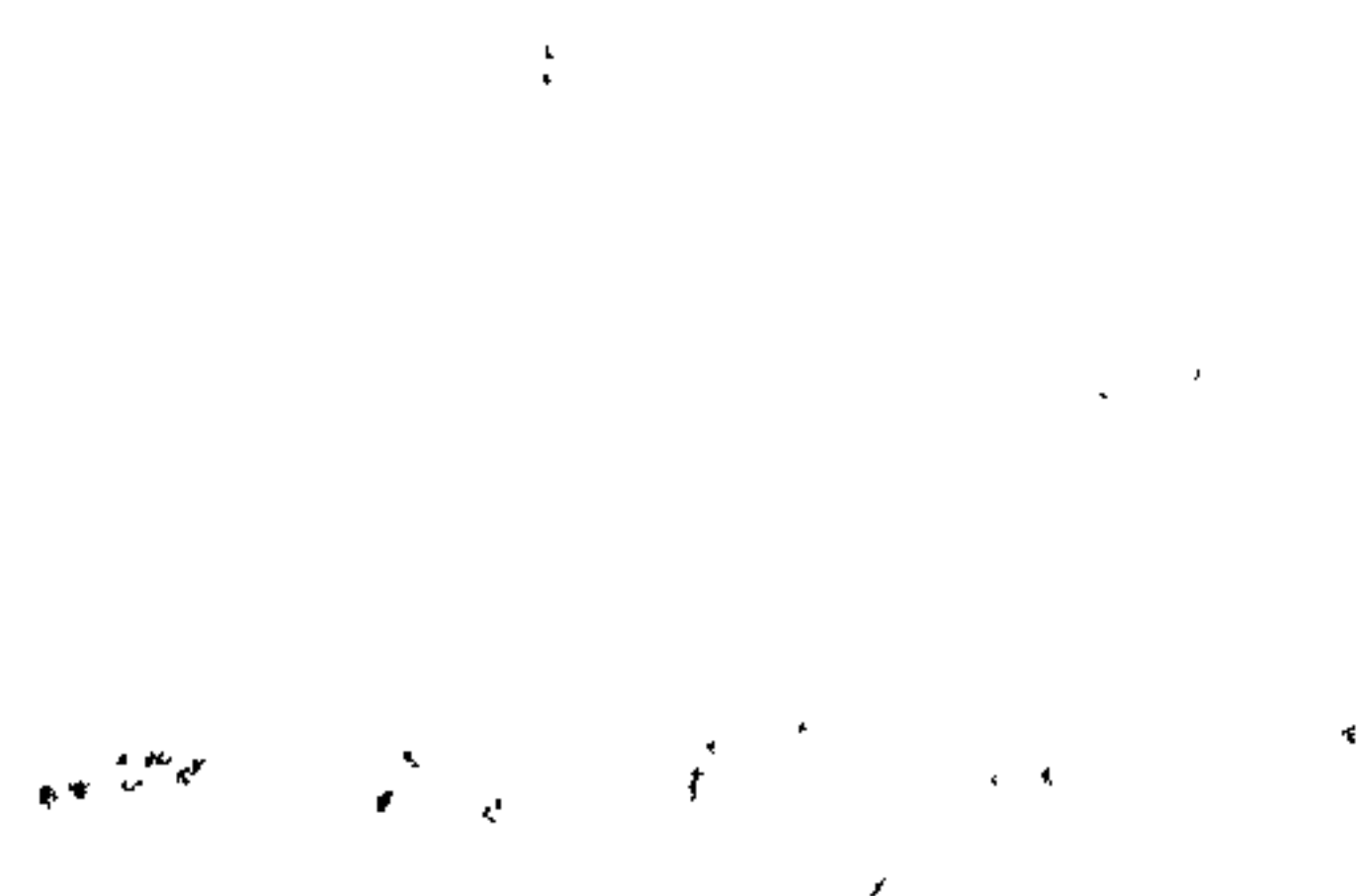


**'Flow' spectrum obtained from the reduction of 5-nitro-isophthalic acid (upper) and a computer simulation (lower) of a mixture of protonated and unprotonated species discussed in the text.**

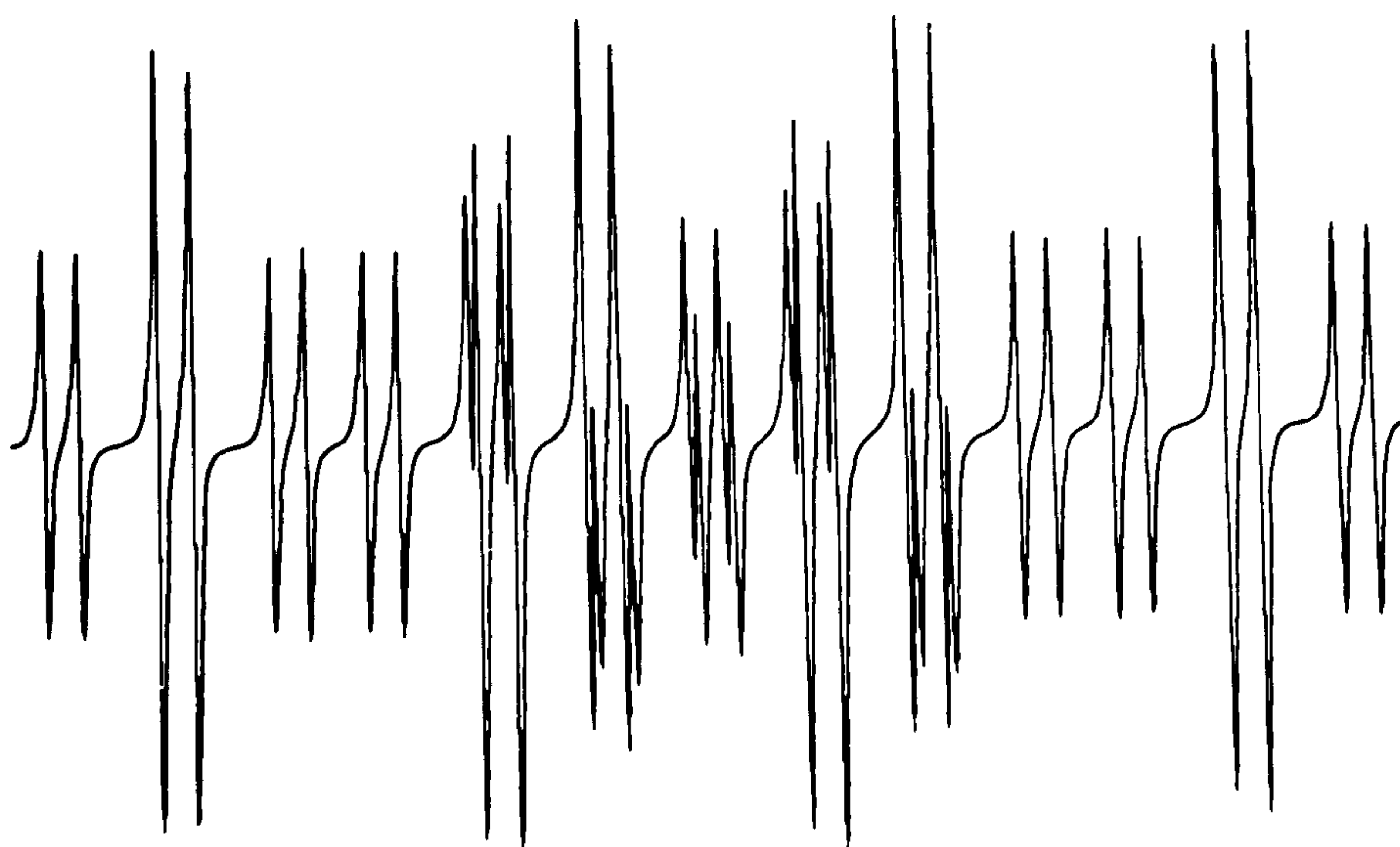
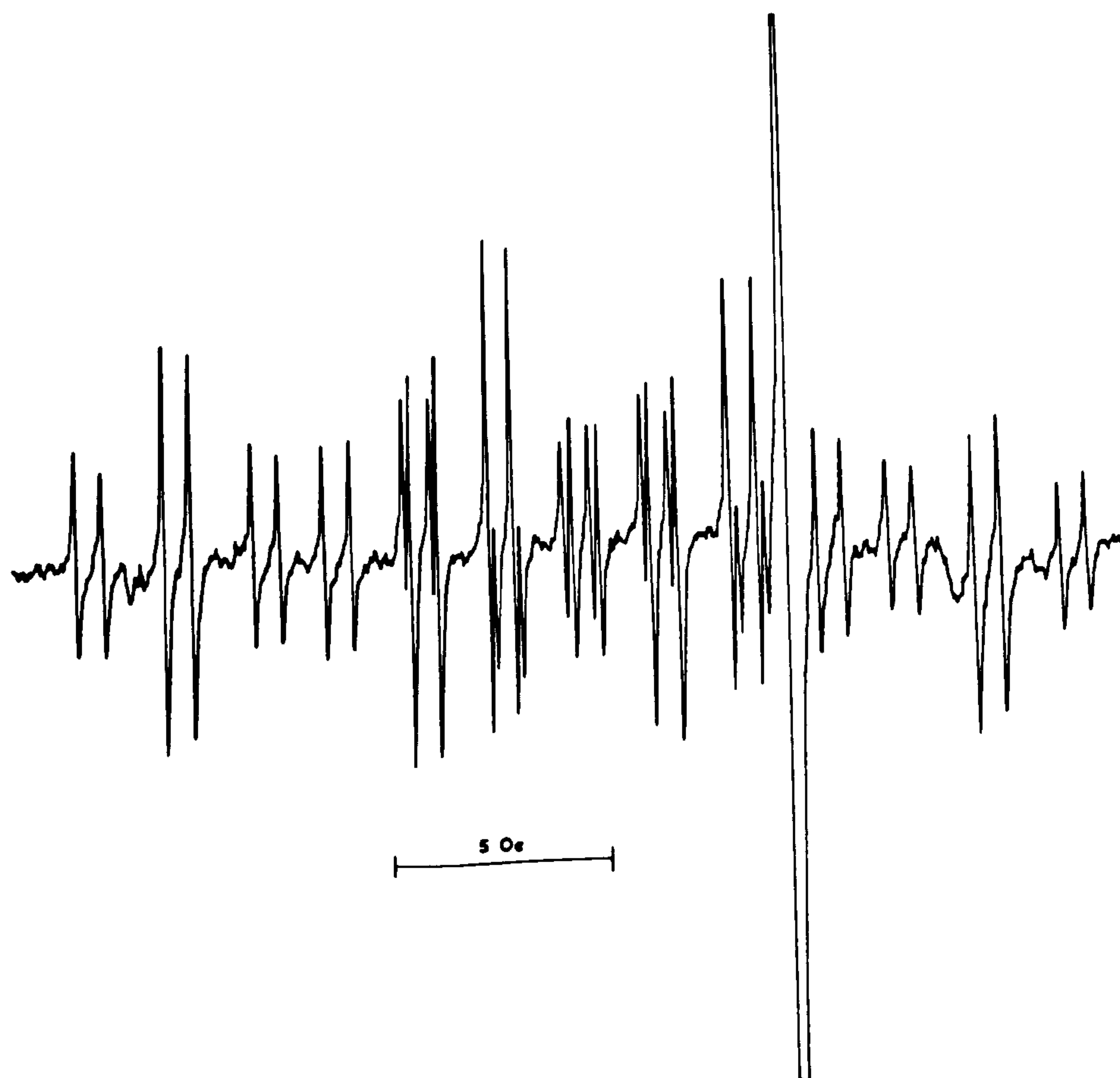


10 Oe





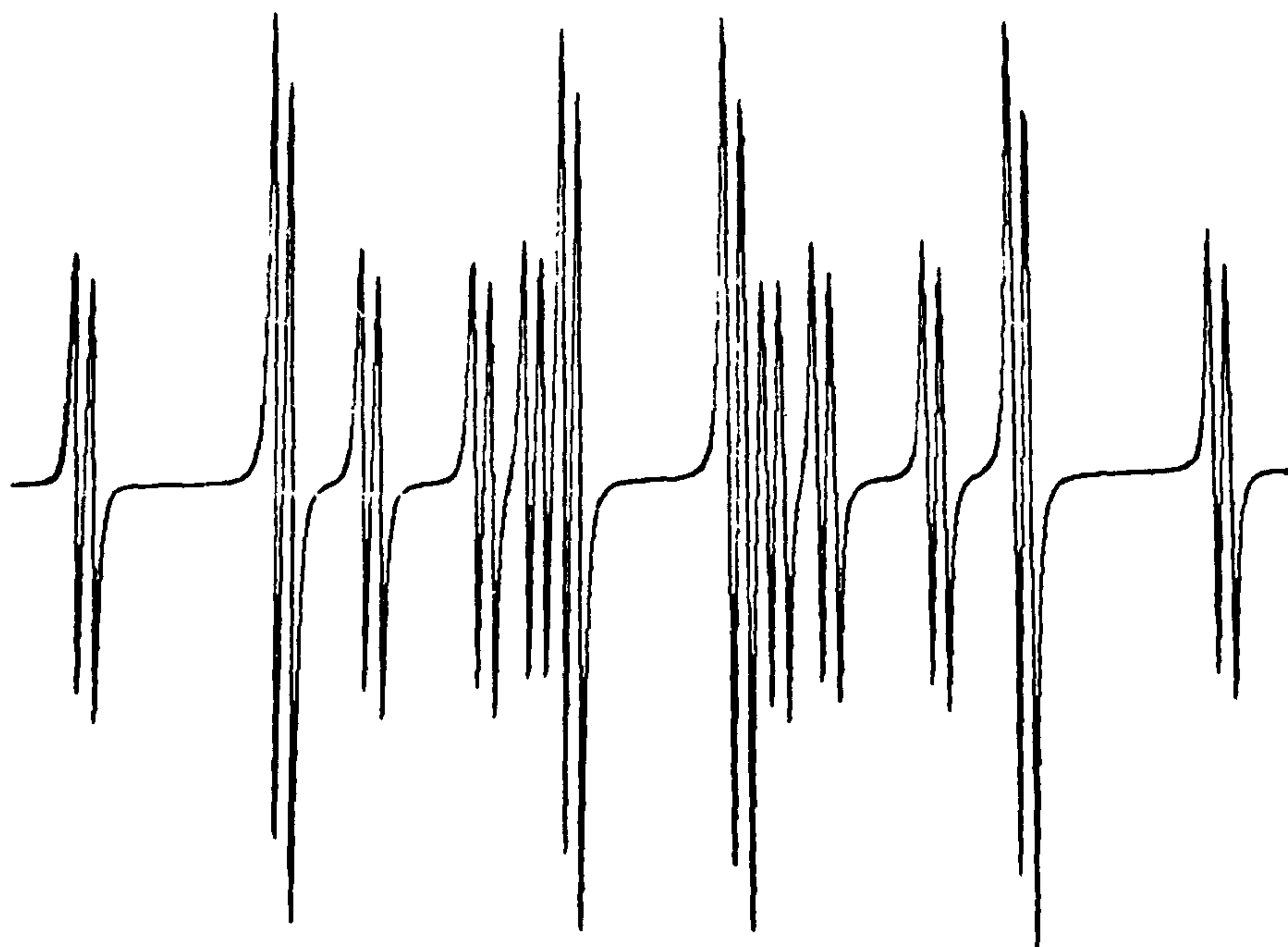
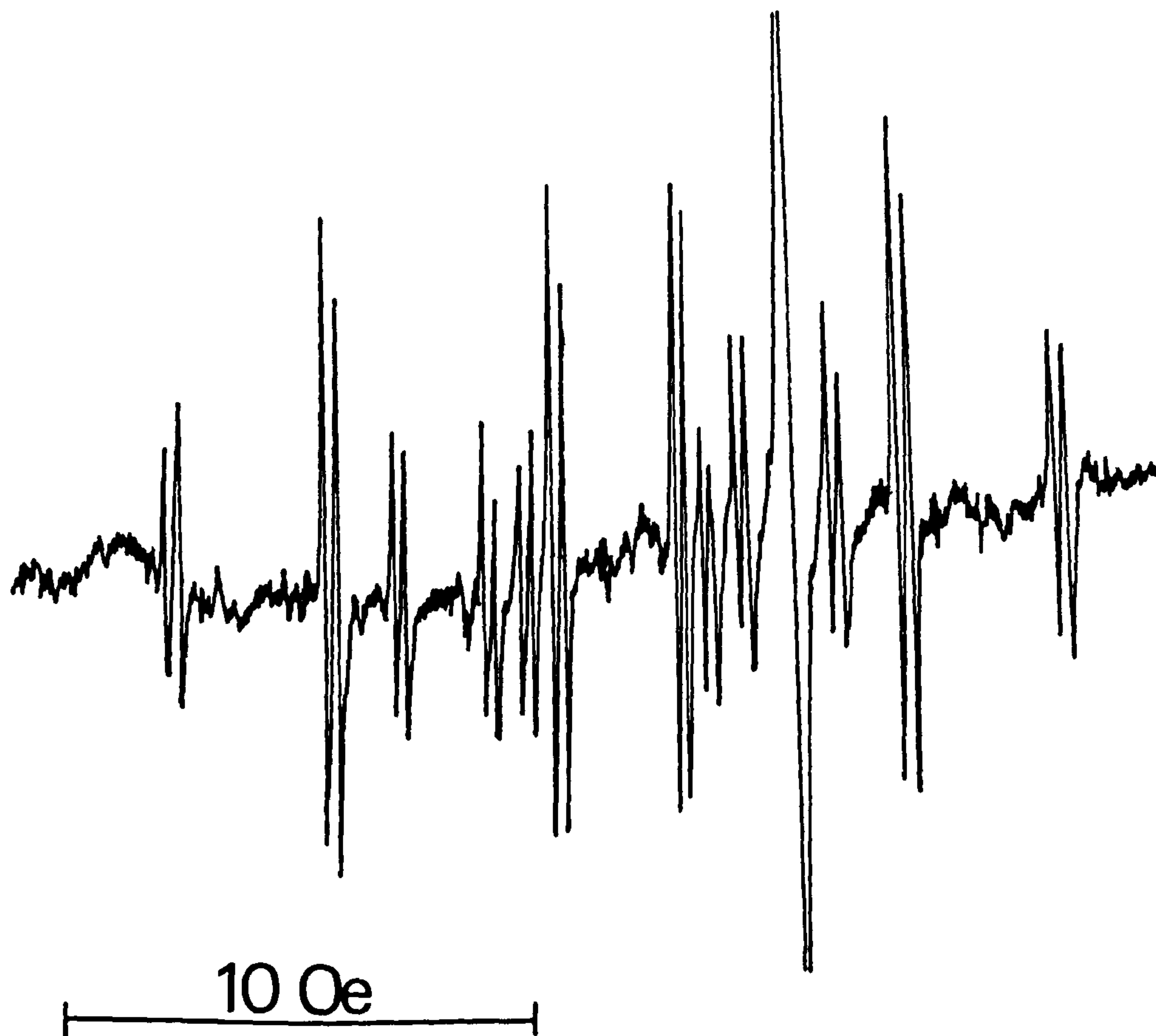
**'Flow' spectrum obtained from reduction of nitro-  
terephthalic acid (upper) and the computer simulation (lower).**





**Spectrum of the radical-anion of 3-fluorobenzoic acid (upper)  
and the computer simulation (lower).**





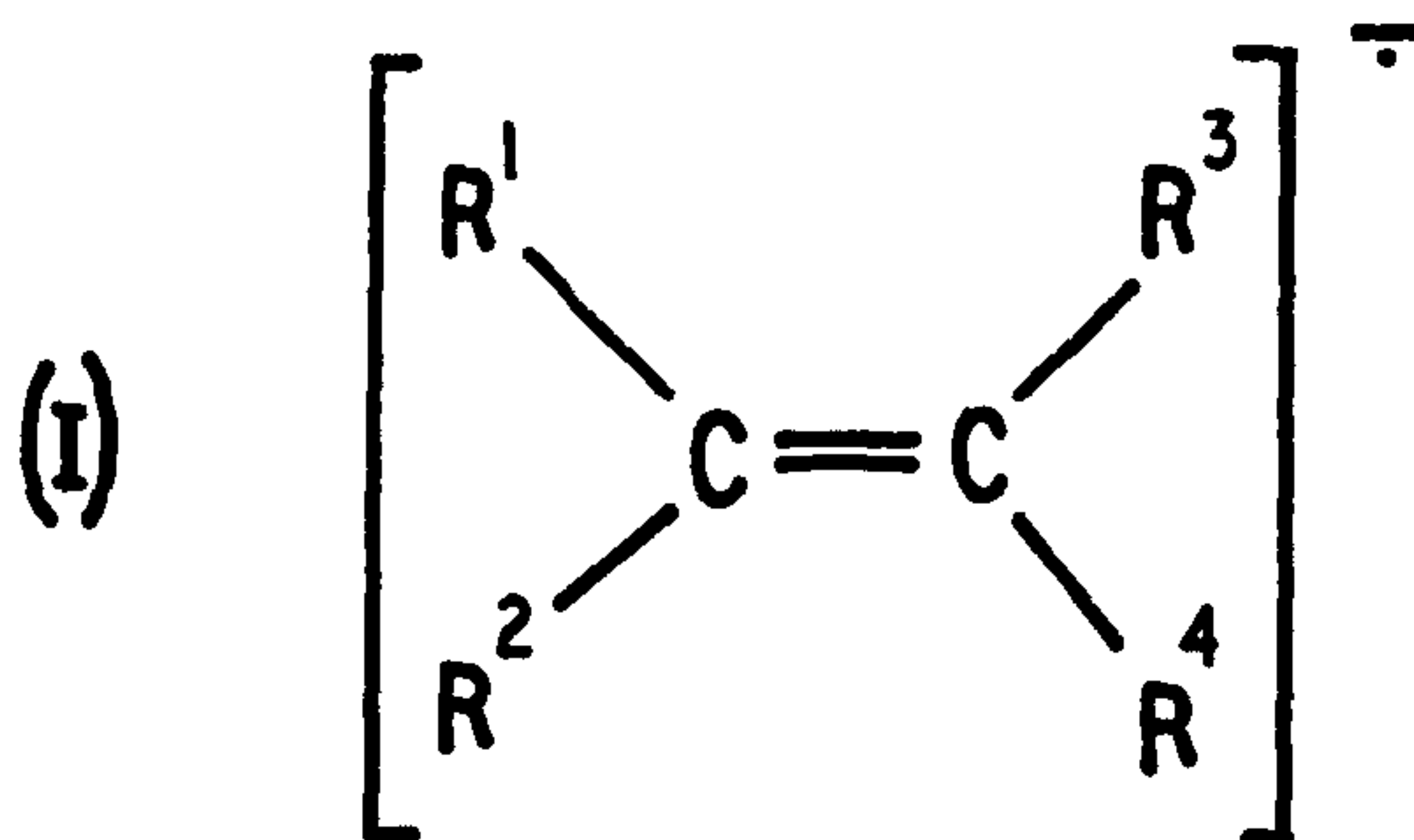
REDUCTION OF STYRENE

AND

RELATED COMPOUNDS

## INTRODUCTION

Interest in radicals produced from vinyl compounds stems predominantly from their participation in polymerisation, and although the e.s.r. spectrum of the unsubstituted styrene radical-anion has not hitherto been observed in solution, spectra have been obtained from phenyl substituted ethylenes of the general formula

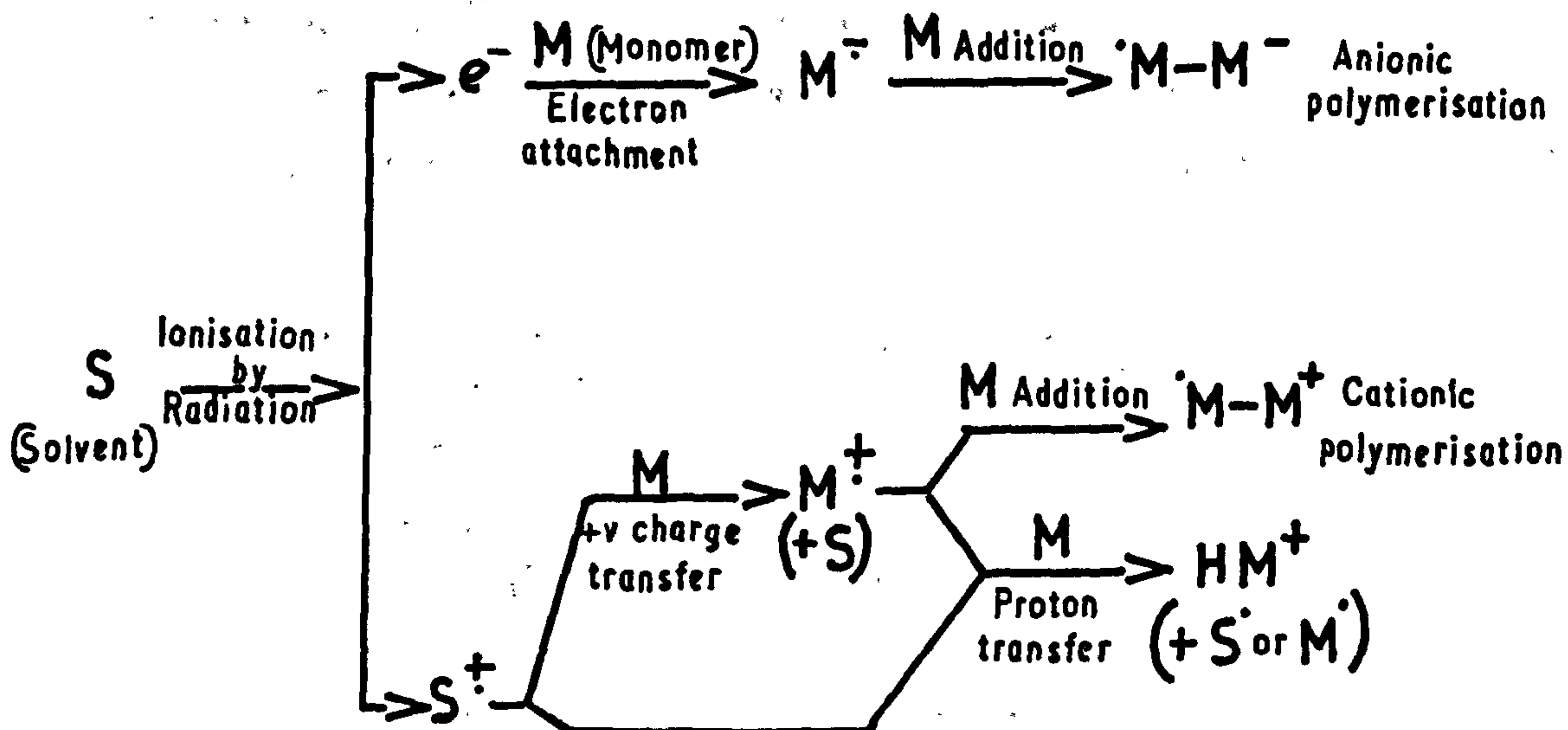


where at least one R group is aromatic. Tetraphenylethylene (TPE), [(I),  $R^1 = R^2 = R^3 = R^4 = C_6H_5$ ], has recently produced a completely analysable spectrum<sup>132</sup> and it appeared from the analysis that the two ortho (and meta) protons in each aromatic ring were not equivalent; hindered rotation of the phenyl group appears to be responsible. Other workers<sup>133, 134</sup> have attempted to observe  $TPE^\cdot$  but resultant spectra were too poor to resolve small coupling constant differences and they were unable to reach any conclusion regarding spin density distribution. A similar history of poor spectra is seen for 1,1'-diphenylethylene (DPE) where Evans<sup>135, 136</sup> claimed to have observed the radical-anion of DPE but which was in fact explained by Staples<sup>137</sup> in terms of an oxidation product from DPE purification, i.e. benzophenone. Other compounds of general formula (I)

have produced radical-anions, i.e. stilbene,<sup>138,139</sup> 1,2-bis (4-pyridyl)-ethylene<sup>138</sup> and 1-phenylprop-1-ene<sup>140</sup>, and in each case restricted rotation was observed.

From pulse radiolysis Swallow<sup>141</sup> concluded that polymerisation of pure styrene proceeds by a radical mechanism while Ueno<sup>142</sup> found that polymerisation was not affected by radical scavengers and the main propagating chain ends were ionic rather than radical, although an investigation by Katayama<sup>143</sup> demonstrated that diphenylpicrylhydrazyl (a radical scavenger) practically inhibited polymerisation of pure  $\alpha$ -methylstyrene. Whether the first step in styrene polymerisation is an ionic or radical one has been shown by O'Driscoll<sup>144</sup> to depend on the catalyst used.

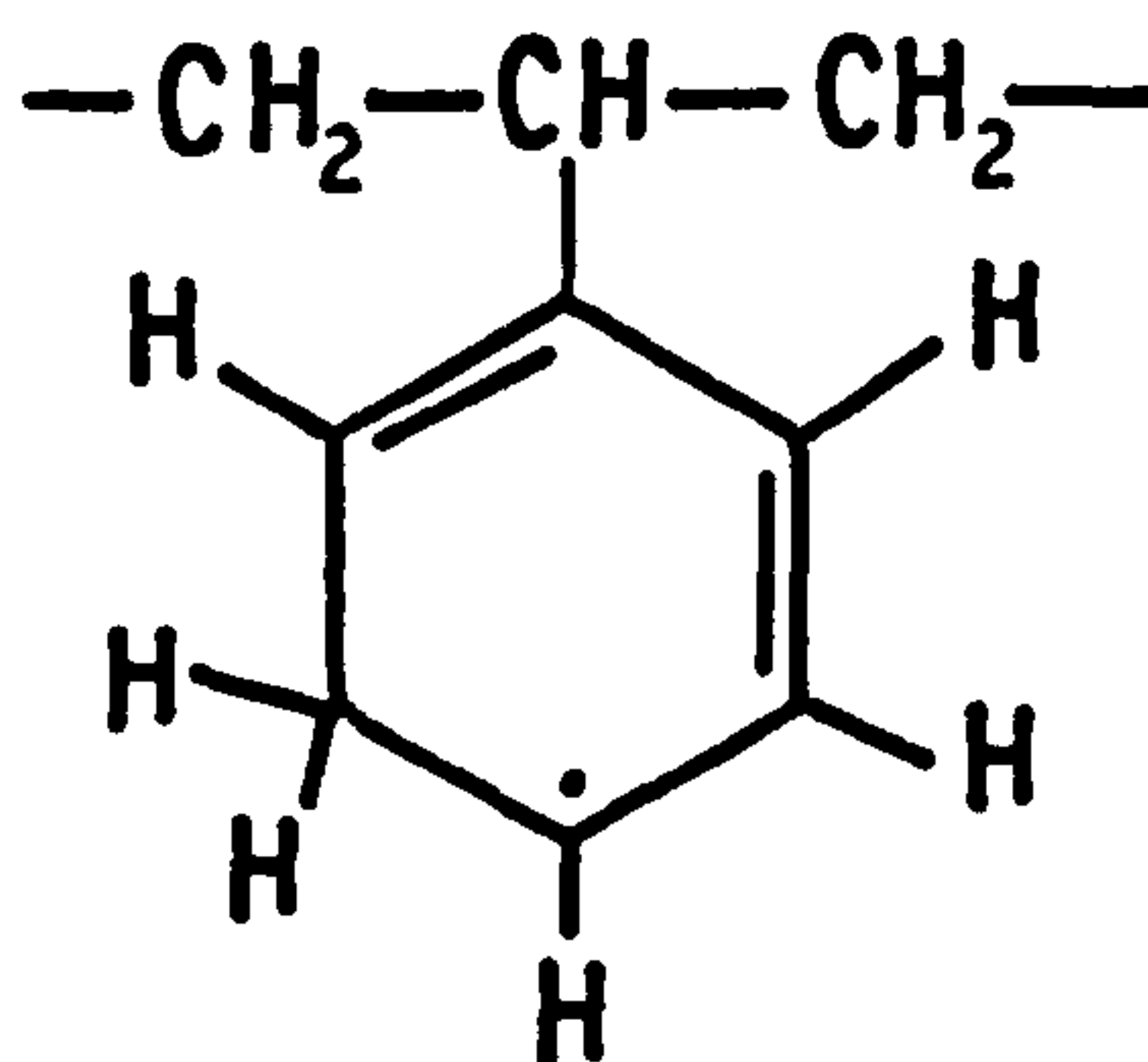
So far as vinyl monomers are concerned ionic propagation proceeds by cationic or anionic polymerisation at the chain ends. The study of the initiation process of radiation-induced ionic polymerisation seeks to elucidate how these ions are formed from primary intermediates. Possible reactions to form these ions in the irradiated solutions may be considered schematically as<sup>145</sup>



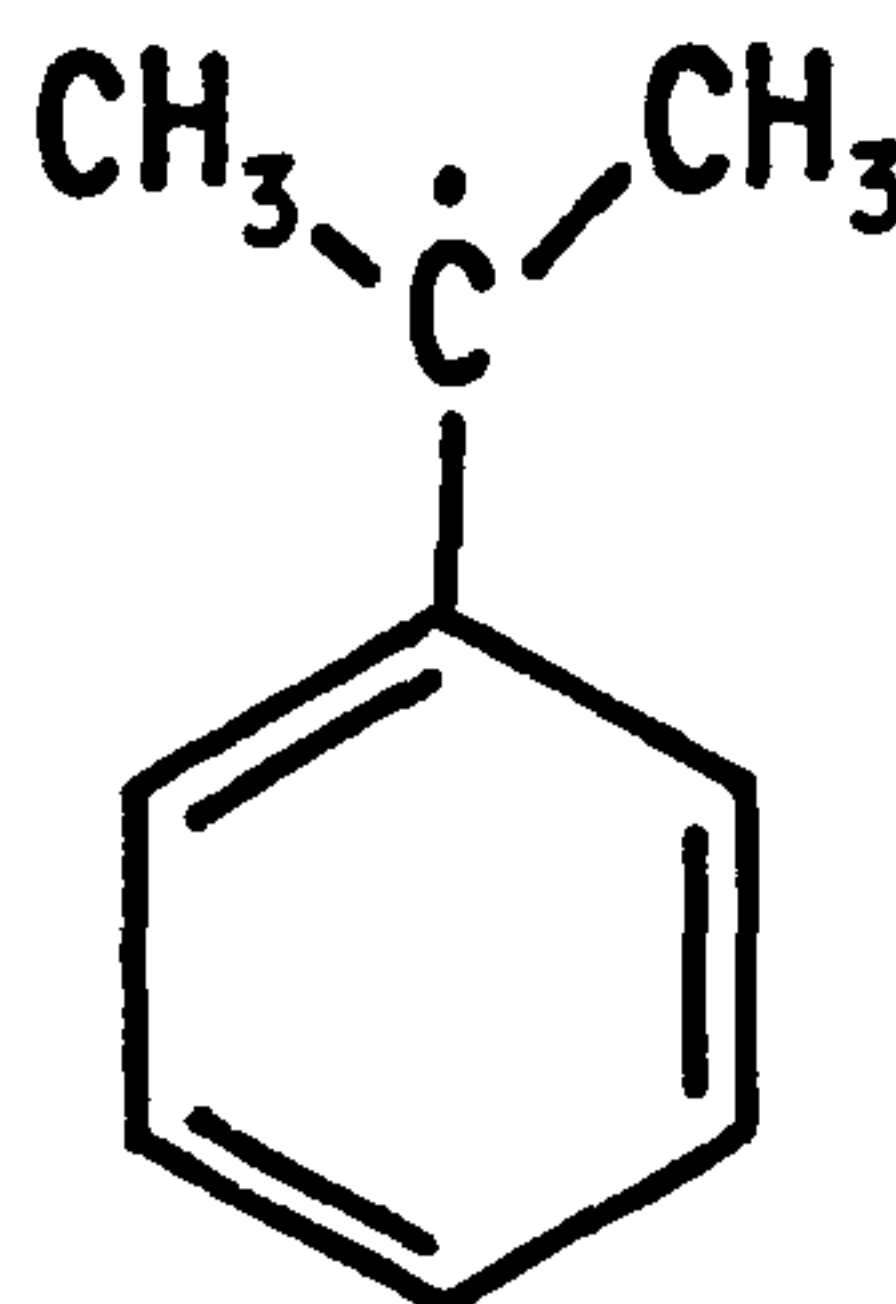
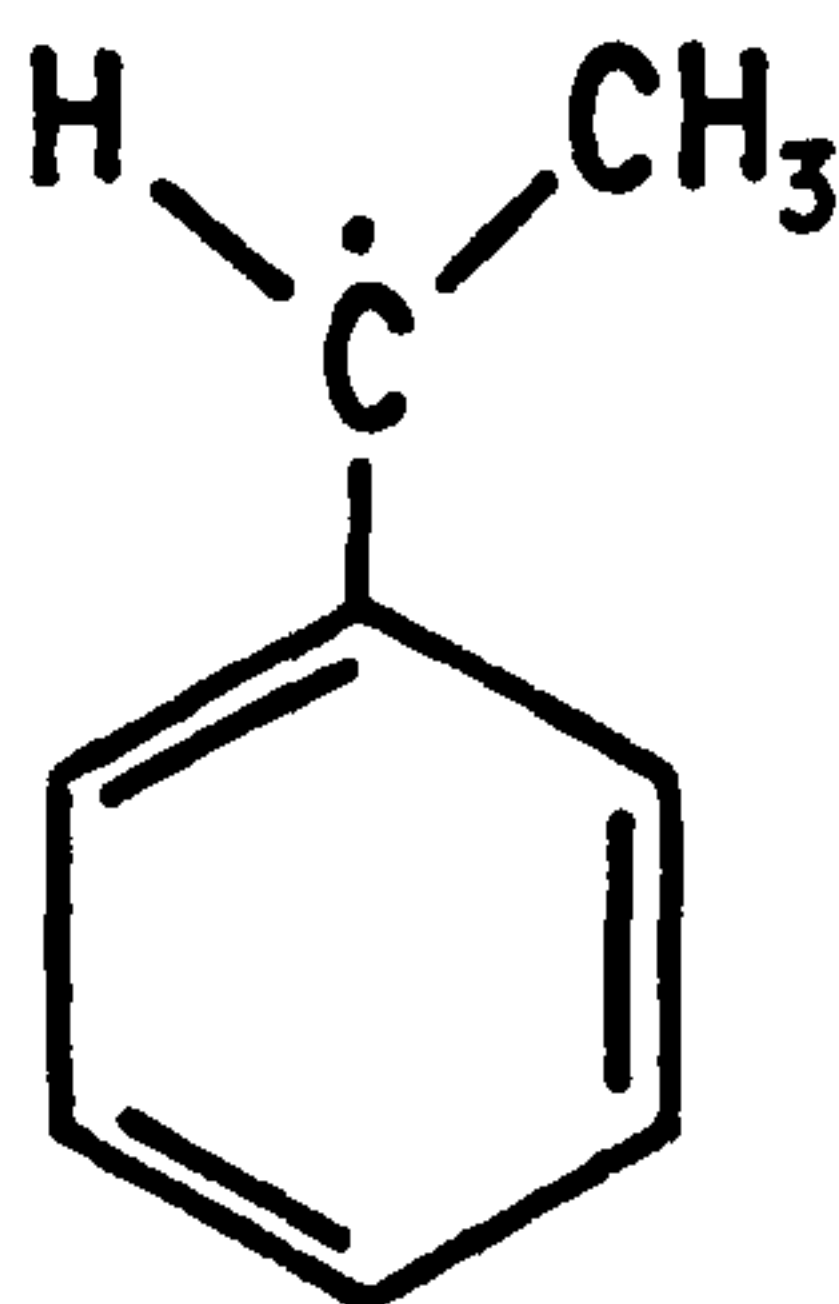


It can be seen from this scheme that ion radicals may play an important rôle in the initiation process, and the observation of ion radicals by means of e.s.r. may give valuable information in the study of the initiation process. The lifetime of these intermediates in liquid solution is so short that it has been difficult or impossible to observe them directly and one convenient way to overcome this difficulty has been to prolong the lifetime by freezing the solution before irradiation; poor spectra are, however, frequently observed from radicals in a solid matrix<sup>146</sup> and consequently most physico-chemical investigations have utilised optical techniques.

Irradiation of polystyrene has given an e.s.r. spectrum<sup>147</sup> corresponding to the cyclohexadienyl structure



Protonation occurs<sup>148</sup> during the  $\gamma$ -irradiation of styrene or  $\alpha$ -methylstyrene in an ethanol glass and the fairly reasonably-resolved spectra are interpreted, with supporting evidence from deuteration, as benzyl type radicals.





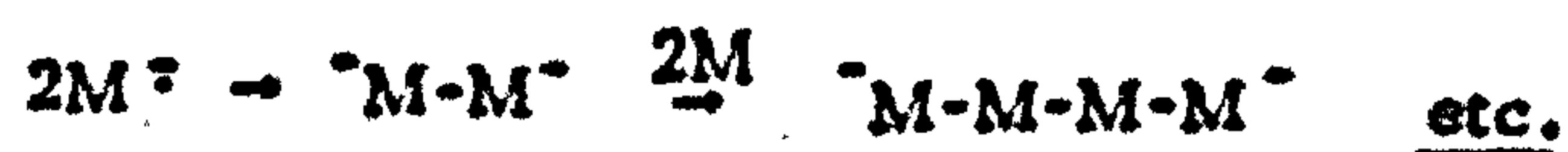
The coupling constants agree well with those for the unsubstituted benzyl radical. The radical-anion is formed by electron capture and followed by proton transfer from the solvent.

From the literature it is apparent that the styrene radical-anion, if present in the first stages of polymerisation, is short-lived and a good candidate for investigation by the sodium/liquid ammonia flow system.

## RESULTS AND DISCUSSION

E.s.r. spectra obtained after the reduction in the flow system of a number of styrene compounds were interpreted as monomer radical-anion spectra; the results are shown in Tables I and II. By far the greatest difficulty encountered was in the analysis of the spectra since restricted rotation of the vinyl group removes the equivalence of ortho (and meta) protons with a consequent increase in the number of coupling constants. Complete analysis was only possible for well-resolved spectra with the total width clearly defined. Computer simulation greatly aided the final stages of spectra interpretation where the accurate matching of coupling constants to within 0.02 G between experimental and theoretical was necessary to confirm the analysis with confidence; more than one hundred such simulations were necessary for confident analysis of  $\alpha$ -methylstyrene. The 4-methylstyrene spectrum has as yet evaded complete analysis but there is no reason to believe it to be due to anything other than the monomer radical-anion since three other methylstyrenes (2-methyl, 3-methyl and  $\alpha$ -methylstyrene) after complete analysis were assigned to monomer radical-anions. No spectra were obtained from reduction of 4-bromostyrene or  $\beta$ -bromostyrene although four fluoro-compounds, viz. 2-, 3- and 4-fluorostyrene and 4-fluoro- $\alpha$ -methylstyrene produced well-resolved spectra.

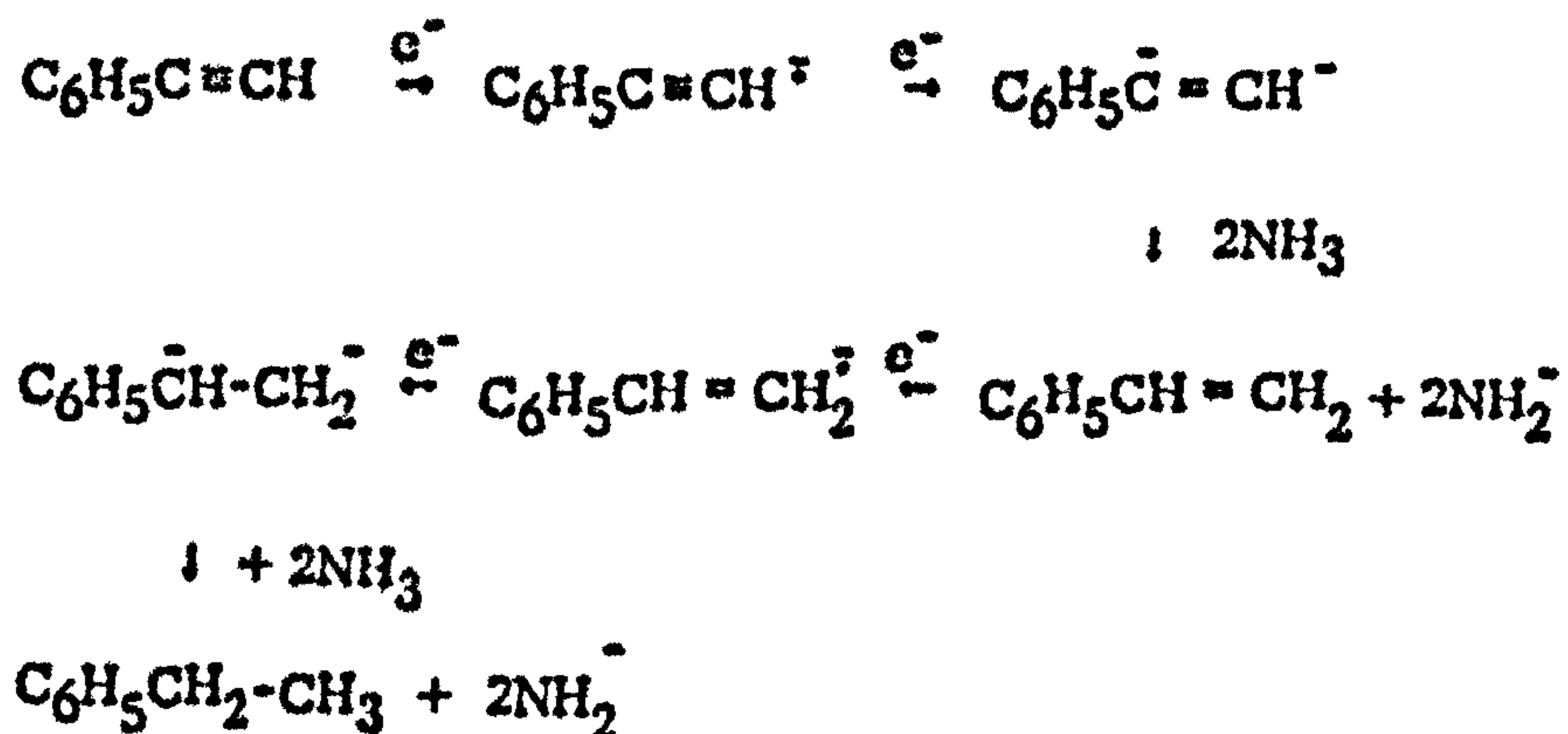
Polymerisation of 4-vinylpyridine in liquid ammonia proceeds by an anionic mechanism<sup>149</sup> after initiation electrochemically; the mechanism is thought to be primary formation of a radical-anion;



Confirmation of the first stage was forthcoming from the flow system where

spectra of the monomer radical-anions were obtained after reduction of 2- and 4-vinylpyridine.

It is appropriate to describe at this point an interesting result from reduction of phenylacetylene. The spectrum obtained consisted of a major species readily interpreted as being due to  $[\text{C}_6\text{H}_5\text{C}\equiv\text{CH}]^{\cdot-}$  with coupling constants of  $A_{2\text{H}} = 3.53 \text{ G}$ ,  $A_{2\text{H}} = 0.56 \text{ G}$ ,  $A_{\text{H}} = 7.16 \text{ G}$ ,  $A_{\text{H}} = 22.79 \text{ G}$ , superimposed on a small complex spectrum. The imposition of a one second delay between the points of mixing and observation increased the intensity of the minor species to the total exclusion of the phenylacetylene radical-anion. The spectrum of the secondary radical matched that of the styrene radical-anion indicating that abstraction of hydrogen from ammonia had occurred to produce styrene. Further protonation of styrene is known to occur<sup>150-152</sup> (as well as production of polymers) during sodium/liquid ammonia reduction to give ethylbenzene in yields up to 50% and hence a possible reaction scheme is

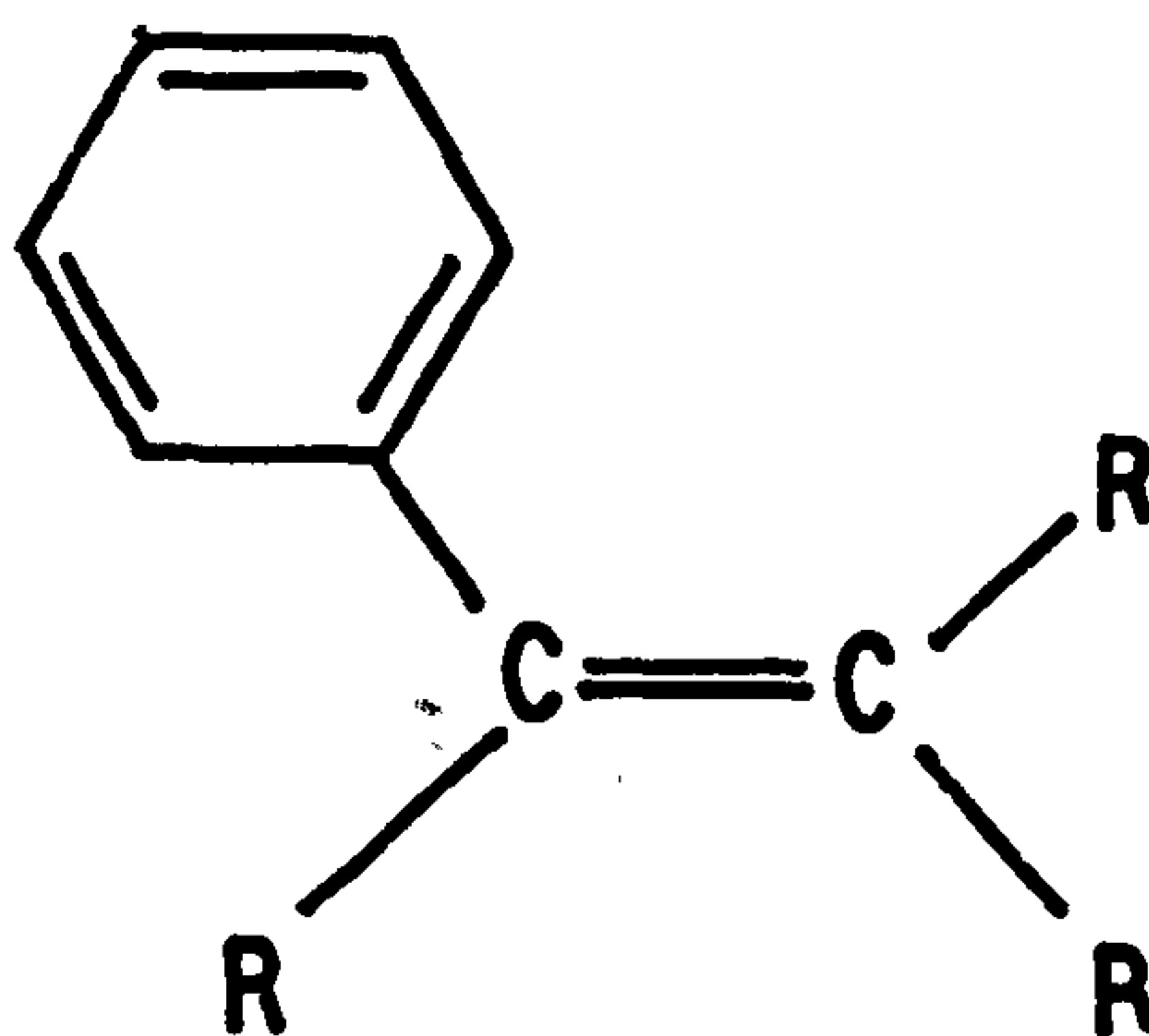


A similar experiment was performed by reducing phenylpropiolic acid  $\text{C}_6\text{H}_5\text{C}\equiv\text{C}-\text{COOH}$ . The spectrum obtained was not due to  $[\text{C}_6\text{H}_5\text{C}\equiv\text{C}-\text{COO}]^{\cdot-}$  but was analysed in terms of seven non-equivalent protons. By analogy with the previous experiment with phenylacetylene, the possibility of the spectrum being due to cinnamic acid was confirmed by reducing an authentic sample of cinnamic acid and comparing the spectra.



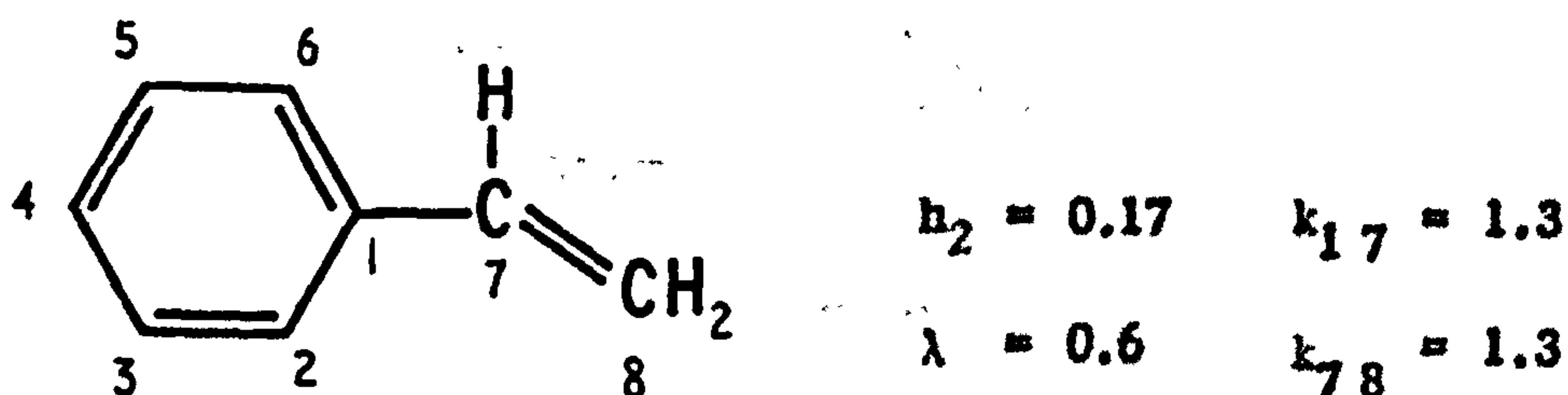
## MOLECULAR ORBITAL CALCULATIONS

The general pattern of aromatic coupling constants in compounds of the formula



is quite well known as, for example, in tetraphenylethylene,<sup>132</sup> stilbene<sup>139</sup> and 1-phenylprop-1-ene.<sup>140</sup> Molecular orbital calculations have proved either impossible<sup>153</sup> or very difficult due to the inequivalence of all aromatic protons. In most of the above cases Coulomb and resonance integrals were kept equal while the McLachlan configuration interaction parameter was given values of 1.0 to 1.2. Two empirical approaches have been successfully used to give inequivalent spin densities at ortho and meta aromatic positions i.e. the  $\alpha$  effect and  $\beta$  effect.<sup>154,122</sup> The former considers a repulsion energy, the latter an imaginary bond, between ortho and ethylenic protons. Reasonable success has been achieved by both methods although Johnson and Chang<sup>138</sup> favour the  $\beta$  effect from a comparison of net charges on the alpha carbon atoms in terephthaldehyde and stilbene. For the present work on styrenes use has been made of the easily manipulable  $\alpha$  effect by giving one ortho aromatic

carbon atom a Coulomb integral of 0.17; other workers<sup>139,154</sup> have used a value of 0.15 - 0.20 with success. The parameters  $h$ ,  $k$  and  $\lambda$  for styrene were altered until the two ortho/para ratios of theoretical spin densities agreed with the same ratios of experimental coupling constants in a similar manner to that used for benzoic acid (Chapter IV). The following parameters



produced ratios of 0.694 and 0.364 (from McLachlan  $\rho$  values) identical to the experimental ratios. The McConnell  $Q_{\text{CH}}^{\text{H}}$  value relating coupling constants to theoretical spin densities was obtained from positions of high spin density (rather than including the less reliable meta positions) yielding the value of 26.9 Oe. Consideration of several styrenes gave a  $Q_{\text{CH}_2}^{\text{H}}$  value of 20 Oe.

The values of  $h$ ,  $k$ ,  $\lambda$  and  $Q$  determined above were used to assign coupling constants to various substituted styrenes with additional methyl, fluorine and carboxyl parameters as in previous chapters. For vinylpyridines the values  $h_{\text{N}} = 0.8$  and  $k_{\text{CN}} = 1.1$  were used (Chapter II).

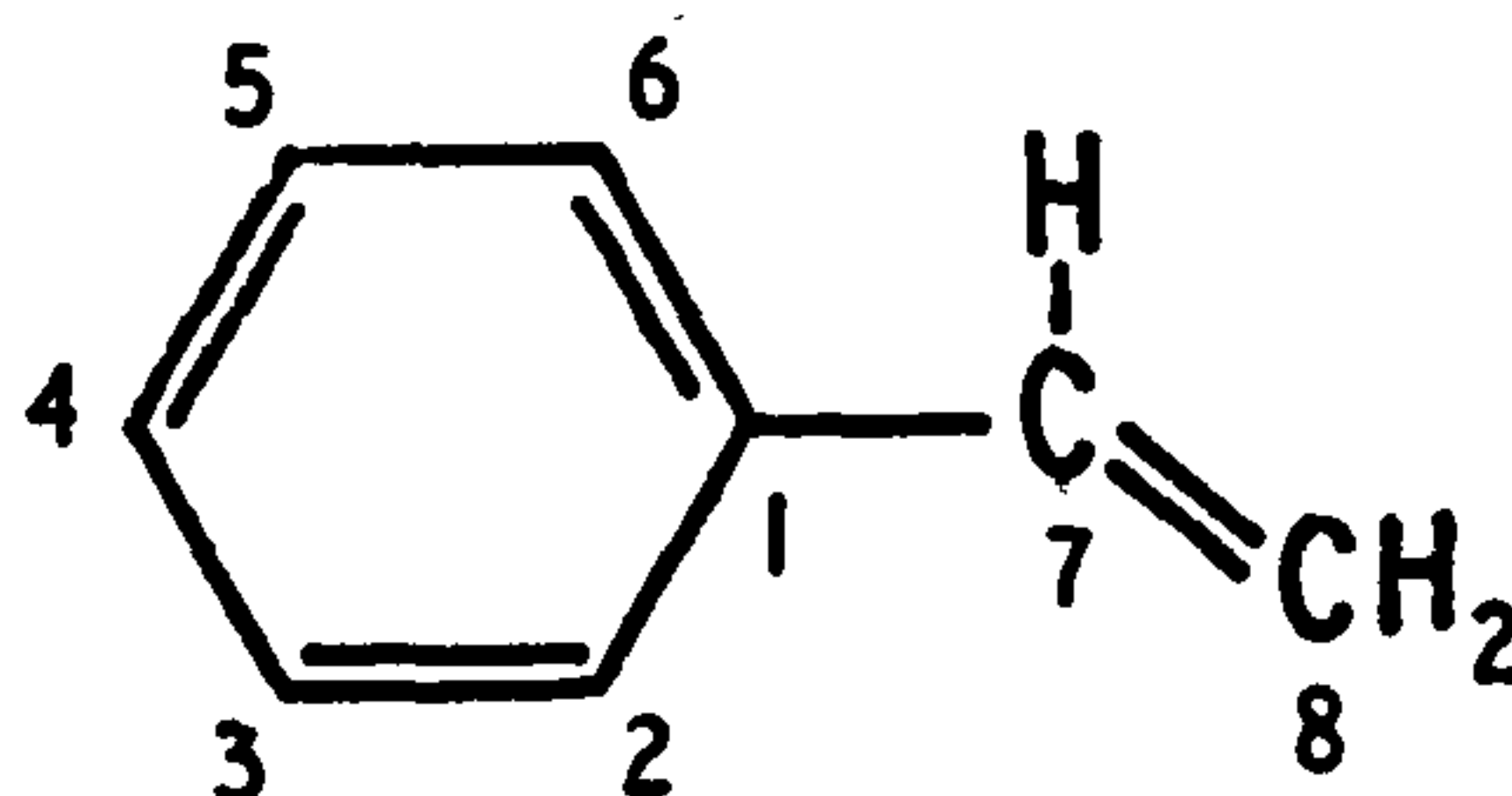
For ortho-fluorostyrene a choice arises as to whether fluorine is in the 2- or 6- position and M.O. calculations favour the 2- position. Similarly meta-fluorine is placed in the 3- position while ortho and meta methyl groups are placed in 6- and 5- positions respectively.



TABLE I

Coupling Constants and Theoretical Spin Densitiesfor Styrenes

Ring positions are numbered as in the following diagram;



Substrate	Position	Experimental		Calculated	
		Coupling constants (Oe)	Spin densities	Hückel	McLachlan
Styrene	2	3.82	0.142	0.134	0.142
	3	0.87	0.032	0.008	-0.024
	4	5.51	0.205	0.182	0.204
	5	0.59	0.022	0.042	0.020
	6	2.00	0.074	0.082	0.074
	7	1.51	0.056	0.085	0.044
	8	7.35	0.367	0.307	0.368
$\alpha$ -methyl-styrene	2	3.44	0.128	0.138	0.146
	3	0.29	0.011	0.008	-0.024
	4	5.07	0.188	0.188	0.213
	5	0.65	0.024	0.045	0.024
	6	2.15	0.080	0.081	0.074
	7	1.31 <sup>a</sup>	0.047	0.080	0.045
	8	6.65	0.333	0.278	0.334
<u>o</u> -methyl-styrene	2	3.77	0.140	0.157	0.171
	3	0.37	0.014	0.002	-0.032
	4	4.92	0.183	0.181	0.203
	5	0.89	0.033	0.065	0.049
	6	1.48 <sup>a</sup>	0.053	0.062	0.049
	7	2.60	0.097	0.034	0.046
	8	7.68	0.384	0.292	0.350

....continued

TABLE I (continued)

Substrate	Position	Experimental		Calculated	
		Coupling constants (Oe)	Spin densities	Spin densities	
				Hückel	McLachlan
<u>m</u> -methyl- styrene	2	3.98	0.148	0.145	0.156
	3	0.64	0.024	0.006	-0.024
	4	5.49	0.204	0.176	0.197
	5	0.86 <sup>a</sup>	0.031	0.045	0.026
	6	2.17	0.081	0.075	0.065
	7	1.52	0.056	0.085	0.044
	8	7.35	0.368	0.307	0.368
<u>o</u> -fluoro- styrene	2	5.89 <sup>b</sup>	0.118	0.116	0.119
	3	0.38	0.014	0.018	-0.011
	4	4.57 <sup>c</sup>	0.170	0.188	0.213
	5	0.94	0.035	0.029	0.004
	6	1.84	0.068	0.099	0.097
	7	0.94	0.035	0.087	0.048
	8	7.51	0.376	0.301	0.360
<u>m</u> -fluoro- styrene	2	3.98	0.148	0.142	0.152
	3	1.22 <sup>b</sup>	0.024	0.006	-0.034
	4	5.23	0.194	0.173	0.200
	5	1.00	0.037	0.044	0.024
	6	2.43	0.090	0.077	0.068
	7	1.53	0.057	0.085	0.044
	8	7.66	0.383	0.307	0.368
<u>p</u> -fluoro- styrene	2	5.29	0.197	0.142	0.153
	3	0.49	0.018	0.004	-0.029
	4	11.17 <sup>b</sup>	0.223	0.176	0.196
	5	1.26	0.047	0.035	0.014
	6	2.53	0.094	0.082	0.076
	7	1.41	0.052	0.089	0.050
	8	8.53	0.426	0.304	0.365

....continued

TABLE I (continued)

Substrate	Position	Experimental		Calculated	
		Coupling	Spin	Spin densities	
		constants	densities	Hückel	McLachlan
		(Oe)			
p-fluoro- <u>α</u> -methyl- styrene	2	4.50	0.167	0.145	0.158
	3	<0.4	0	0.004	-0.029
	4	13.34 <sup>b</sup>	0.267	0.181	0.204
	5	1.09	0.041	0.039	0.917
	6	1.80	0.067	0.081	0.075
	7	1.70 <sup>a</sup>	0.061	0.084	0.050
	8	6.34	0.317	0.275	0.330
4-vinyl- pyridine	2	2.49	0.092	0.097	0.086
	3	0.47	0.017	0.042	0.028
	4	3.95 <sup>c</sup>	0.138	0.153	0.159
	5	2.12	0.079	0.082	0.076
	6	1.02	0.038	0.070	0.051
	7	0.32	0.012	0.061	0.015
	8	8.30	0.415	0.302	0.370
2-vinyl- pyridine	1	3.44	0.128	0.073	0.066
	2	<0.4	0	0.048	0.025
	3			0.195	0.217
	4	3.36 <sup>c</sup>	0.118	0.136	0.133
	5	<0.4	0	0.001	-0.026
	6	4.39	0.163	0.148	0.158
	7	0.73	0.027	0.073	0.025
	8	7.72	0.386	0.325	0.397
cinnamic acid	2	3.87	0.144	0.128	0.150
	3	1.18	0.043	0.002	-0.028
	4	4.91	0.183	0.143	0.170
	5	0.81	0.030	0.153	-0.011
	6	3.20	0.119	0.104	0.120
	7	8.08	0.300	0.184	0.193
	8	3.02	0.151	0.176	0.177

<sup>a</sup> methyl proton coupling; <sup>b</sup> fluorine coupling; <sup>c</sup> nitrogen coupling.

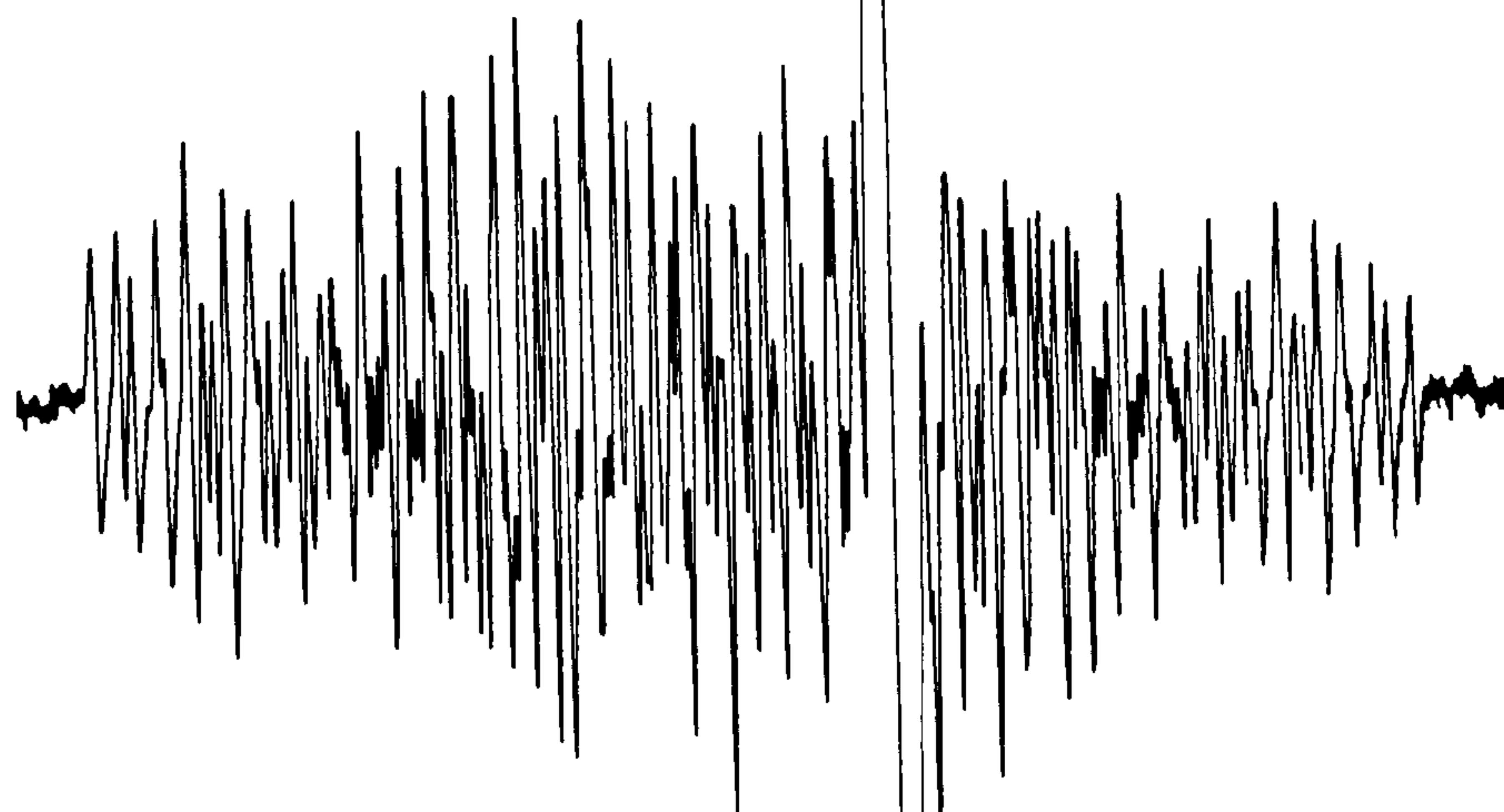
TABLE II

Calculated g-Values for Radical-anions of  
Styrene and Related Compounds

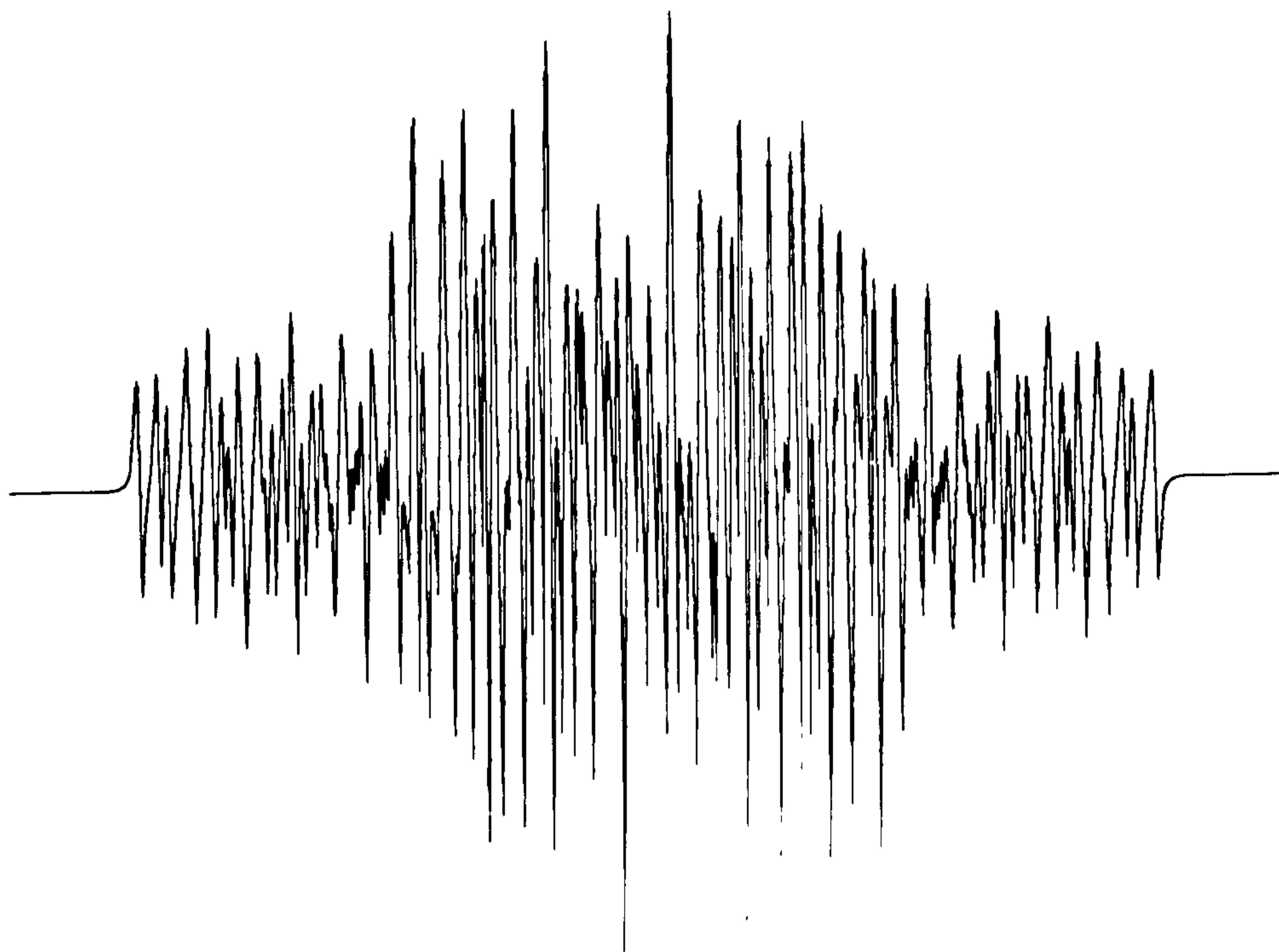
<u>Substrate</u>	<u>g-Value</u>
Styrene	2.0027
$\alpha$ -Methylstyrene	2.0027
<u>o</u> -Methylstyrene	2.0027
<u>m</u> -Methylstyrene	2.0027
<u>o</u> -Fluorostyrene	2.0027
<u>m</u> -Fluorostyrene	2.0027
<u>p</u> -fluorostyrene	2.0029
<u>p</u> -fluoro- $\alpha$ -methylstyrene	2.0029
2-vinylpyridine	2.0029
4-vinylpyridine	2.0030
cinnamic acid	2.0030

**Spectrum of the radical-anion of styrene (upper)  
and the computer simulation (lower).**

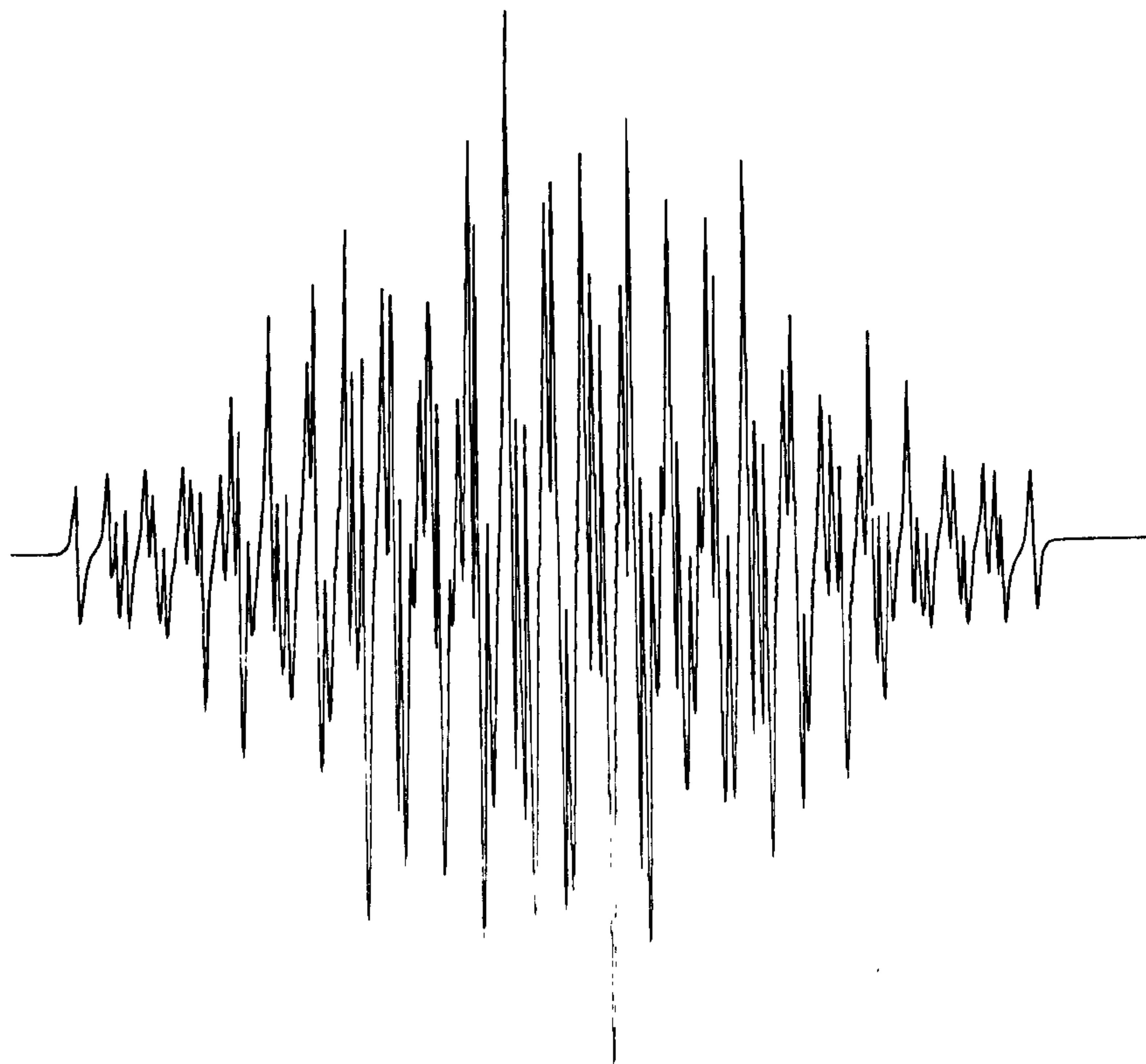
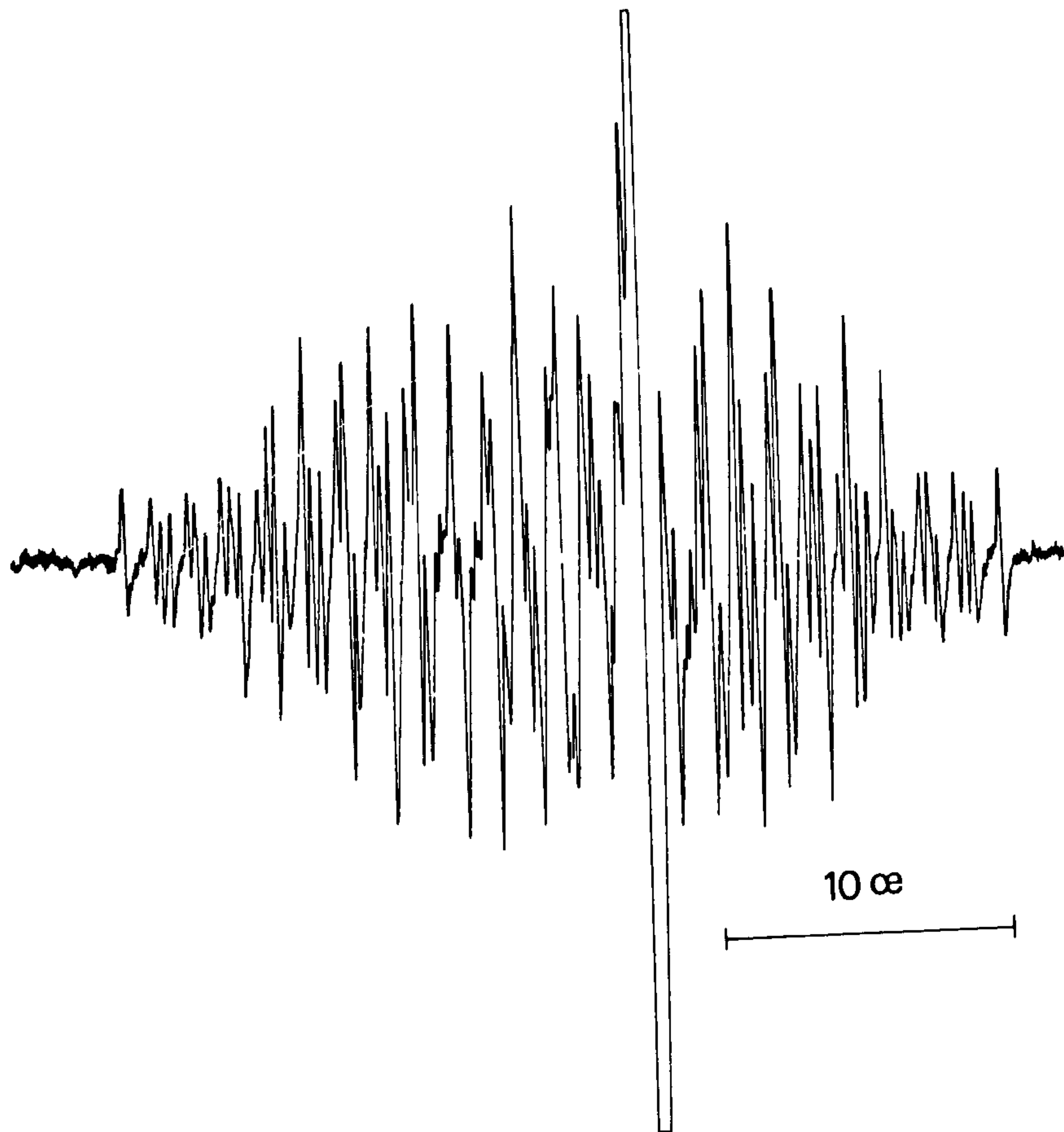




10 Oe

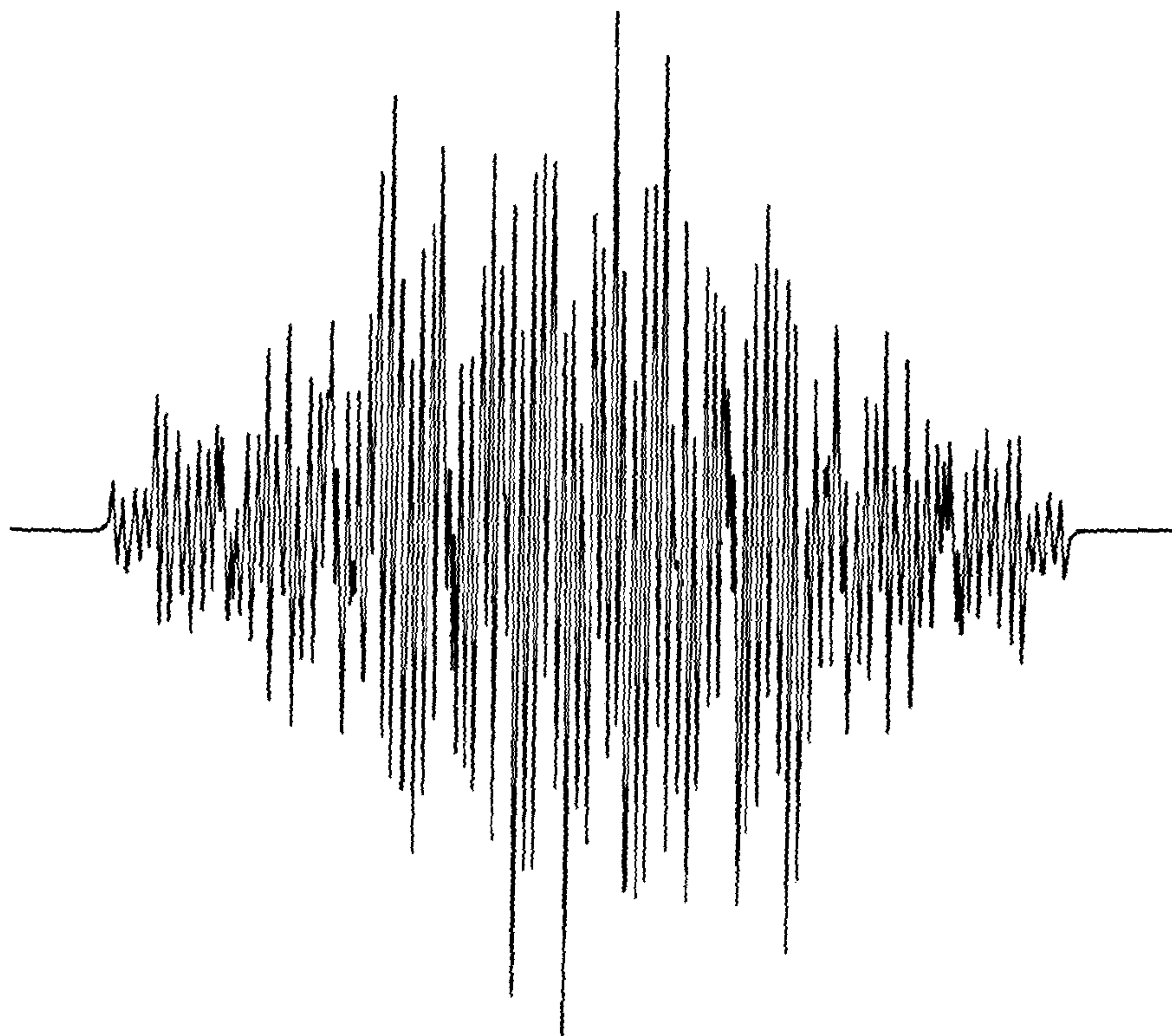
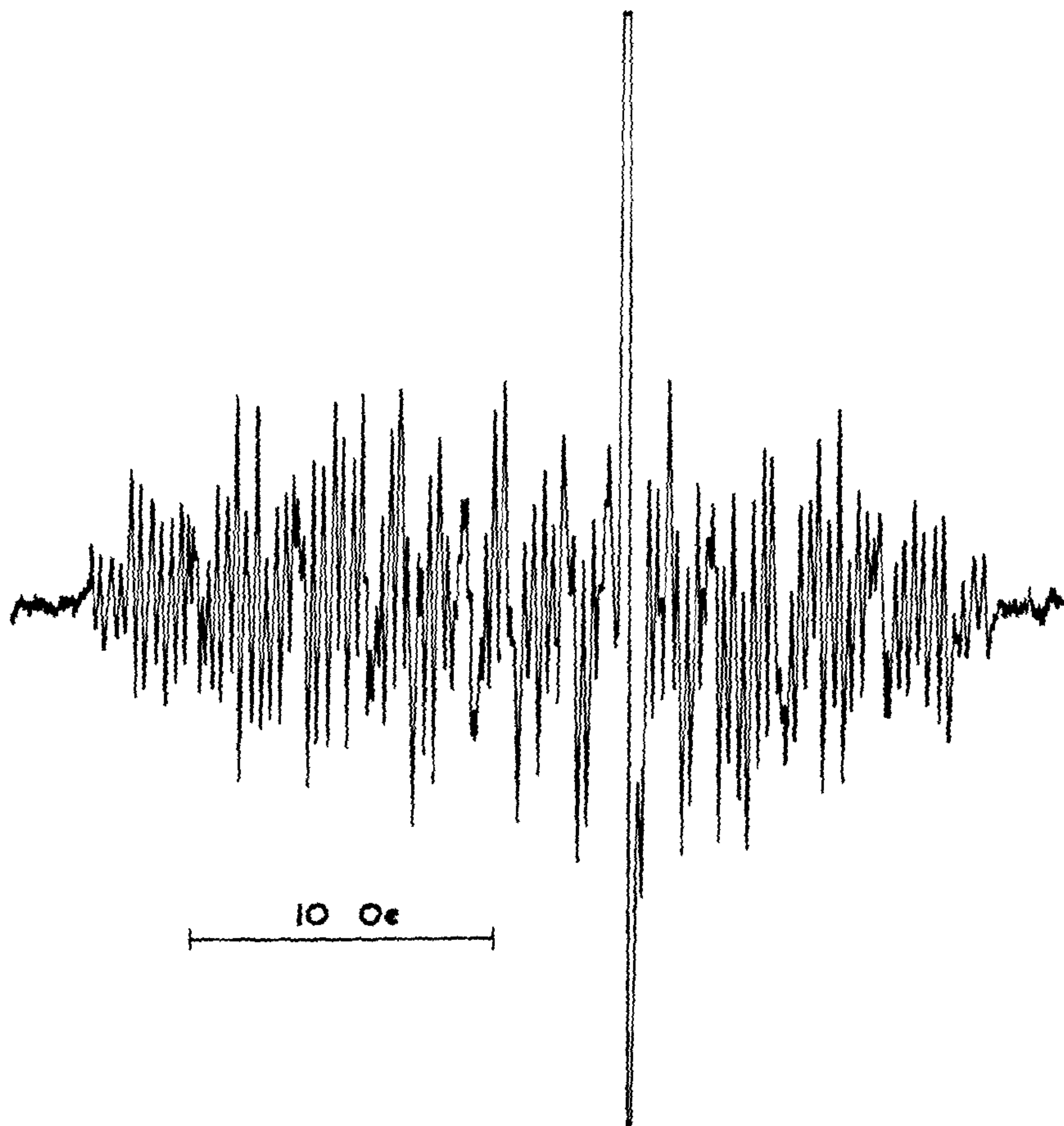


Spectrum of the radical-anion of meta-fluorostyrene (upper)  
and the computer simulation (lower).



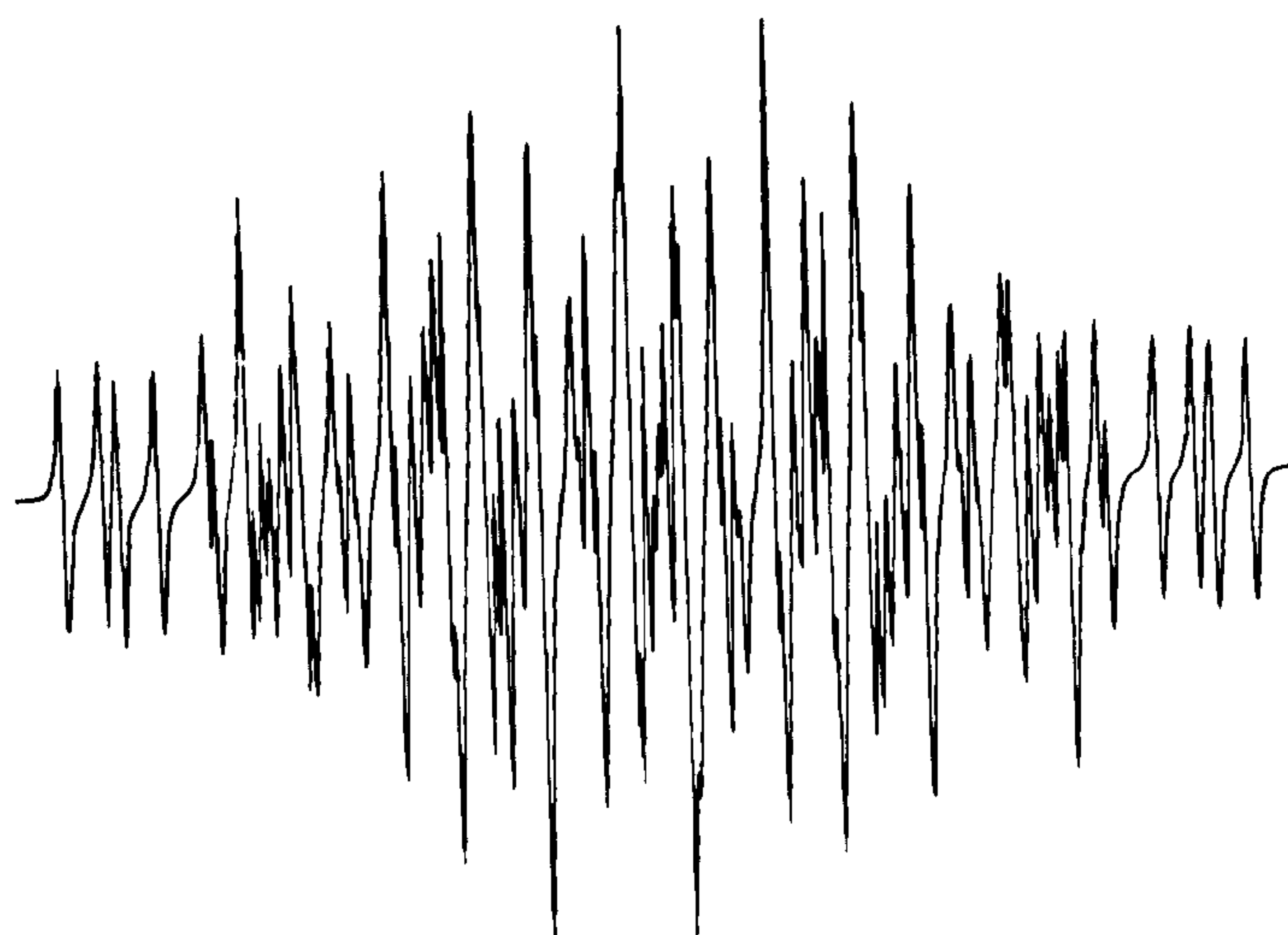
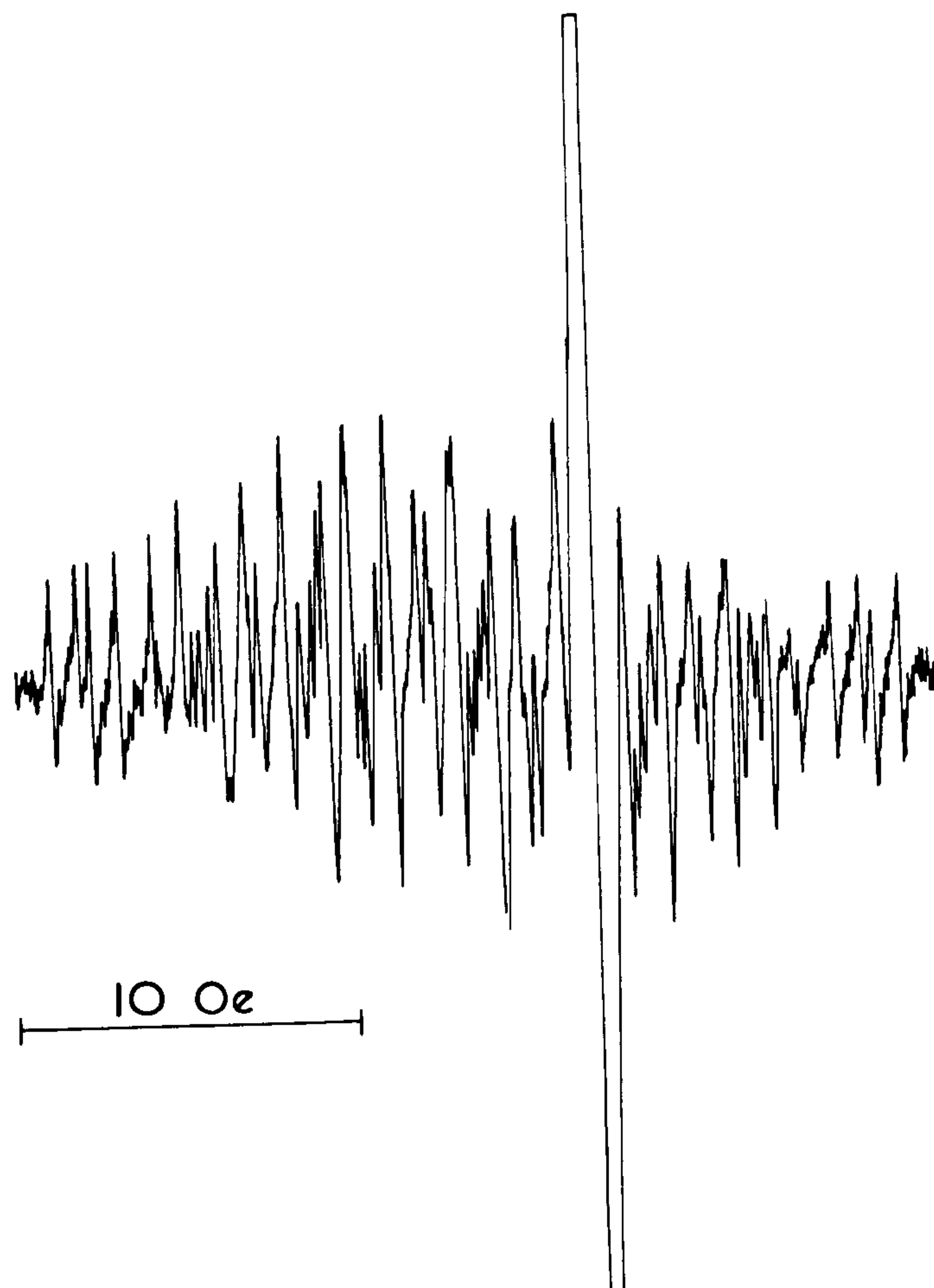


Spectrum of the radical-anion of  $\alpha$ -methylstyrene (upper)  
and the computer simulation (lower).

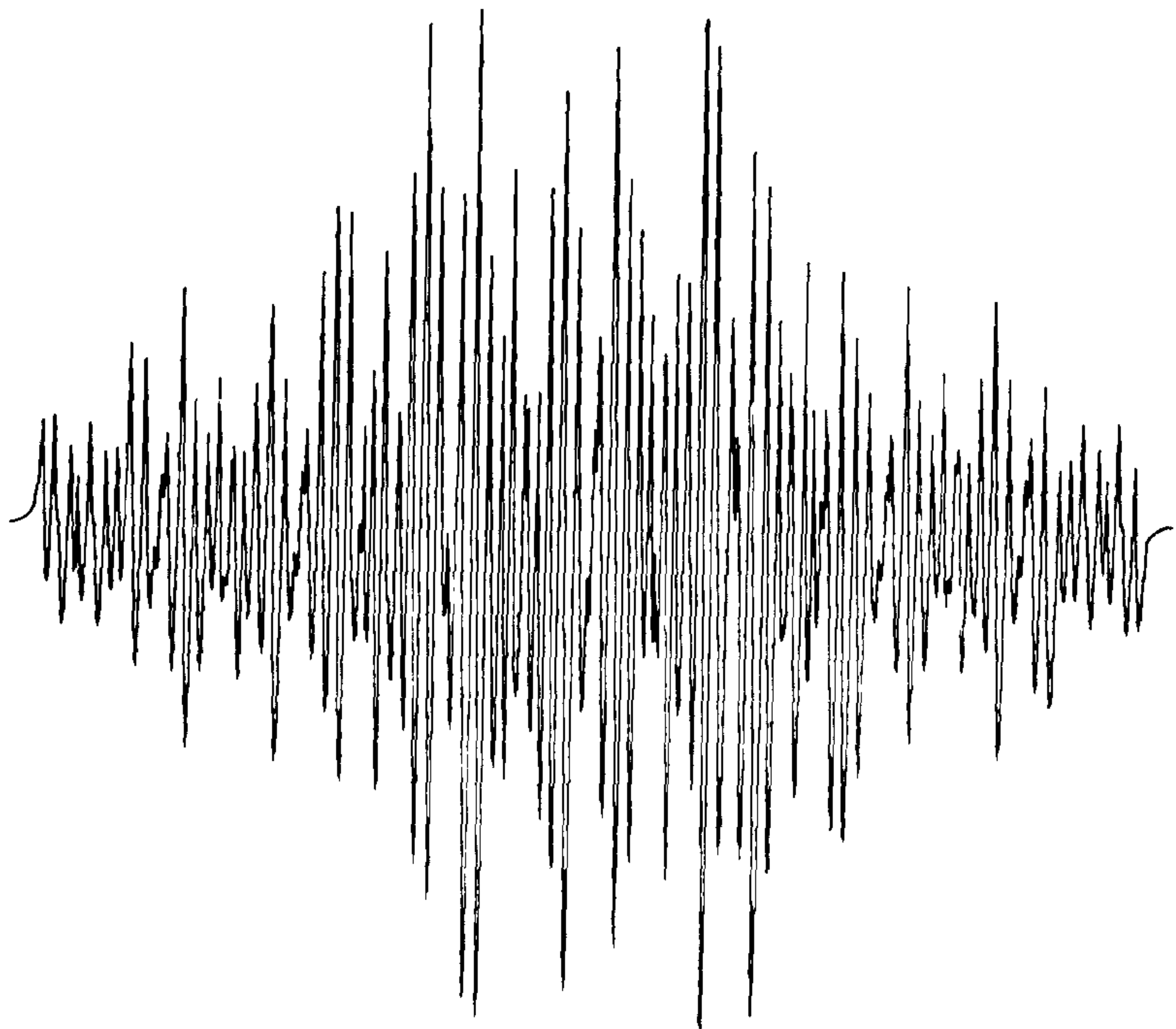
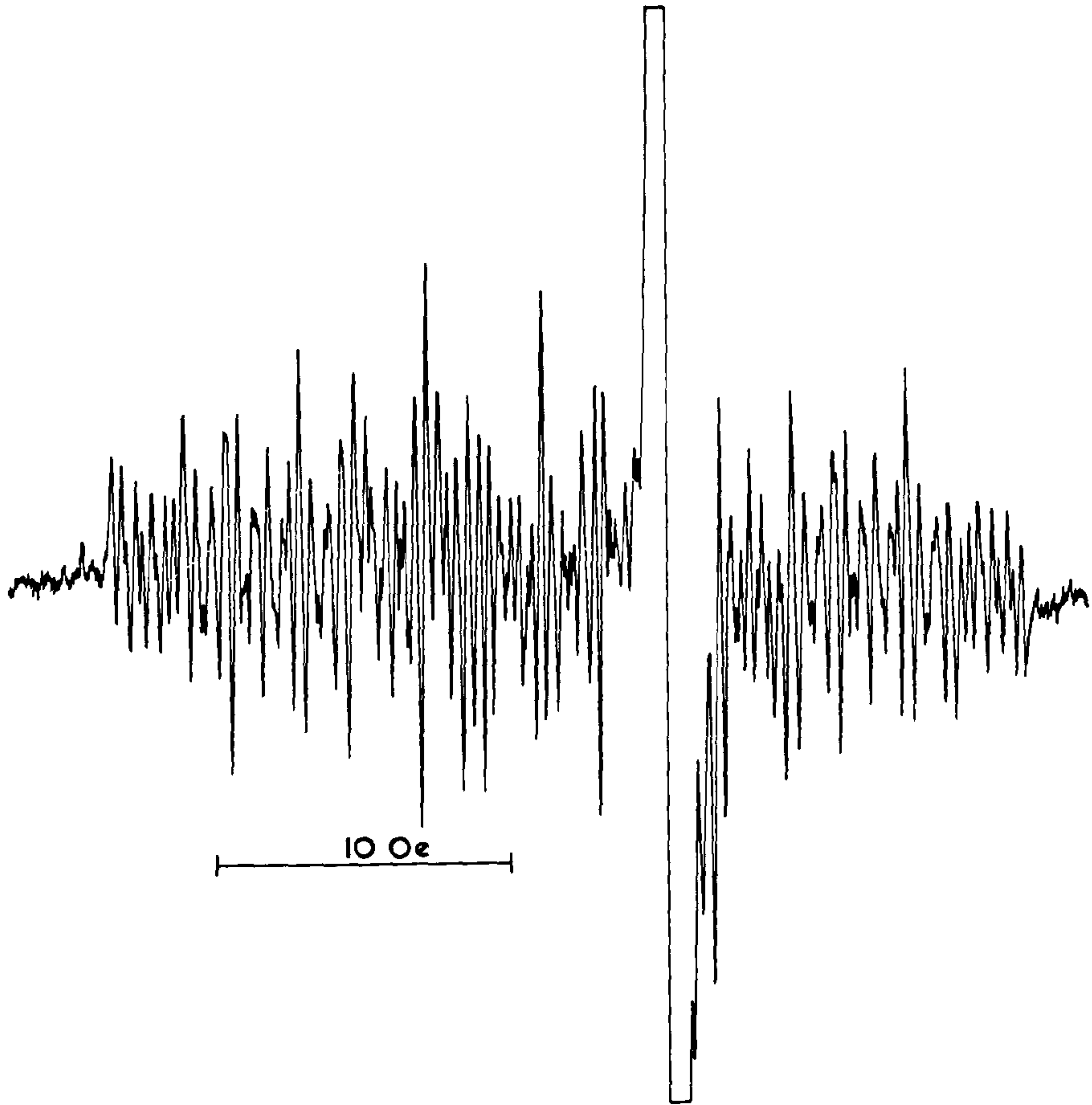




**Spectrum of the radical-anion of cinnamic acid (upper)  
and the computer simulation (lower).**



**Spectrum of the radical-anion of 4-vinylpyridine (upper)  
and the computer simulation (lower).**

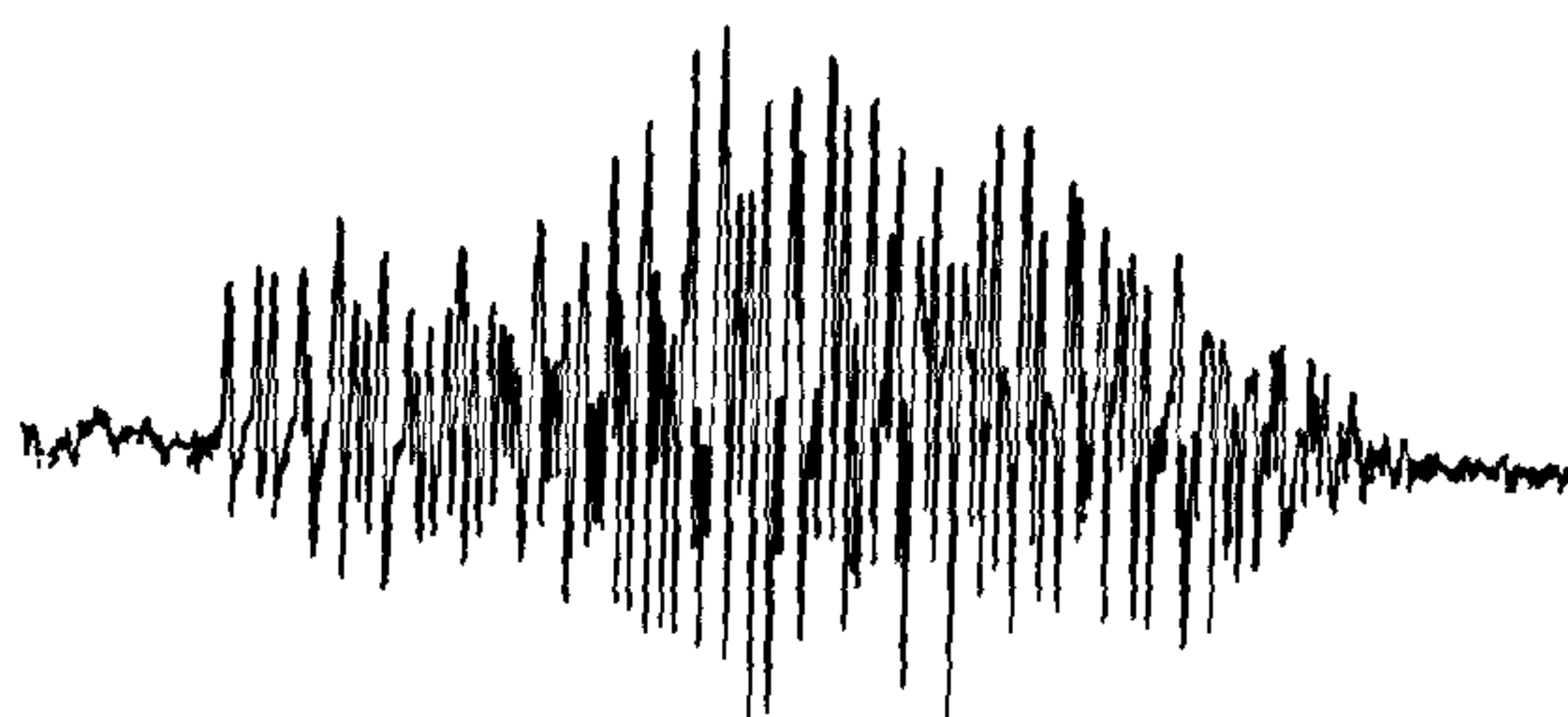
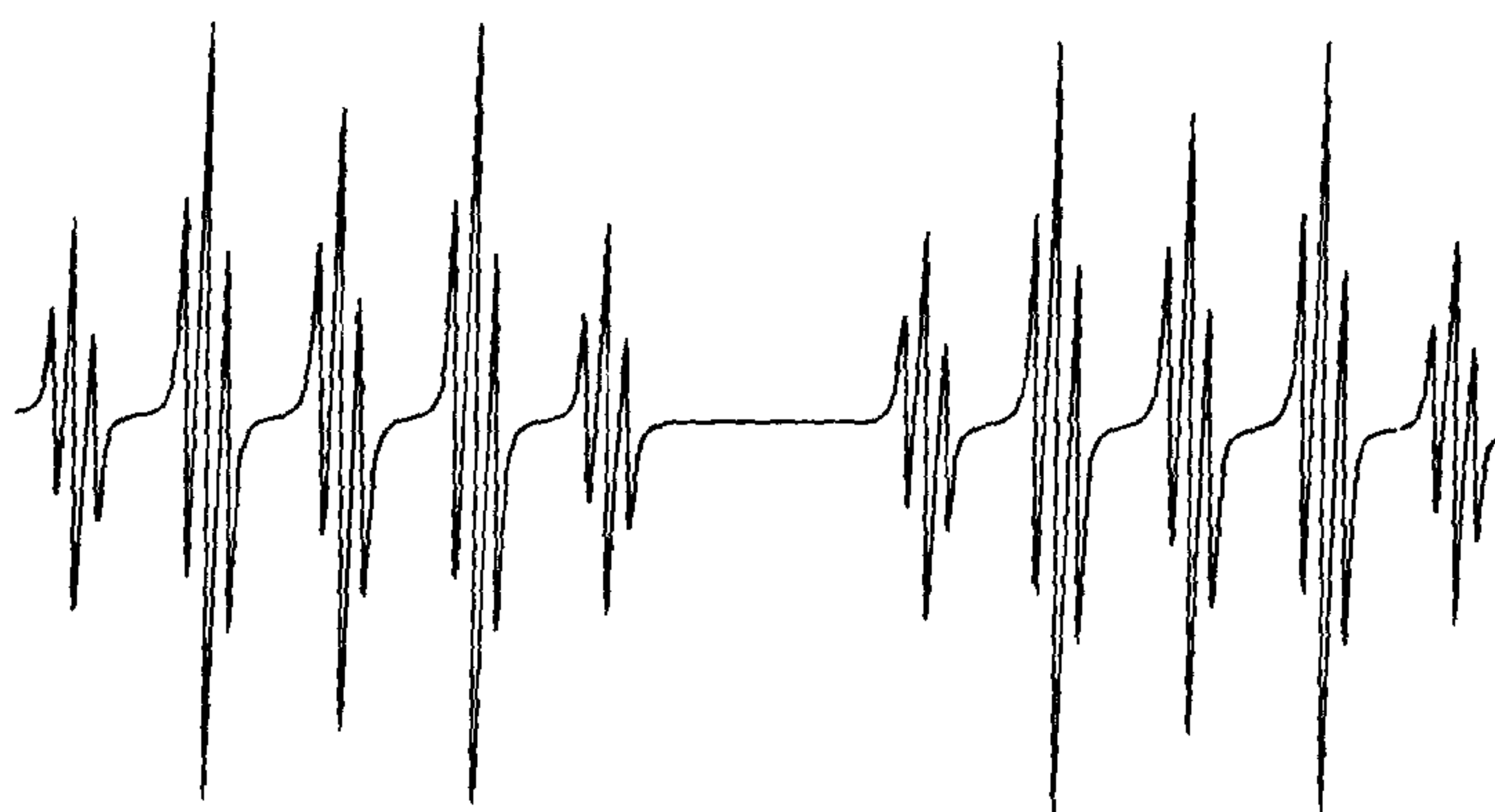
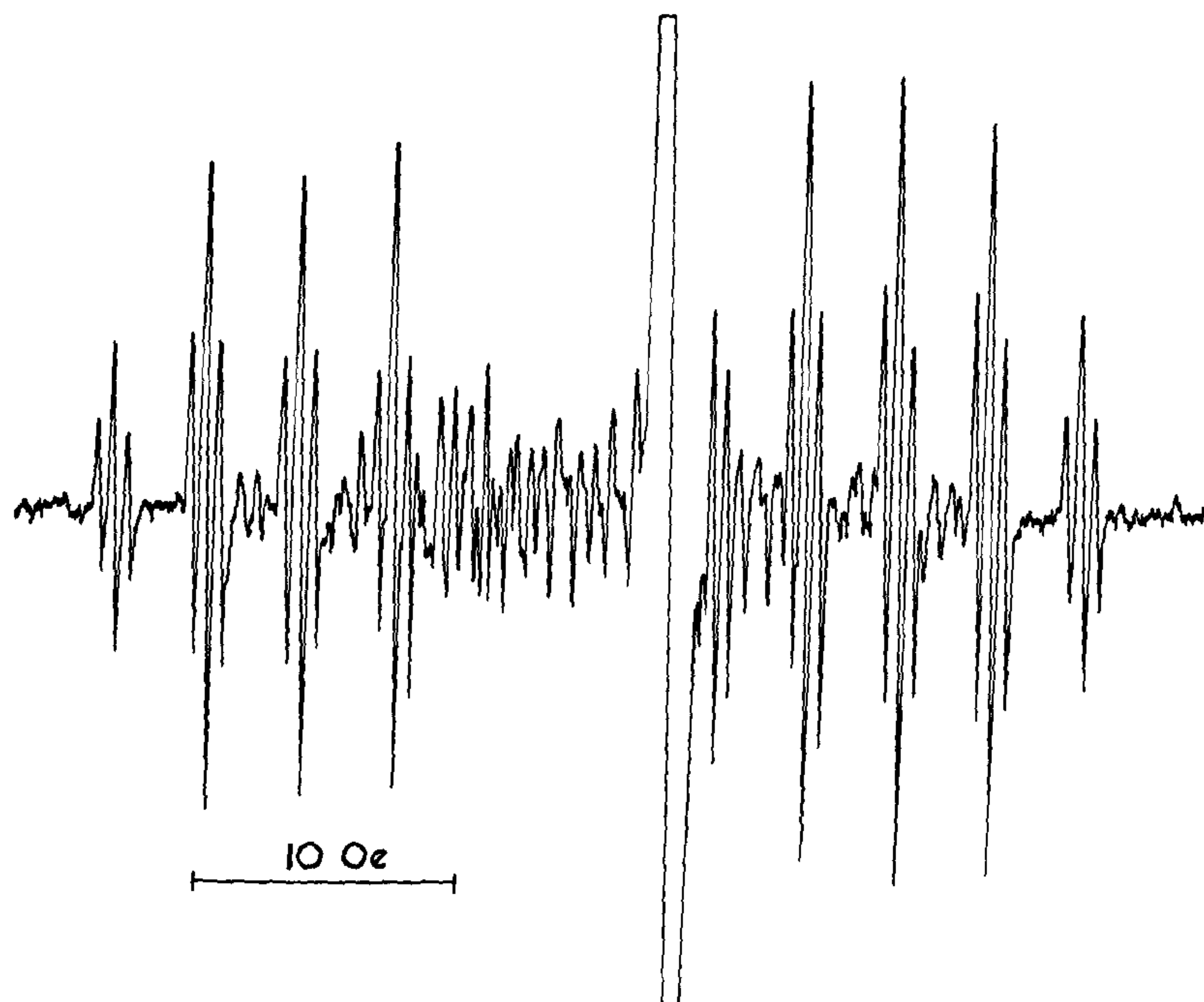


**Upper:** Mixed spectrum obtained from the reduction of phenylacetylene.

**Centre:** Computer simulation of the dominant phenylacetylene radical-anion.

**Lower:** Spectrum obtained from observation 1 sec. after mixing phenylacetylene and  $e_{\text{solv}}^-$ . The coupling constants agree with those for the styrene radical-anion.





REDUCTION OF AROMATIC CARBOXYLIC

ACID AMIDES

AND

$\alpha, \beta$ -UNSATURATED KETONES

## INTRODUCTION

In order to test the scope of the new flow system many compounds were investigated; a substantial number of these produced either poor spectra (e.g. anisonitrile) or no spectra at all (e.g. cyclopentadiene), but well-resolved spectra were obtained from two or three members of at least two groups of compounds. These groups are (a) aromatic carboxylic acid amides and (b)  $\alpha, \beta$ -unsaturated ketones, and because, at the time of writing, only a few spectra from each group have been obtained the discussion which follows is necessarily more superficial than that in previous chapters; indeed in most cases a complete assignment of coupling constants has not been made.

## AROMATIC CARBOXYLIC ACID AMIDES

Reduction of benzamide can take place either at the amide function or at the aromatic ring. Kuehne and Lambert<sup>155</sup> during reduction of benzamide by sodium in liquid ammonia with added ethanol obtained no isolable quantities of dihydro- or tetrahydro- derivatives; reduction of the amide group produced benzylamine. This was unexpected since benzamides behave as monobasic acids in liquid ammonia<sup>156,157</sup> and the formation of the anion should protect the carbonyl group. However, replacement of ethanol by tert. butanol in the reaction gave 1,4-dihydrobenzamide, indicating that the product of reduction depends on the pKa of benzamide in a particular solvent; the easier the formation of the anion the greater the resistance of the amide group to reduction.

E.s.r. spectra of radicals from many imides<sup>158-160</sup> and some substituted amides<sup>83,154</sup> have been recorded. Voss<sup>161</sup> has electrolysed substituted thiobenzamides in acetonitrile but broad lines and poor resolution led to only a few of the many coupling constants for each molecule being determined, while thiobenzamide itself and other simple thiobenzamides gave no spectra. Broad lines for the e.s.r. spectrum of para-nitrobenzamide radical-anion were explained<sup>83</sup> by unresolved amide group coupling, while Fraenkel<sup>154</sup> noticed 'peculiar line shapes' for the spectrum of terephthalamide radical-anion which on cooling produced many more lines and an unanalysable spectrum assumed to be due to the presence of two isomers. Proton nuclear magnetic resonance evidence has been used to indicate slow rotation about the carbonyl-to-phenyl bond in many ortho-<sup>162-165</sup> and one meta-substituted<sup>166</sup> benzamides while benzamide itself in dioxane has been shown<sup>167</sup> to have a dihedral angle of 37°.

In an attempt to investigate such steric hindrance effects further some

substituted benzamides and benzamide itself were reduced in the flow system. Five benzamides gave well-resolved analysable spectra and the results are shown in Table I. Two amides (benzoylhydrazine and N,N-dimethylbenzamide) gave poor spectra while thlobenzamide and cinnauamide gave well-resolved spectra which so far have evaded analysis. A related compound, benzoylcyanide, gave a spectrum which has also not yet been analysed, but appears to resemble closely that from benzamide.

Those spectra which were analysed clearly show inequivalent ring protons and while unresolved amide group coupling may have been responsible for some line broadening, as discussed by some authors<sup>154</sup>, restricted rotation might have contributed to some extent. A single amide proton (as expected) is seen for para-fluoro- and para-methylbenzamide, while no amide protons are observed for benzamide, meta-fluorobenzamide and ortho-methylbenzamide, presumably because of the small amount of unpaired spin density on the amide group (as shown by  $A^N$ ) giving a value for  $A^H_{CONH_2}$  too small to be resolved.

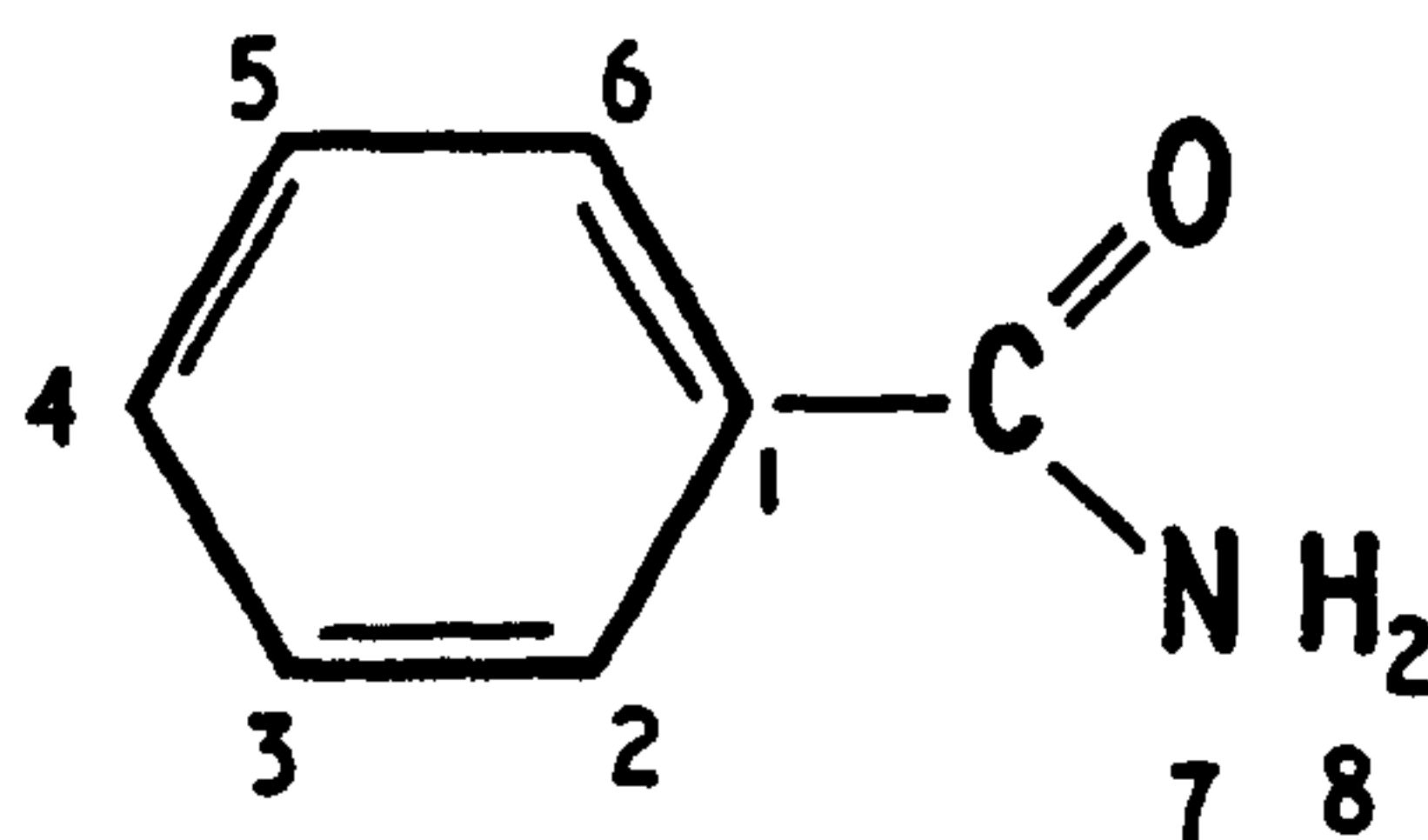
Coupling constants have been assigned by comparison with known substituted benzamides and more definite assignments should be forthcoming on completion of Hückel and McLachlan molecular orbital calculations.



TABLE I

Coupling Constants and g-Values Obtained  
for Radical-anions of Benzanides

Ring positions are numbered as in the following diagram



Substrate	Position	Coupling constants <sup>a</sup> (G)	g-Value
Benzamide	2	3.37	2.0033
	3	0.67	
	4	10.74	
	5	0.89	
	6	3.95	
	7	0.98	
	8	-	
<u>o</u> -Methylbenzamide	2	3.99 <sup>b</sup>	2.0032
	3	1.09	
	4	11.98	
	5	0.44	
	6	3.53	
	7	0.73	
	8	-	
<u>p</u> -Methylbenzamide	2	2.24	2.0031
	3	1.06	
	4	7.94 <sup>b</sup>	
	5	0.87	
	6	4.08	
	7	2.99	
	8	1.06 <sup>c</sup>	

....continued

TABLE I (continued)

Substrate	Position	Coupling constants (Oe)	g-Value
<u>m</u> -Fluorobenzamide	2	5.27	2.0030
	3	2.49 <sup>d</sup>	
	4	8.78	
	5	0.26	
	6	2.96	
	7	0.99	
	8	-	
<u>p</u> -Fluorobenzamide	2	5.36	2.0036
	3	1.11	
	4	17.05 <sup>d</sup>	
	5	1.45	
	6	5.94	
	7	2.10	
	8	1.11 <sup>c</sup>	

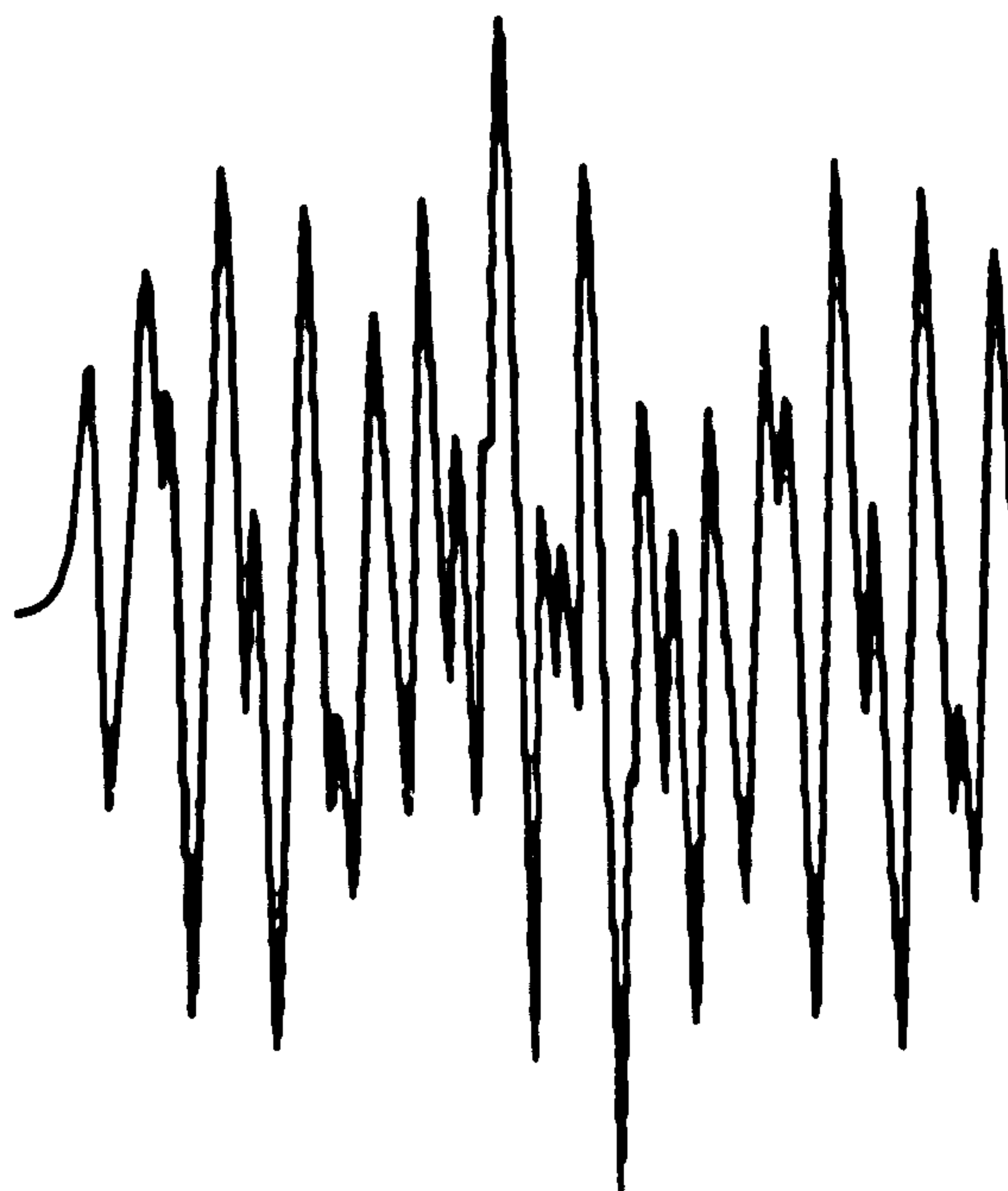
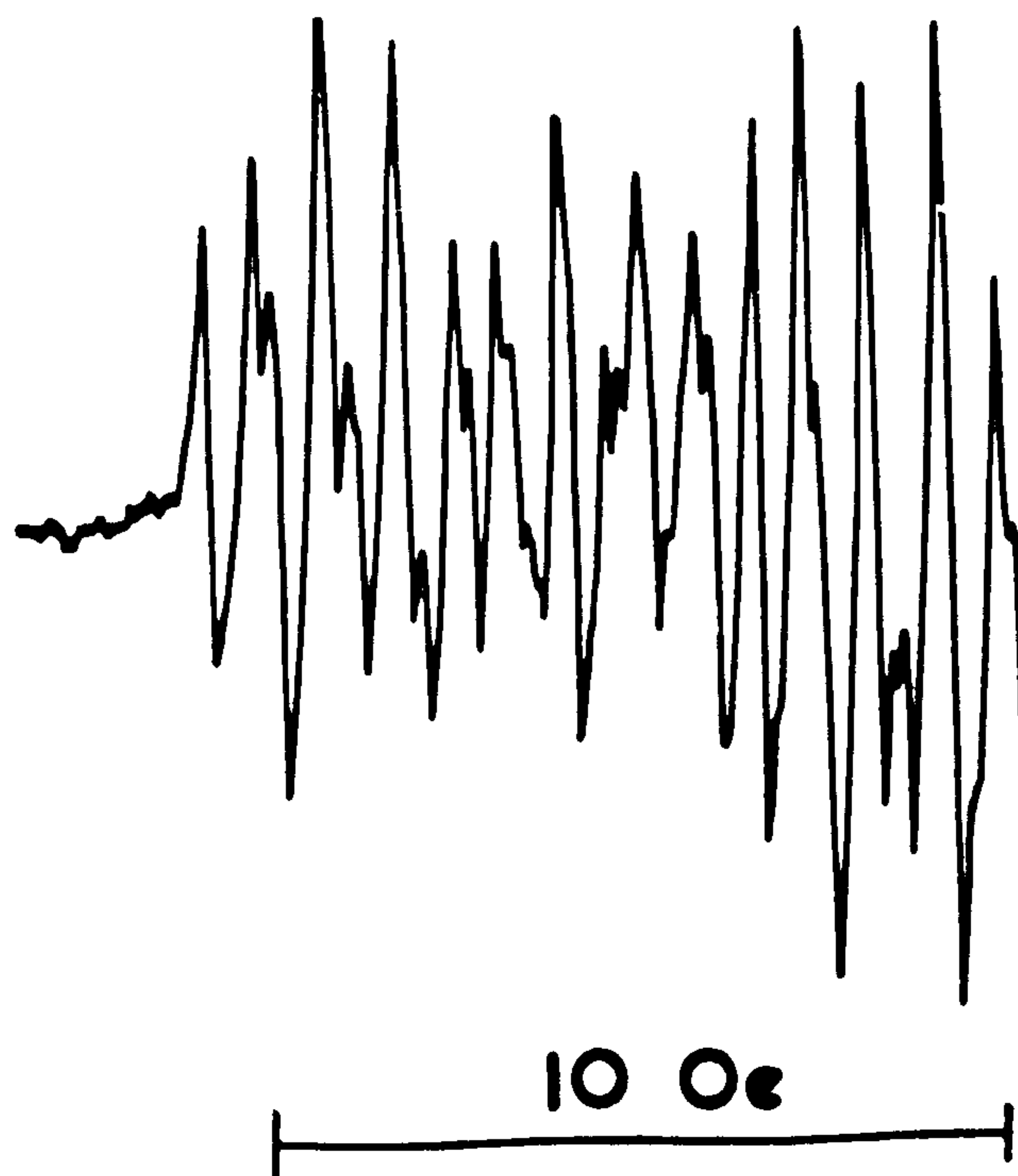
<sup>a</sup> Uncertainty in assignment of some coupling constants.

<sup>b</sup> Methyl proton coupling.

<sup>c</sup> Coupling due to one proton.

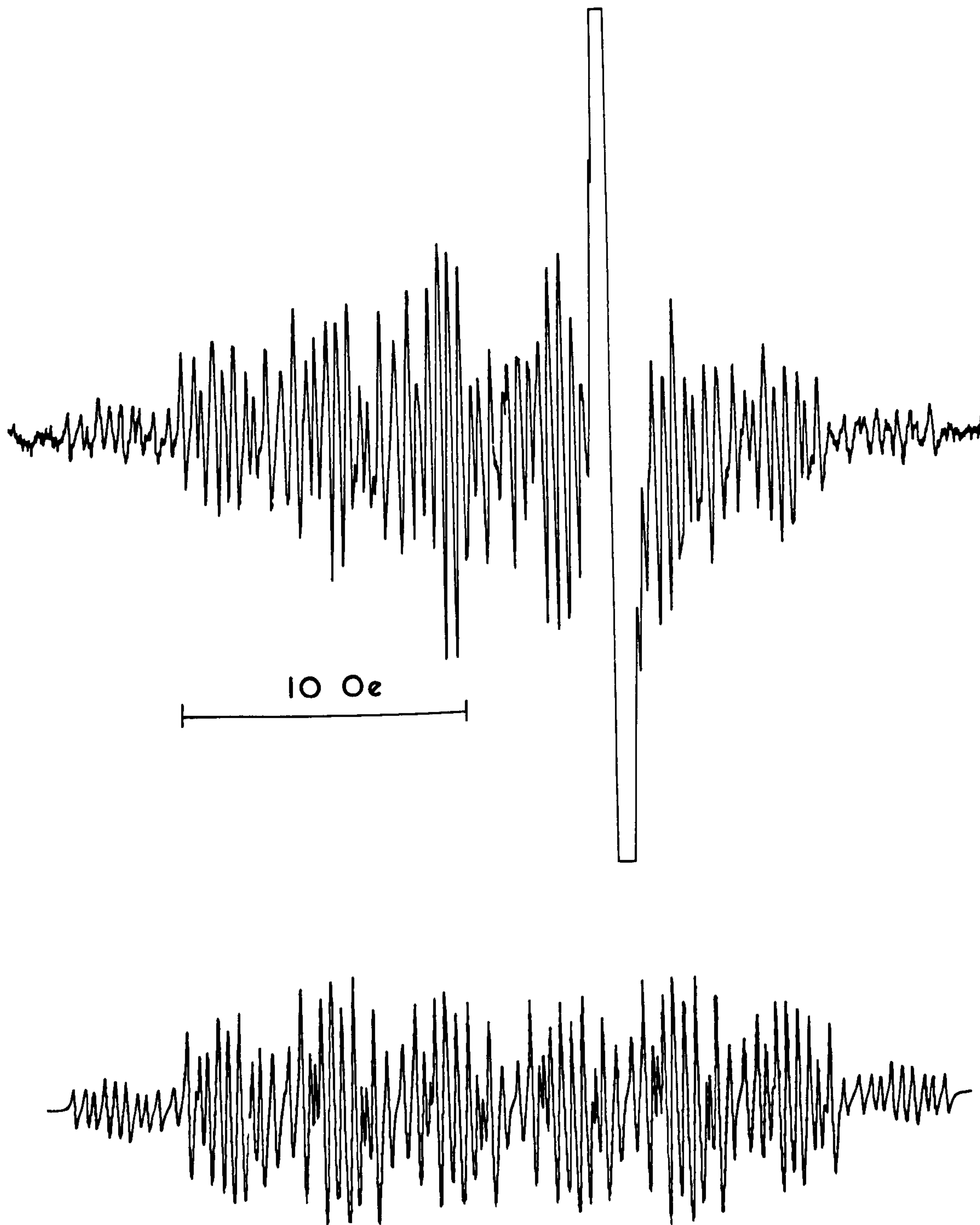
<sup>d</sup> Fluorine coupling.

Half-spectrum of the benzamide radical-anion (upper)  
and the computer simulation (lower).

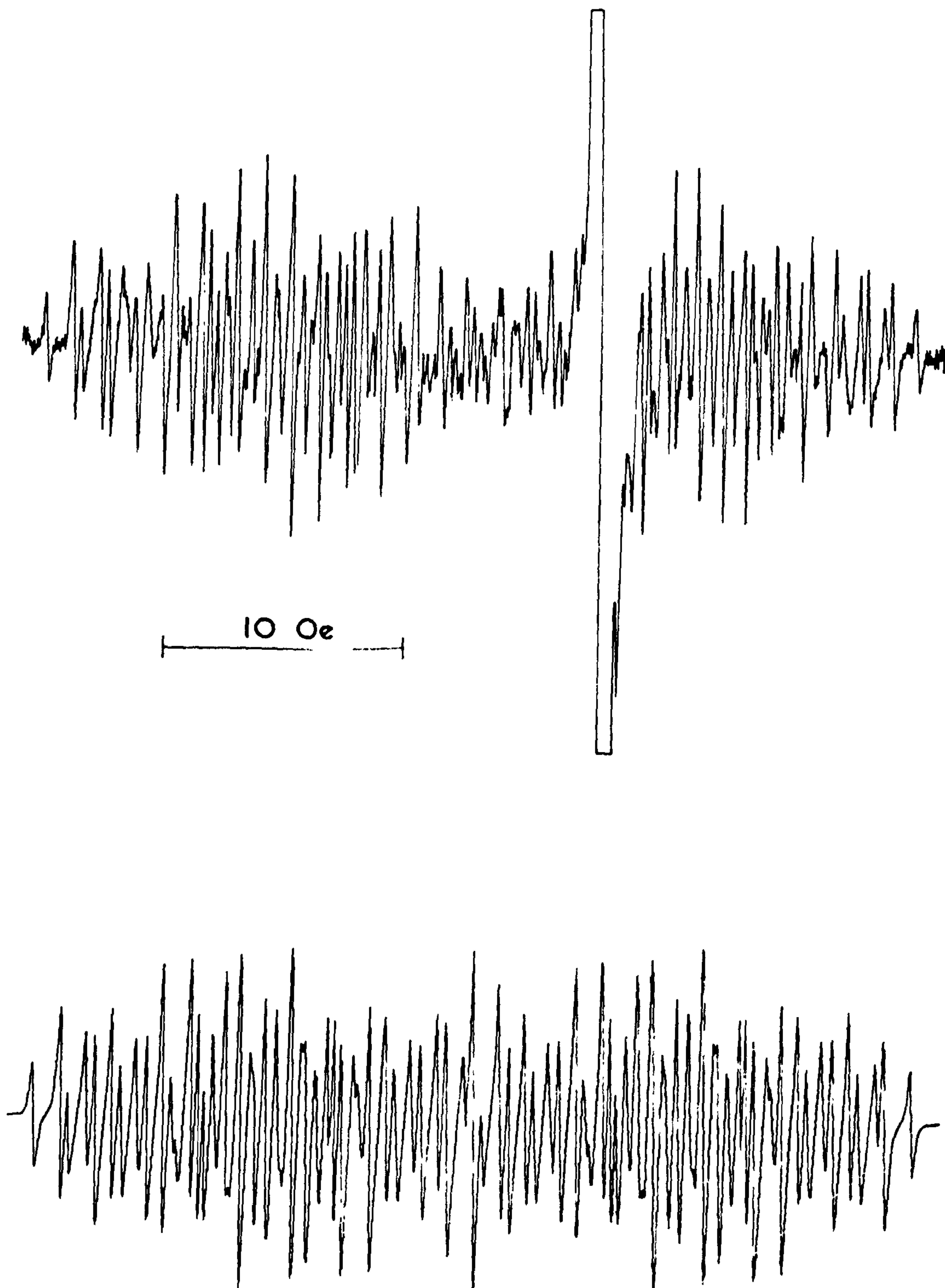


Spectrum of the radical-anion of ortho-methylbenzamide (upper)  
and the computer simulation (lower).



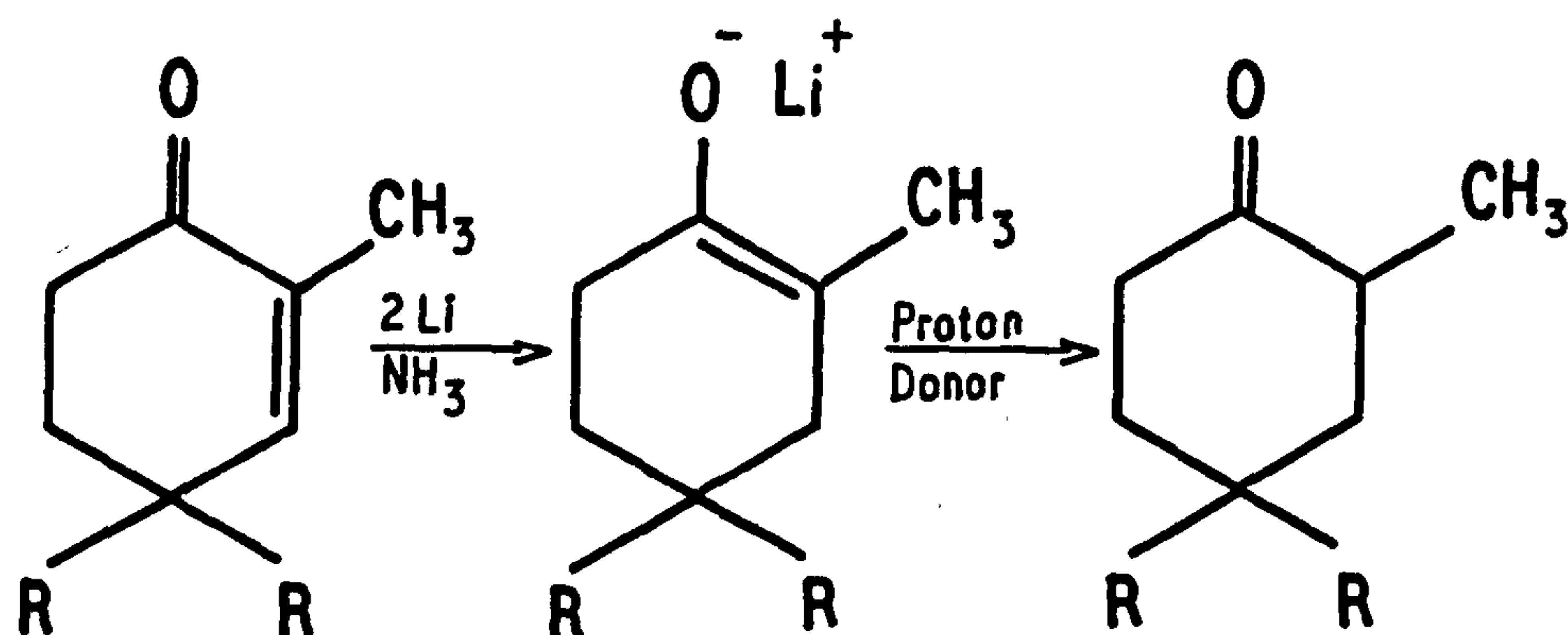


Spectrum of the radical-anion of para-fluorobenzamide (upper)  
and the computer simulation (lower).



## $\alpha, \beta$ -UNSATURATED KETONES

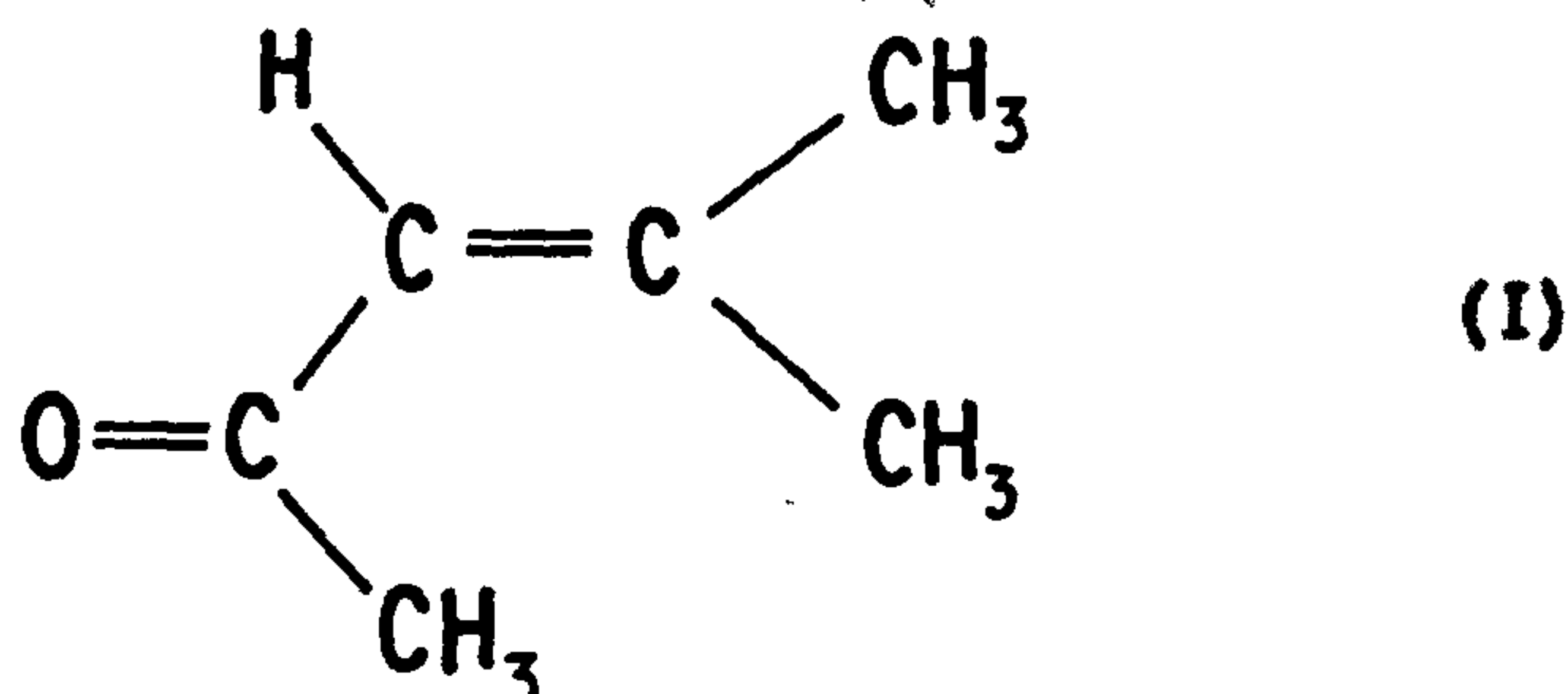
The results obtained from reduction of three ketones i.e. mesityl oxide, 3,5,5-trimethyl-2-cyclohexen-1-one (isophorone) and 2-cyclohexen-1-one are given in Table II. Isophorone, mesityl oxide and other  $\alpha, \beta$ -unsaturated ketones have been reduced by potassium in hexamethylphosphoramide by Angibeaud<sup>168</sup> to give the corresponding saturated ketones and the mechanism is discussed by Smith<sup>169</sup> for the similar reducing medium of lithium in liquid ammonia,



Yields of saturated ketone without added proton donor are lower due to amide side reactions. Depending on the conditions, mesityl oxide can be reduced not only to the saturated ketone but also to products involving reduction of the ketone group.<sup>170</sup> Polymerisation is also known to occur for some  $\alpha, \beta$ -unsaturated ketones, e.g. the polarographic reduction of  $\text{C}_6\text{H}_5\text{CH}=\text{CHCOR}$ <sup>171</sup> and of cyclohexenone.<sup>172</sup> The results for the ketones shown in Table II indicate that spectra observed in the present work are due to the primary radical-anions rather than from further reduction products. Other  $\alpha, \beta$ -unsaturated ketones for which e.s.r. spectra have been obtained hitherto are the tropone radical-anion,<sup>173</sup>

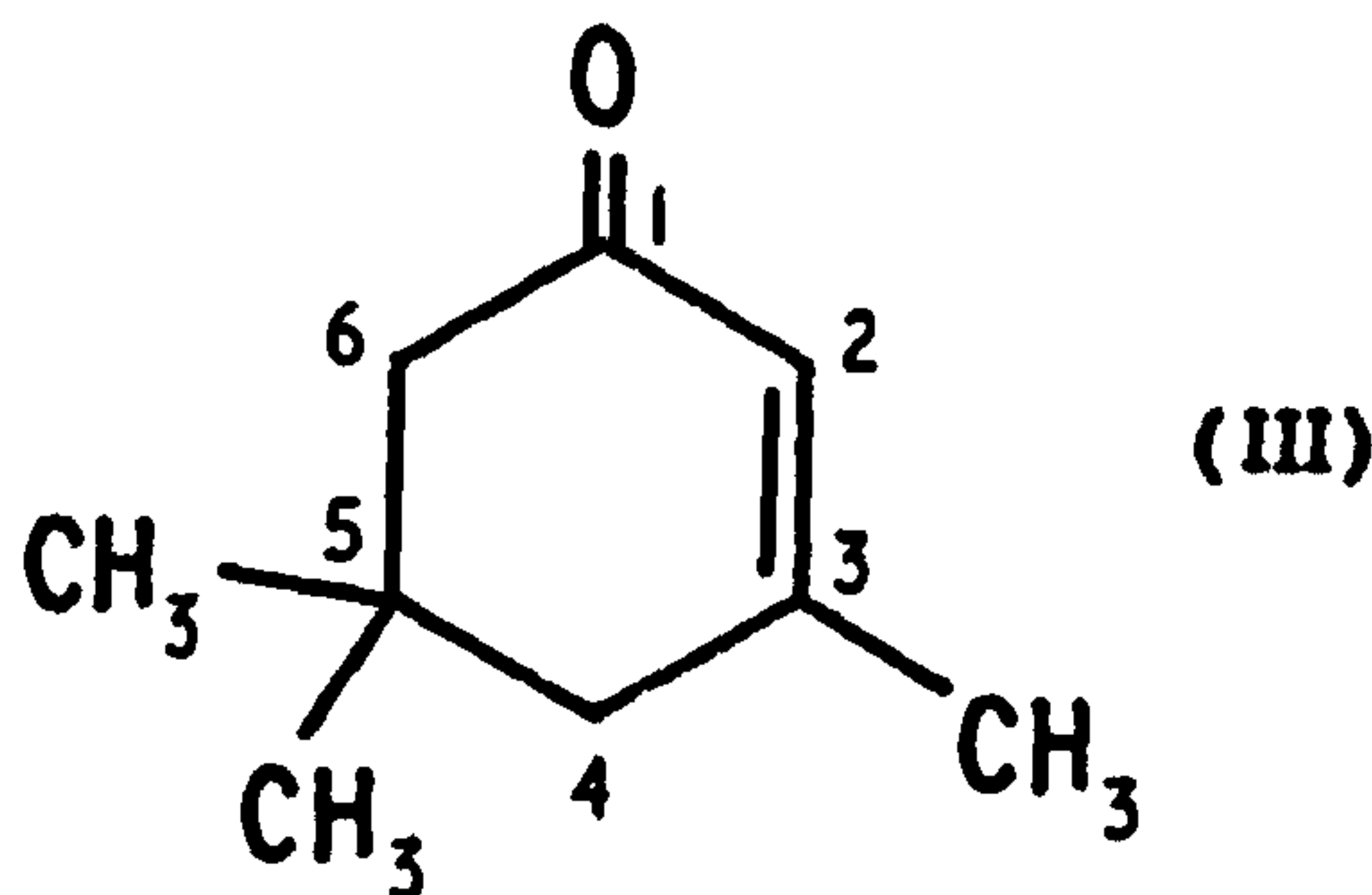
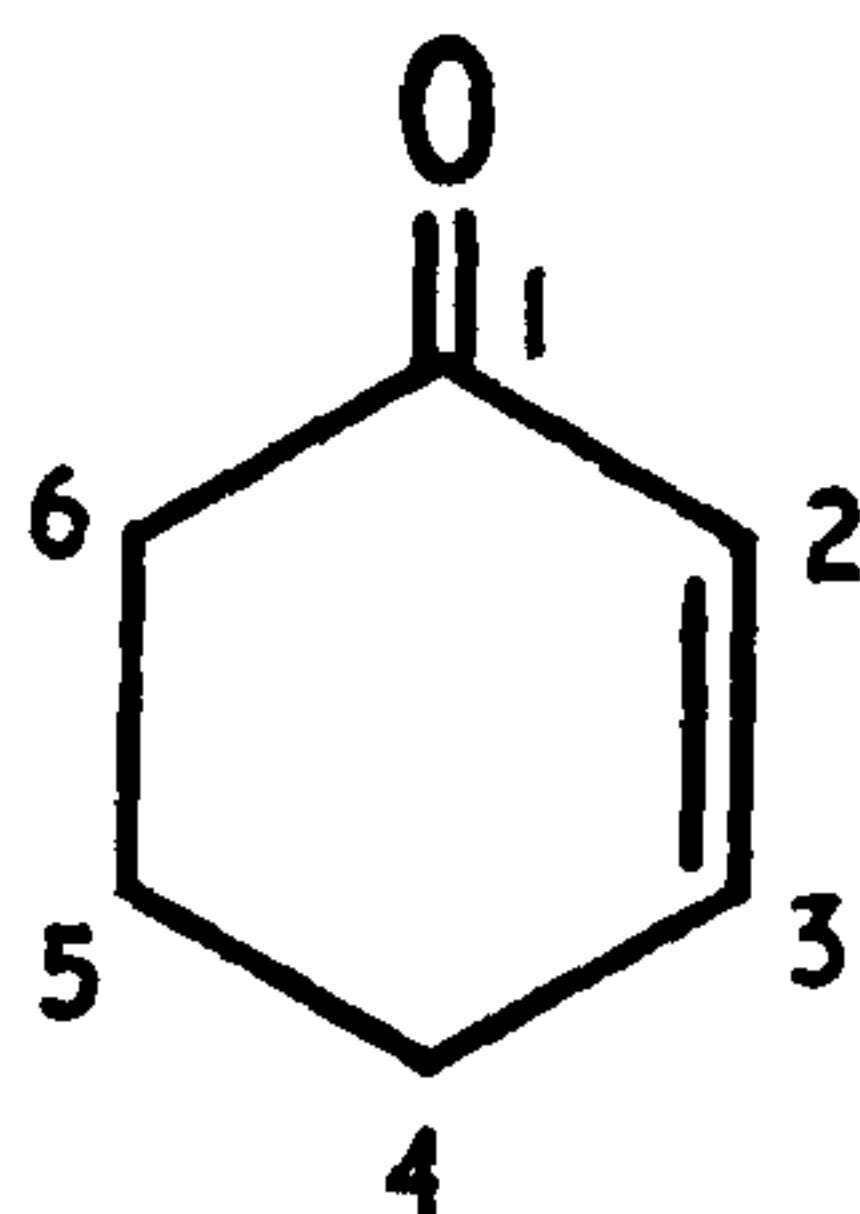
4,4-dimethyl-2-cyclohexen-1-one<sup>174</sup> and, a similar class of compounds, the cyclohexanediones.<sup>175</sup> The second of these, although showing a poorly-resolved spectrum, is helpful in the coupling constant assignment of the present radical-anions.

For mesityl oxide (I)



the assignment appears to be straightforward; six equivalent protons from the two methyl groups on  $\beta$ - carbon, three equivalent protons from the  $\alpha$ -methyl group and one proton attached to  $\alpha$ - carbon.

For 2-cyclohexen-1-one (II) and isophorone (III)

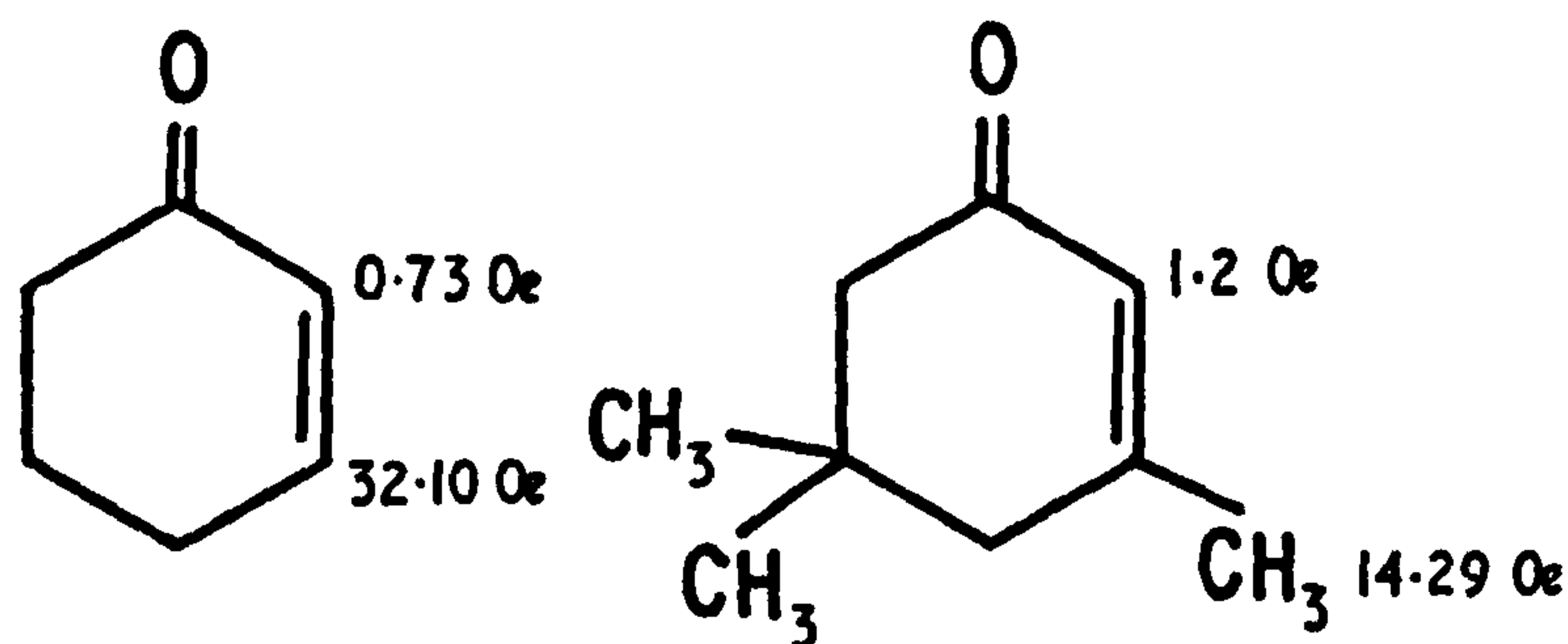


assignment is not so straightforward. From mesityl oxide for which assignment has been made and isophorone, where the  $\beta$ -methyl coupling constant is easily obtained from the e.s.r. spectrum, the  $\beta$ - carbon atom '3' must have a fairly high unpaired spin density. From mesityl oxide and 4,4-dimethyl-2-cyclohexen-1-one (IV)<sup>174</sup>, the  $\alpha$ - carbon '2' must be small and from (I), (IV) (where Hückel M.O. calculations have been



performed) and semidiones<sup>176</sup> the methylene group at position '4' in the cyclohexene structure should be fairly large. To accommodate the remaining coupling constants the structure of the molecules must be considered in the light of conformational analysis. Cyclohexenes,<sup>177</sup> cyclohexanones,<sup>176</sup> and other six membered alicyclic compounds<sup>178</sup> are known to exist in either 'chair' (or 'half-chair' for cyclohexenes) or 'boat' forms which are constantly flipping from one conformer to another. At varying conditions such as temperature and molecular substitution one or other conformation may be preferred, or the barrier to flipping may be small enough to allow fast transformation to take place from one conformer to the other giving effectively equal environments for, e.g., two methylene protons which would be unequal in one conformer. For the substituted cyclohexenones considered above it is obvious that one conformer is preferred and axial and equatorial methylene protons give different coupling constants.

From the discussion so far the following assignments can be made;



with the rest of the coupling constants to be assigned to the 4- and 6-positions.

Reduction of more  $\alpha, \beta$ -unsaturated ketones is at present in progress and exact and complete assignment of coupling constants may be made from further results. Russell<sup>176</sup> has been able to determine conformational lifetimes and ratios of conformers present and these determinations may

also be possible for (II) and (III) by similarly comparing results to the radical-anions of substituted  $\alpha, \beta$ -unsaturated decalones where coupling constants are thought to be due to pure axial and equatorial bonds.

TABLE II

Coupling Constants and g-Values Obtained forRadical-anions of  $\alpha,\beta$ -Unsaturated Ketones

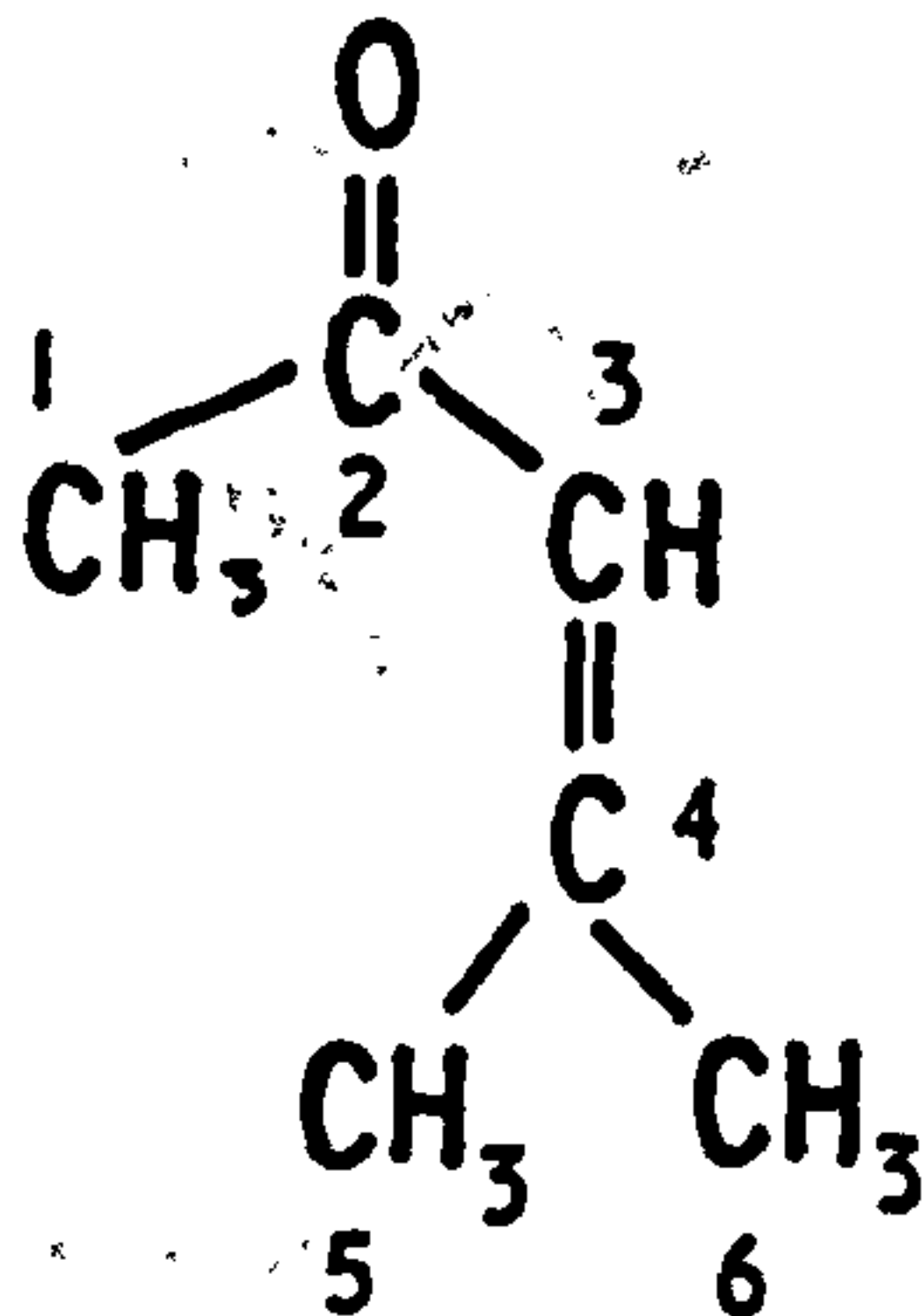
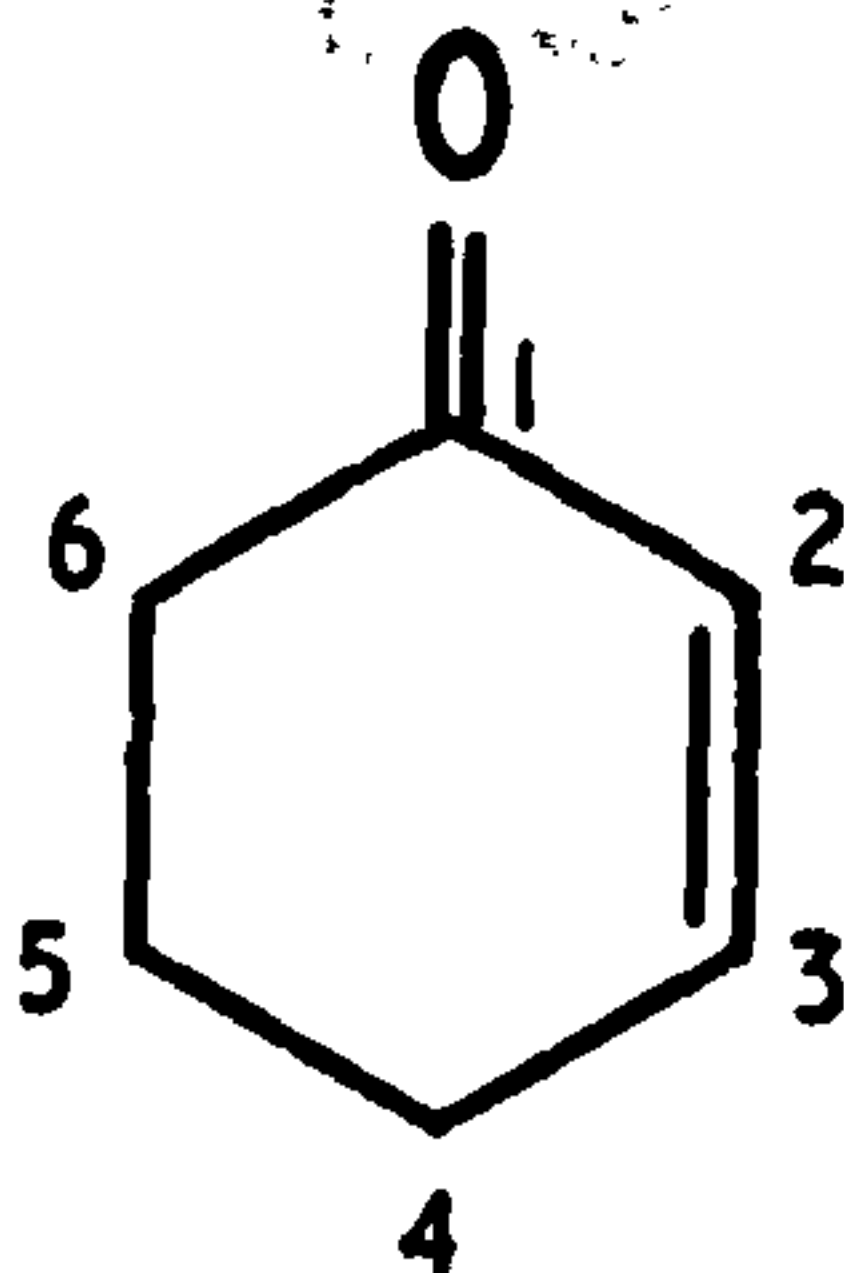
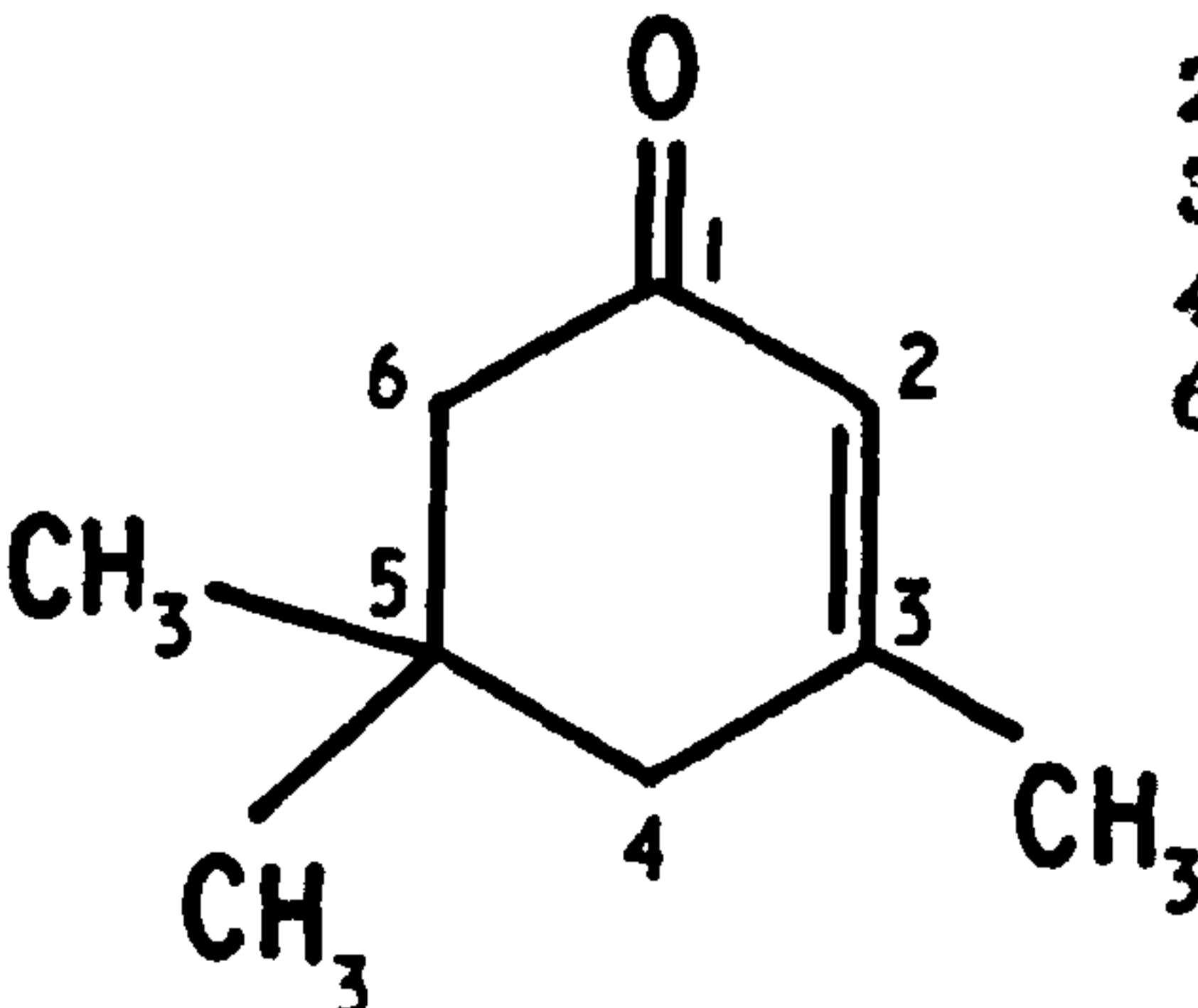
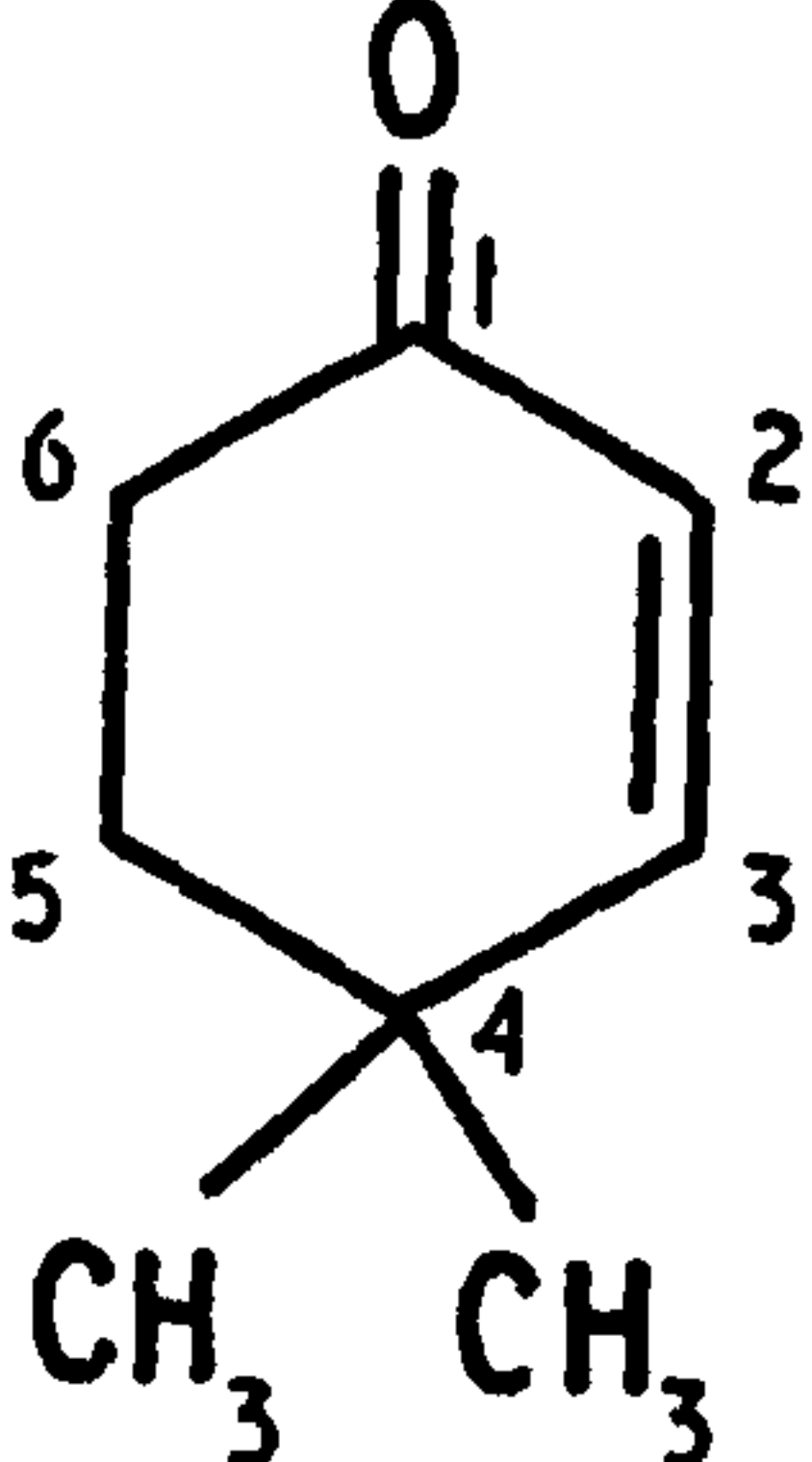
Substrate	Position	Coupling <sup>a</sup> constants (G)	g-Value
Mesityl oxide			
	1	4.65	2.0023
	3	0.75	
	5,6	6.30	
2-Cyclohexen-1-one			
	2	0.73	2.0076
	3	32.10	
	4	0.73, 12.98	
	6	0.73, 17.47	
Isophorone			
	2	1.20	2.0037
	3	14.29	
	4	4.35, 13.66	
	6	6.89, 22.55	
....continued			

TABLE II (continued)

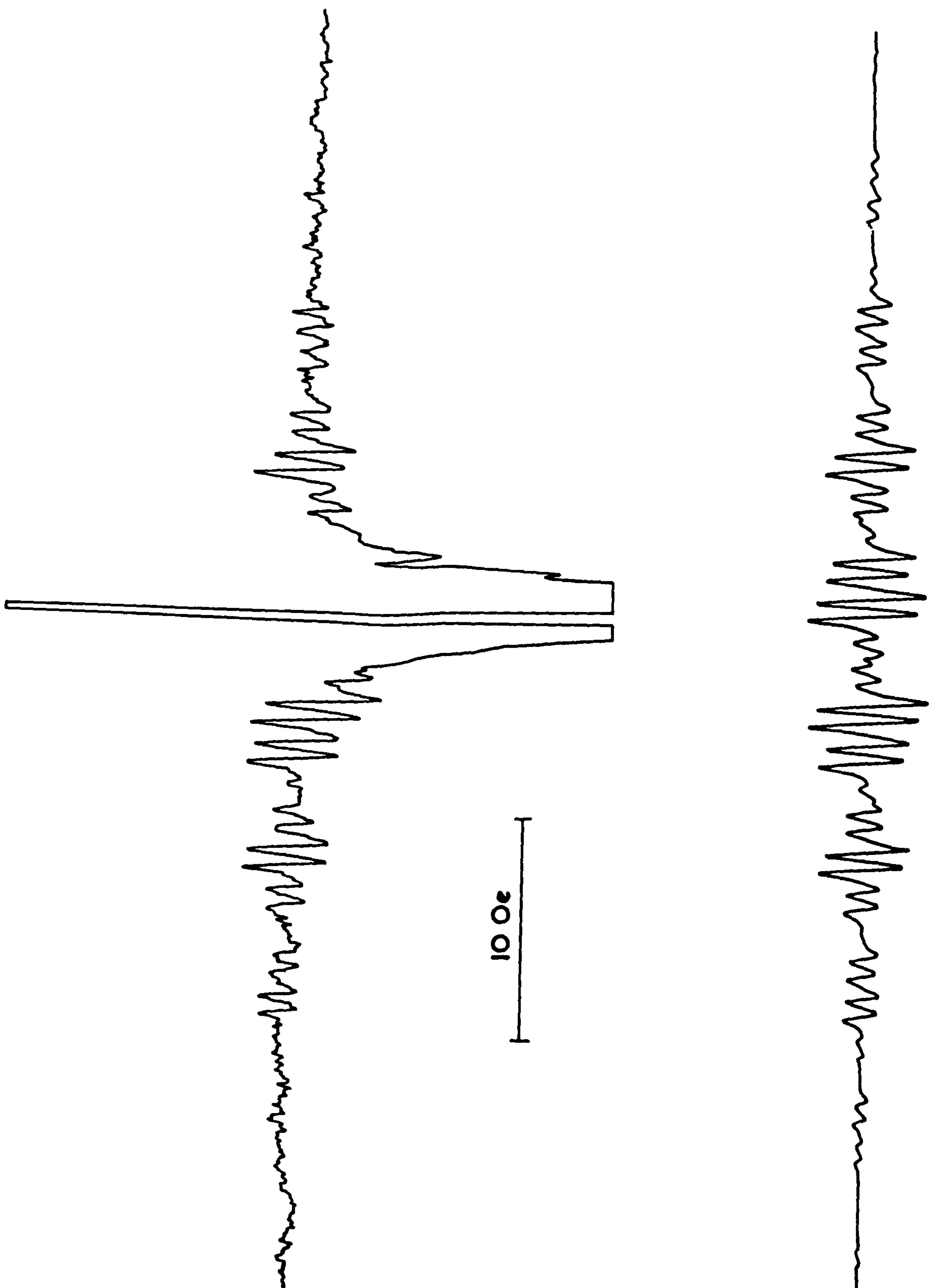
Substrate	Position	Coupling constants (G)	g-Value
4,4-Dimethyl-2-b cyclohexen-1-one		1.72	2.0046
		5.16	
		5.87, 5.87	

<sup>a</sup> Assignment of coupling constants is uncertain.

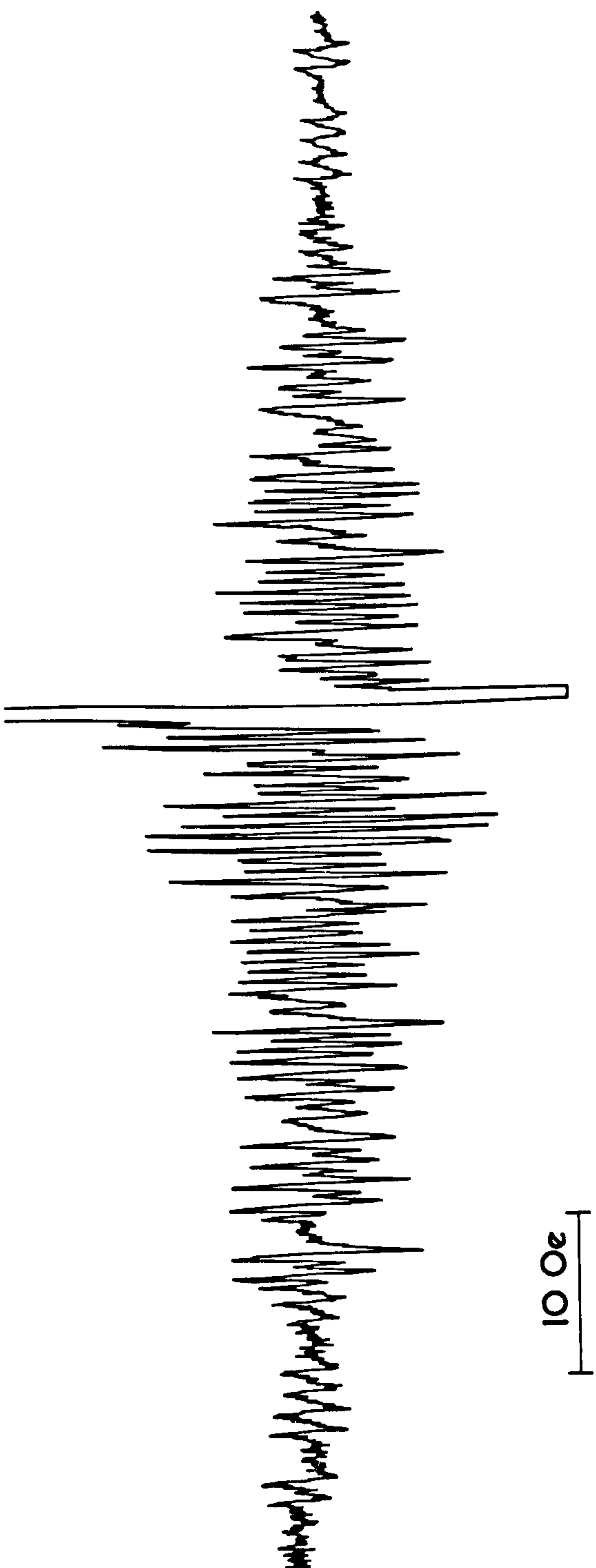
<sup>b</sup> Results from ref. 174 included for comparison.

Spectrum of the radical-anion of mesityl oxide (upper)  
and the computer simulation (lower).





**Spectrum of the radical-anion of isophorone (upper)  
and the computer simulation (lower).**



**EXPERIMENTAL**

## DESIGN OF FLOW MIXER

Several techniques for providing a high concentration of short-lived free radicals for e.s.r. observation were mentioned in the introductory chapter and the flow method in particular was discussed. A very successful design of rapid-flow apparatus is that of Dixon and Norman<sup>18</sup> which consists of an e.s.r. aqueous flat cell modified to allow two solutions to mix just prior to entering the narrow part of the cell; a diagram of the mixer is shown in Fig. 1 and examples of its use are given in refs. 18-21.

Experiments in which the Dixon and Norman mixer was used with liquid ammonia solutions were abandoned for two reasons. First, it was felt that the aqueous e.s.r. cell would be unable to withstand the high pressures often encountered in the first stages of flowing; second, the poor initial spectra obtained indicated that the time lapse between mixing and observation was too long. In an effort to remedy these faults a mixing cell was designed based on an apparatus of Moskowitz and Bowman<sup>182</sup> whose mixer was formed by packing a glass tube with capillary tubes, heating and drawing out to a point. The drawn-out point was cut off in such a way as to present a flat mixing plane with a cross-section consisting of a number of holes half of which belonged to capillary tubes and half to interstices. Solution A was passed down the capillary tubes, solution B down the interstices and Moskowitz and Bowman quoted extremely short intervals of time for complete mixing. Although the first few results of the present work were obtained with a mixing cell very similar to that used by Moskowitz and Bowman the difficulty of producing the correct cross-sectional pattern at the nozzle consumed a large amount of time and glassware.

In order to facilitate construction the basic design was modified in such a way as to allow for separate preparations of the mixing-cell jacket and a



number (10-20) of drawn out capillary tubes; the latter are placed in the jacket and cut off to form a flat mixing plane in the manner previously discussed. A diagram of this mixer is shown in Fig. II and it can be seen that a plug of Araldite is necessary to hold the capillary tubes in place and to separate solutions A and B in the main body of the mixer. Fixed to the nozzle by Araldite is the flow tube of approximately 2 mm internal diameter which is the maximum diameter allowed by the dielectric constant of liquid ammonia (22.4 at  $-33.4^{\circ}\text{C}$ ). Difficulties were encountered with the Araldite plug which, owing to the different coefficients of expansion of glass and Araldite, often caused the glass jacket to crack during the flow of cold solutions with the result that cell lifetimes of only approximately 2-3 flow experiments were common. Cracking of the glass was prevented to some extent by using a softer-setting grade of Araldite and to a large extent by inserting a film of compressible Evo-Stik between the Araldite and the glass.

Although use of the mixing-cell provided some very well-resolved e.s.r. spectra, which is a good test of adequate mixing characteristics, further mention should be made of criteria (discussed in Chapter I) for a good mixing-cell.

Cavitation (the production of bubbles due to high flow rates) must be absent since it would cause intermittent detuning of the e.s.r. spectrometer; this did not occur during the present work. The rate of mixing was tested visually by running solutions of acids and bases with colour indicators; no unchanged indicator colour was observed immediately after the nozzle. During an average run approximately four litres of liquid ammonia passed through the cell in about 15 minutes; flow rates were thus of the order of 4-5 ml per sec. For efficient mixing and to reduce deviations from 'mass-flow' to a minimum, turbulent flow must occur for

which the minimum critical velocity is given by Reynold's equation (see Chapter I). The critical velocity,  $u_c$ , is given by

$$u_c = \frac{1,000 \eta}{\rho \times r} \text{ cm/sec}$$

and the value for liquid ammonia at  $-33^\circ \text{C}$  in a flow tube of 2 mm internal diameter is 37.32 cm/sec or 1.17 ml/sec which is well below flow rates actually used. However, increased turbulence at the nozzle might be obtained if turbulent flow occurs in the capillary tubes just prior to mixing. Assuming each capillary tube (and cross-section of interstitial holes) to have an average diameter of 0.25 mm the critical velocity for turbulence would be 300 cm/sec or 0.587 ml/sec in each capillary. For a flow experiment with a cell containing ten capillary tubes through which pass two litres of solution in 15 minutes the flow rate in each tube is approximately 0.22 ml/sec i.e. below  $u_c$ .

### TWO-STAGE MIXER

A two-stage mixing-cell was developed for the purpose of investigating the pyridine/ethanol reduction discussed in Chapter II. The prototype is shown in Fig. III and although its construction was somewhat more difficult than the single-stage mixer the basic principles remain the same. A modification of the prototype was necessary (shown in Fig. IV) in order to overcome the problem of solution pressures working against each other before reaching the nozzle resulting in greatly differing flow rates of solutions A, B and C.

### A. TYPICAL FLOW EXPERIMENT

A typical experiment involved the preparation of  $10^{-3}$  -  $10^{-2}$  M solutions both of sodium and of the compound under investigation in liquid ammonia. The flow set-up is shown diagrammatically in Fig. V. The solutions were driven under pressure of nitrogen into the mixing-cell via narrow-bore tubes well lagged with solid carbon dioxide chips. The temperature of the mixed solutions in the flow tube was monitored with a thermocouple attached to a galvanometer and usually found to be between  $-50^{\circ}$  and  $-40^{\circ}$  C. Difficulty was often encountered when a particular batch of liquid ammonia contained impurities causing decomposition of the solvated electron solution. In those cases where rapid decomposition of solvated electron solution occurred the batch of ammonia was discarded, but for slow decomposition (giving hydrogen) the solutions were often used, the hydrogen bubbles (which would detune the spectrometer) being caught in a gas trap placed just before the mixing-cell.

Only short spectrum recording times were possible (100-500 sec) because of the high flow rates used and this resulted in some loss of resolution for many compounds although for spectra such as 2-fluoropyridine (Chapter II) it would be difficult to improve resolution on a longer scan time.

### THE STATIC REDUCTION EXPERIMENT

The static reduction technique for observing stable radical-anions was carried out by adding a minute amount of compound to a 0.1 M solution of sodium in liquid ammonia. The tube was then placed in the spectrometer cavity and kept at the required temperature by passing a stream of



precooled nitrogen gas round the tube using a variable temperature apparatus supplied with the e.s.r. spectrometer. With practice observations could be begun within half a minute of mixing.

### THE SPECTROMETER

The e.s.r. spectrometer used was a Decca Radar X 1 employing a Newport Instruments M 2 7" magnet system. Spectra were recorded on X - Y and Y - T recorders.

### DETERMINATION OF g-VALUES

The g-value (and field value) of the solvated electron peak was calculated by comparison with potassium peroxyaminedisulphonate (Fremy's salt), for which  $g = 2.0055$  and diphenylpicrylhydrazyl (DPPH),  $g = 2.0036$ , giving  $g_{\text{e solv}} = 2.0011$  which compares well with the figure of 2.0012 given by Pastor.<sup>183</sup> g-Values for radical-anions were obtained by measuring the separation between the centre of a spectrum and the solvated electron peak, converting to magnetic field units (after running a sample of Fremy's salt in dilute KOH which has a three line spectrum of 13.07 Oe separation) and using the equation  $h\nu = g\beta H$ .

### MATERIALS USED

Compounds were in most cases purified by distillation or recrystallisation where quantity of material allowed, but in two instances, 2,4,6-collidine and iodobenzene, distillation alone did not free the compounds from interfering impurities. The collidine contained an impurity of 3,5-lutidine

which was removed by first preparing the picrate and recrystallising five times, which gave 2,4,6-collidine picrate melting at  $156^{\circ}\text{C}$  (lit.<sup>184</sup>  $156^{\circ}\text{C}$ , cf. 3,5-lutidine picrate m.p.  $229^{\circ}\text{C}$ ). The collidine was then regenerated by eluting with benzene from an alumina chromatographic column.

Styrenes were purified from stabiliser by washing with 4M NaOH and water and drying with Drierite followed by calcium hydride before distilling at reduced pressure.

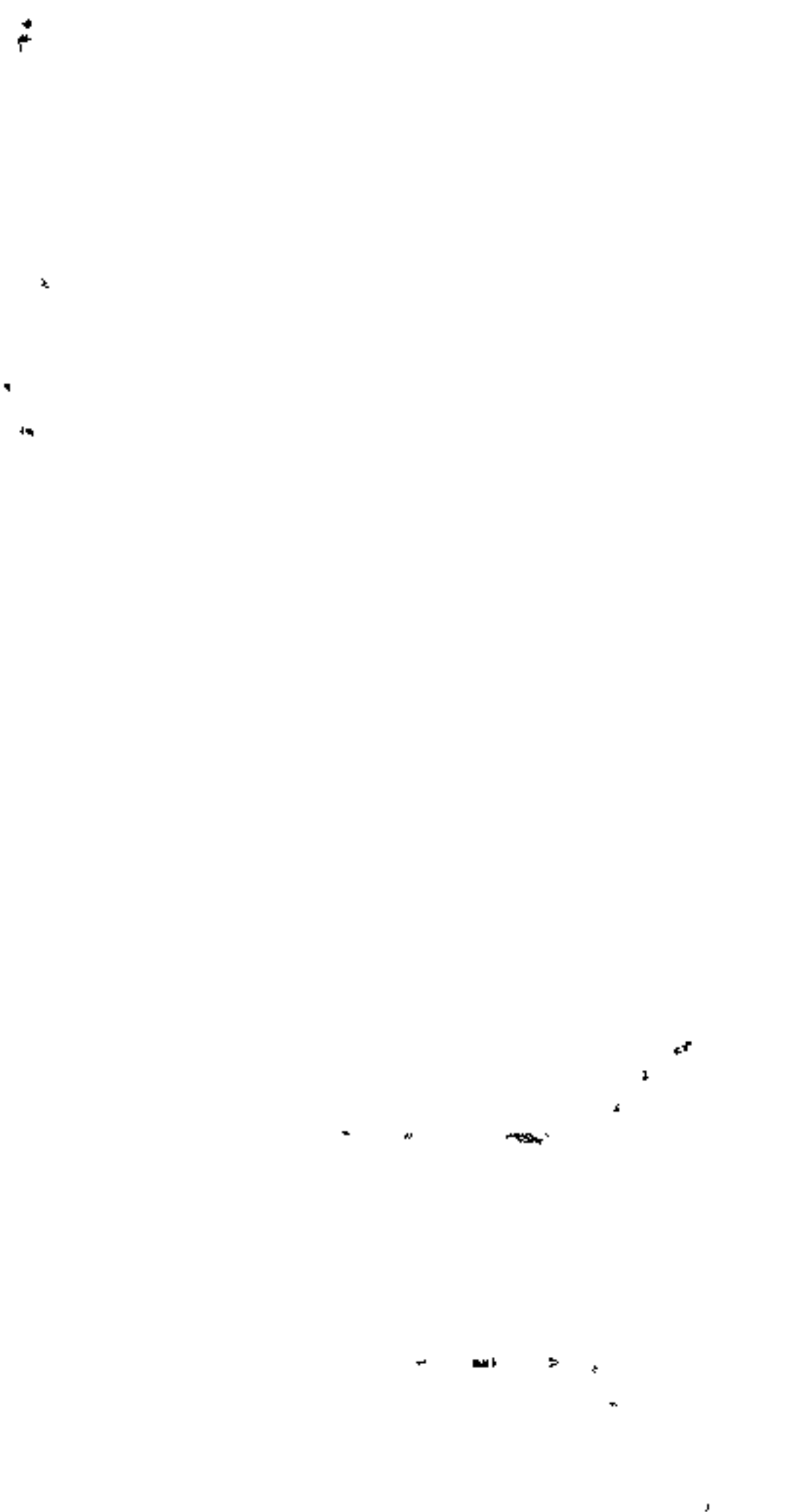
Iodobenzene could not easily be separated from a nitrobenzene impurity and was therefore prepared in the laboratory by the method of Baker and Waters<sup>185</sup> where there was no possibility of the presence of nitrobenzene occurring in the product.

Compounds not commercially available were prepared in the laboratory. 2,6-Pyridinedicarboxylic acid N-oxide was prepared by the method of Heywood and Dunn<sup>186</sup> and 2,6-pyridinedicarboxylic acid diethyl ester using the method of Barnes and Fales.<sup>187</sup>

### COMPUTER PROGRAMS

Computation of electron spin densities was performed with a program supplied by Dr. D.M. Hirst, modified by Dr. G.T. Neal, on an Elliott 4130 system computer. Programs for the computer simulation of e.s.r. spectra were provided by Dr. O.W. Howarth and Dr. G.T. Neal.

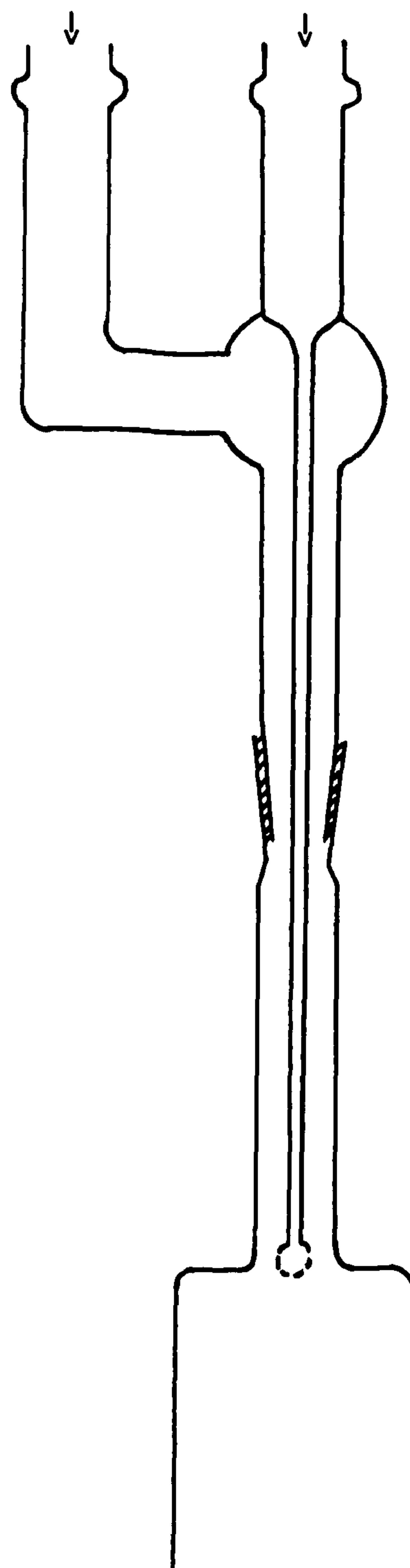




**Fig. 1. The Dixon and Norman mixing-cell.**

SOLUTION B

SOLUTION A



**Fig. II. Mixing-cell developed to obtain the results  
discussed in the present work.**

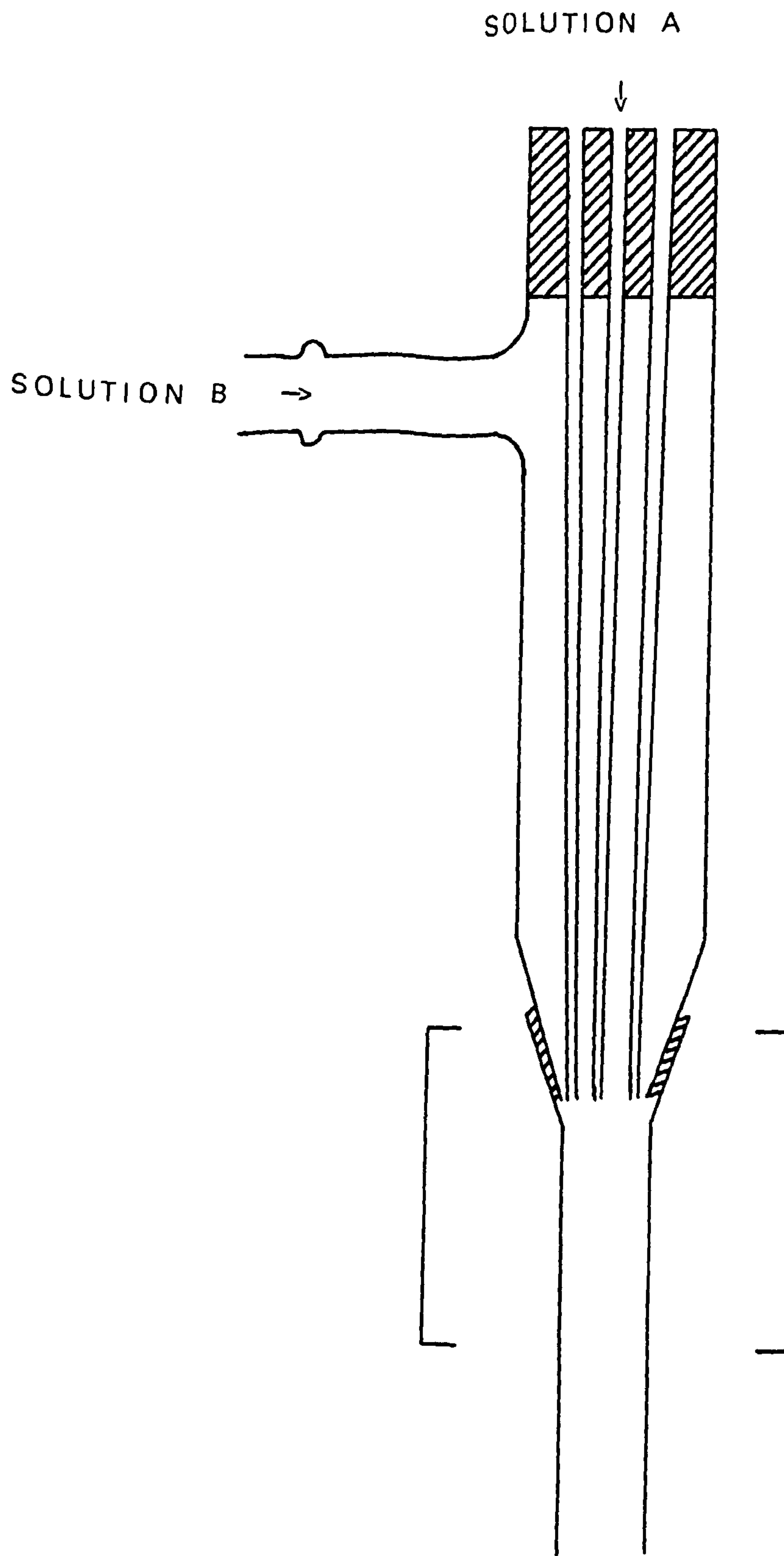


Fig. III. Two stage mixing-cell: prototype.



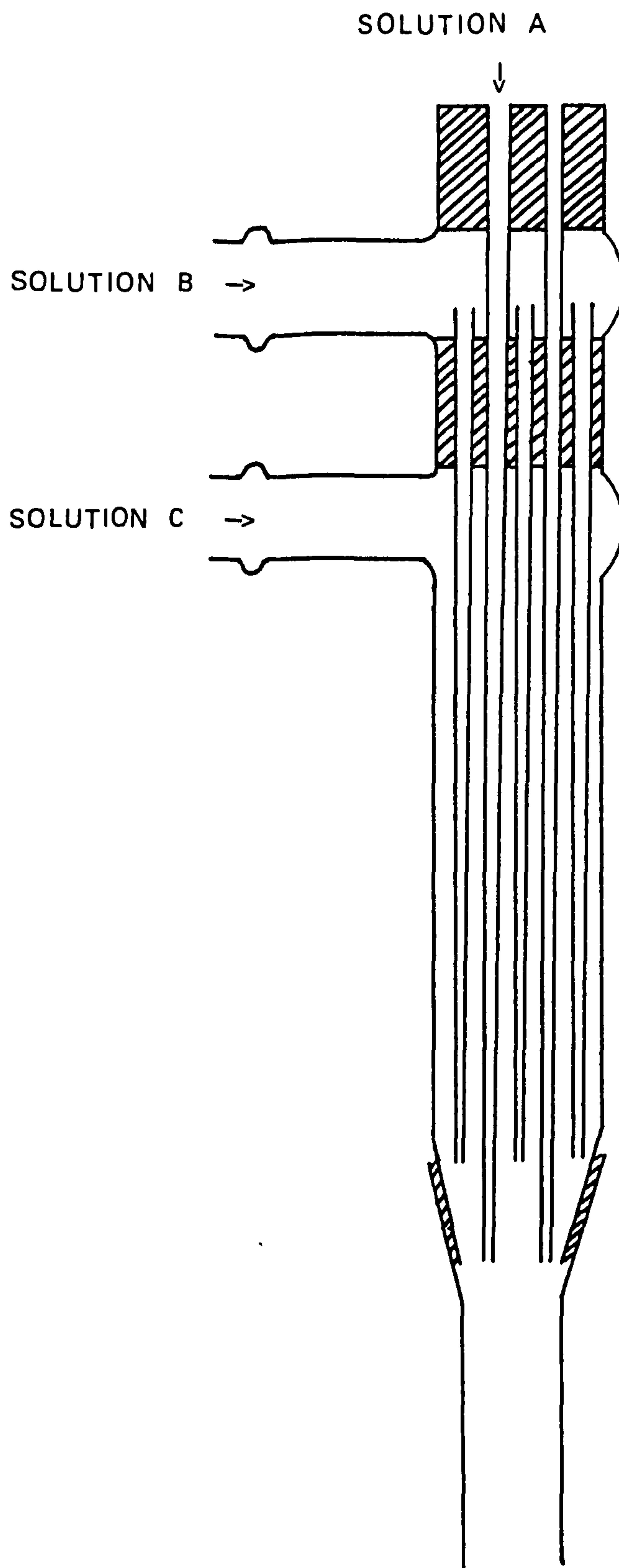


Fig. IV. Two stage mixing-cell: modification of the prototype.

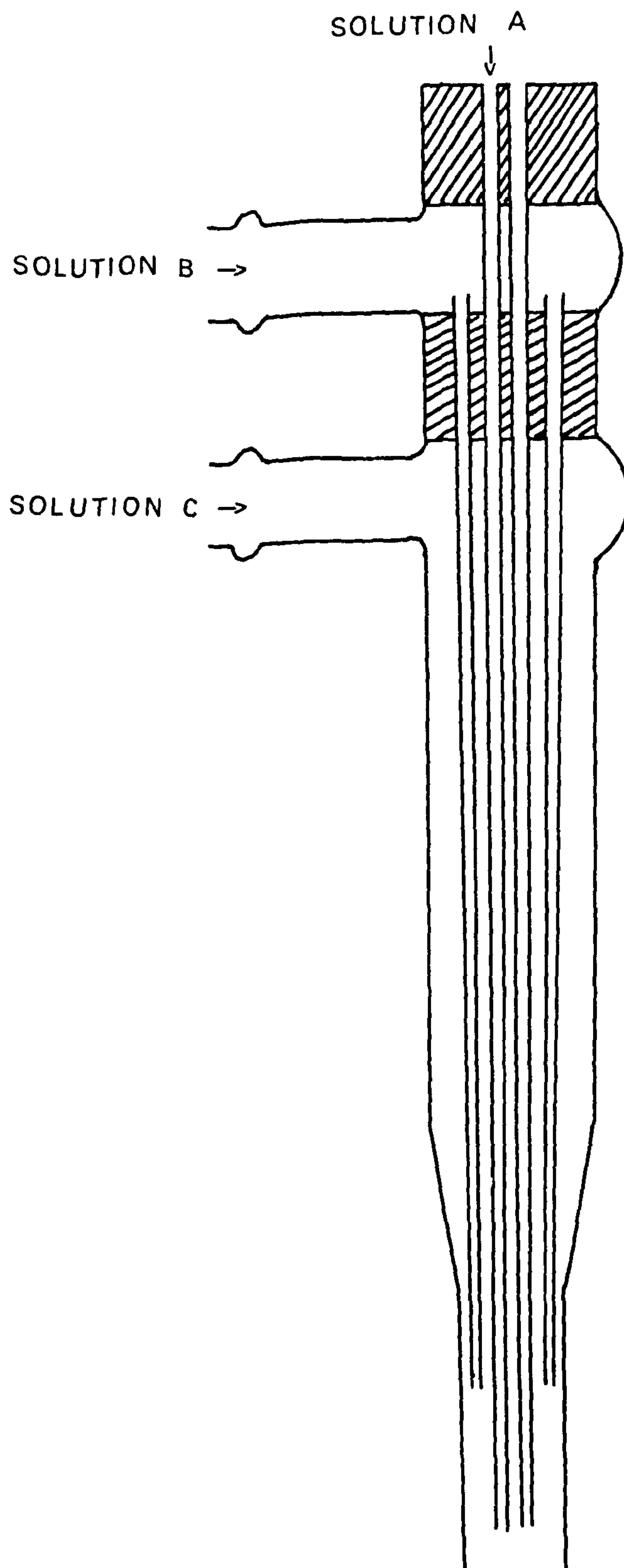
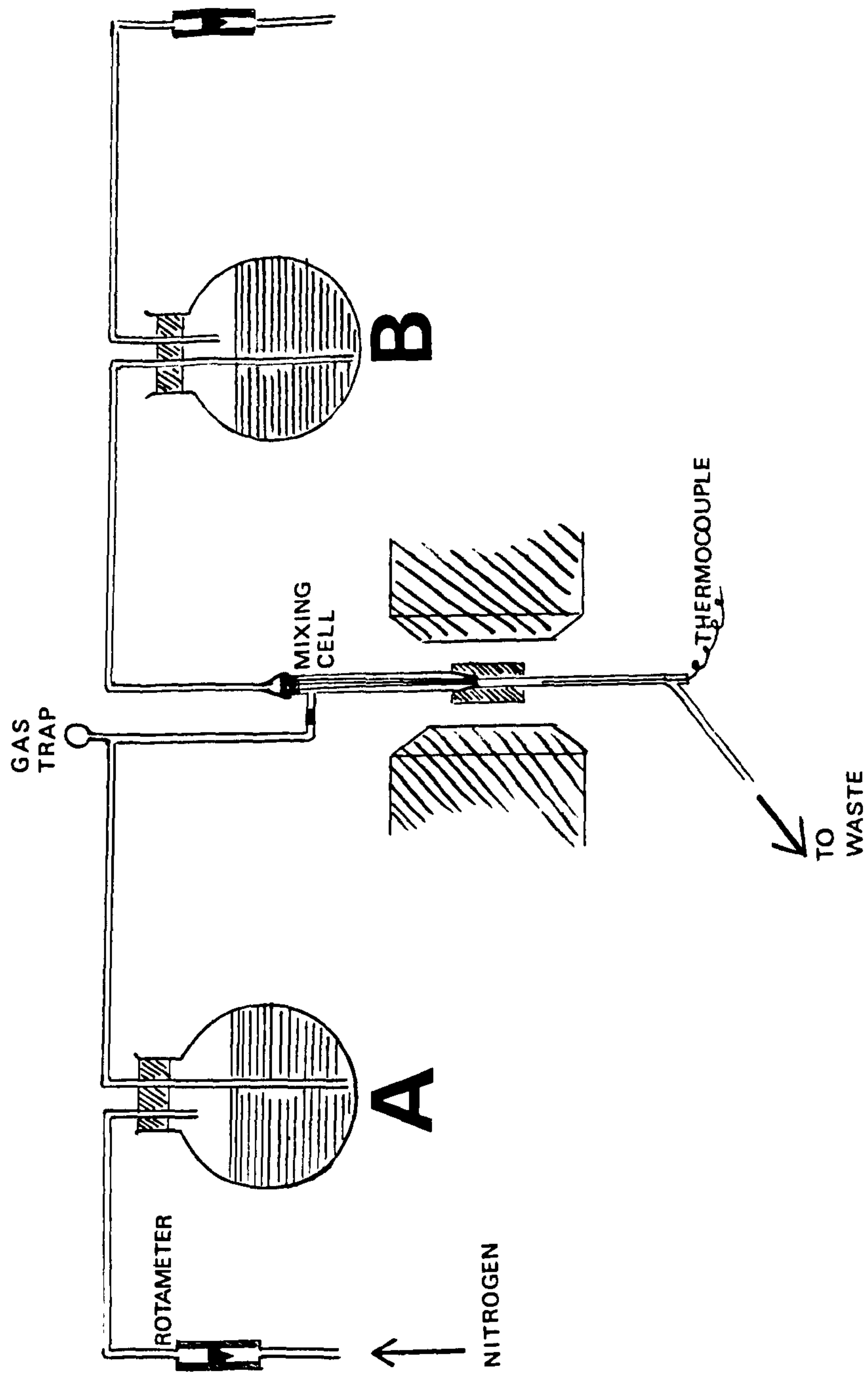


Fig. V. Rapid flow apparatus.

# RAPID FLOW APPARATUS





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## ABSTRACT

A rapid flow method for the production of radical-anions for electron spin resonance (e.s.r.) observation is described whereby liquid ammonia solutions of sodium and substrate are mixed in the cavity of the spectrometer. The mixing-cell consists of several capillary tubes placed in a glass jacket narrowing at one end to form a nozzle. Liquid ammonia solutions are passed under pressure of nitrogen through capillary tubes and interstices and radical-anions can be observed within a few milliseconds of mixing.

Results are presented in five chapters. The reduction of pyridine and substituted pyridines is described in Chapter II; with the exception of one mono- and all dicarboxylic acid derivatives, simple monomer radical-anions are formed. Pyridinecarboxylic acids ionise in liquid ammonia solution and in some cases the ionised proton attaches itself to the radical-anion forming an N- protonated species. N- protonation is also seen for pyridine itself when reduced in the presence of a large excess of ethanol, a strong acid in ammonia. A complementary static reduction technique is used to observe reduction on a longer time scale where several dimeric products are observed, for example 2,6-dimethylpyridine gives 2,2',6,6'-tetramethyl-4,4'-dipyridyl radical-anion.

Carbon halogen bond-cleavage occurs rapidly when aryl halides, except fluorides, are reduced (Chapter III). The halogen atom in fluoro-benzonitriles shows varying degrees of lability; for example, a mixed spectrum of halogenated and dehalogenated radical-anions is seen for para-fluorobenzonitrile while even after the insertion of a one second delay between points of mixing and observation only the halogenated radical-anion is observed for meta-fluorobenzonitrile.

Aromatic carboxylic acid reduction (Chapter IV) produces the expected radical-anions, with the exception of two nitro di-acids which produce a mixture of radicals on the flow system, and a spectrum possibly corresponding to a radical-anion similar to the parent nitro di-acid on static reduction. Analysis of the major flow spectrum again indicates a protonated species.

Styrenes and benzamides show non-equivalent ring protons resulting in complex spectra (Chapters V and VI). The 'alpha effect' is used in Hückel and McLachlan molecular orbital calculations for styrenes where one ortho ring position is given a small Coulomb integral value.

The results of the reduction of some  $\alpha,\beta$ -unsaturated ketones are discussed in Chapter VI. Analysis of the spectrum of mesityl oxide radical-anion is straightforward, while slow 'ring-flip' from one conformer to another is responsible for inequivalent methylene protons in isophorone and 2-cyclohexen-1-one.