

FAST REACTION KINETICS BY E.S.R. METHODS

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Abstract - Kinetic information can be obtained from e.s.r. spectra both through the determination of radical concentrations as a function of conditions and through line-broadening effects. Applications of the former method have usually been combined with radical generation either by photolysis within the spectrometer cavity or by a rapid redox reaction in conjunction with a flow system; the scope and limitations of the method are discussed, and the examples chosen reveal several structure-reactivity relationships. The method based on line-broadening is applicable to processes which occur on a time-scale which is of the same order as appropriate hyperfine splitting intervals for the radicals concerned; the examples chosen give information about the rates of conformational changes.

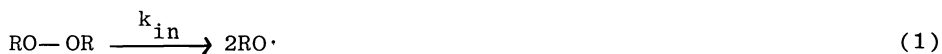
INTRODUCTION

The electron spin resonance spectra of free radicals yield information of four types: hyperfine splittings, g -factors, line-widths, and concentrations. The first two in turn provide information about structural features of the radicals; and both line-widths and concentrations can give kinetic information. The first phase of the application of e.s.r. to organic radicals, beginning in about 1960, was largely concerned with the elucidation of structural features, but in the last decade kinetic applications have become at least as important.

This Paper will be concerned mainly with the kinetic data which can be derived from measurements of radical concentrations as a function of reaction conditions. This is because the method is applicable to radicals and their reactions of all types; rate constants up to the diffusion-controlled limit can be determined. In contrast, line-width measurements can yield rate constants only when these are within a relatively small range.

STATIC SYSTEMS: PHOTOCHEMICAL TECHNIQUES

Photolysis, particularly of peroxides (frequently di-*t*-butyl peroxide, DTBP) has been widely used to initiate radical reactions for e.s.r. study. The success of the method depends on the efficiency of the photolysis coupled with the fact that alkoxy radicals react very rapidly with most organic compounds; in spite of the rapidity with which the resulting radicals usually react further, a steady-state radical concentration which is above the limit detectable by e.s.r. (ca. $10^{-7}M$) can be produced. For example, consider the simple system in which all alkoxy radicals $RO\cdot$ are scavenged by a compound $R'H$ to give radicals $R'\cdot$ which decay only by bimolecular combination to give non-radical (molecular) products:

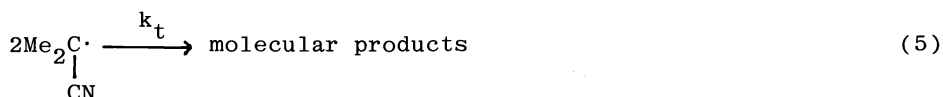
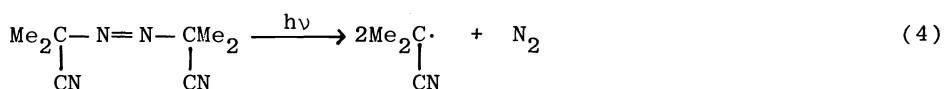


Steady-state treatment gives

$$d[R'\cdot]/dt = 2k_{in} [RO_2R] - 2k_t [R'\cdot]^2 = 0$$

Even when $2k_t$ is ca. $10^9 \text{ M}^{-1} \text{ s}^{-1}$, as is usually the case for unhindered carbon-centred radicals, it follows that, with $[RO_2R] = 0.1\text{M}$, $[R'\cdot] > 10^{-6}\text{M}$ provided that $k_{in} > 10^{-2} \text{ s}^{-1}$, and this condition can usually be achieved with a suitable ultraviolet lamp.

Kinetics of bimolecular radical termination. The rotating sector technique has been combined with e.s.r. spectroscopy to measure the rates of radical termination. Radicals have been generated either by a high-energy electron beam (2.8 MeV) which is pulsed electronically (Ref. 1) or by ultraviolet irradiation. For example, Weiner and Hammond (Ref. 2) employed a rotating sector which provided equal light and dark periods of ca. $2 \times 10^{-3} \text{ s}$; during the light periods, a steady-state concentration, $[R\cdot]_0$, of 2-cyanopropyl radicals was set up by photolysis of azobisisobutyronitrile,



and decay curves for $R\cdot$ during the dark periods were accumulated by a computer which was triggered off by the rotating sector. The decay kinetics are given by

$$-d[R\cdot]/dt = 2k_t [R\cdot]^2$$

$$\text{i.e. } 1/[R\cdot]_t = 1/[R\cdot]_0 + 2k_t t$$

$$\text{and } k_t = 4/(3[R\cdot]_0 \Delta t)$$

where Δt is the time for $[R\cdot]$ to fall from 3/4 to 1/4 of its starting concentration $[R\cdot]_0$. The rate constant obtained was $(2.2 \pm 1.0) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ at room temperature in benzene solution.

In another application of the rotating sector method in which radicals $R\cdot$ were generated by photolysis of DTBP in the presence of the parent RH, values of $2k_t$ were obtained of which those in Table 1 are illustrative. It was noted that, except for $\cdot\text{CCl}_3$, $\log k_t$ correlates surprisingly well with molecular weight, and the suggestion was made that, with increase of molecular weight, the radius for diffusion increases whereas that for reaction is almost unchanged (Ref. 3). Polar effects possibly serve to retard the decay of $\cdot\text{CCl}_3$.

TABLE 1. Values of $2k_t$ from the rotating sector method

$R\cdot$	$10^{-9} \times 2k_t / \text{M}^{-1} \text{ s}^{-1}$	$T/^\circ\text{C}$
$\cdot\text{CH}_3$	11 ± 1.0	-18
$\cdot\text{CMe}_3$	8.1 ± 0.3	25
$\cdot\text{CCl}_3$	0.12 ± 0.02	-75 to -15
$\cdot\text{SiMe}_3$	5.5 ± 0.2	25
$\cdot\text{GeMe}_3$	3.6 ± 0.2	-65
$\cdot\text{SnMe}_3$	2.8 ± 0.3	-65

Kinetics of intramolecular radical reactions. If, in addition to its bimolecular decay, a radical takes part in a reaction which leads to another radical, the rate constant for that reaction can be obtained provided that the spectra of both initial and final radicals can be observed. The following are four examples of intramolecular free-radical processes which have been studied in this way.

The 5-hexenyl radical A was generated from tris(5-hexenyl)phosphine with $\text{Bu}^t\text{O}\cdot$ (from DTBP/hv) in isopentane, and the spectra of both A and the radical to which it cyclises, B, were monitored. The steady-state concentration of B is



given by

$$d[\text{B}]/dt = k_c[\text{A}] - 2k_t[\text{B}]^2 - 2k'_t[\text{A}][\text{B}] = 0$$

where k_t and k'_t are the bimolecular termination rate constants for $\text{B} + \text{B}$ and $\text{B} + \text{A}$, respectively. Since both A and B are primary radicals of the same molecular weight, it may be assumed that $k_t = k'_t$. It follows that

$$k_c/2k_t = ([\text{B}]^2/[\text{A}]) + [\text{B}]$$

The ratio $k_c/2k_t$ was determined by measuring $[\text{B}]$ and $[\text{A}]$, and $2k_t$ was measured independently by generating B in the same solvent from tris(cyclopentylmethyl)-borane with $\text{Bu}^t\text{O}\cdot$. It proved possible to determine both $[\text{A}]$ and $[\text{B}]$ in the temperature range 188–228 K, and this yielded the Arrhenius parameters:

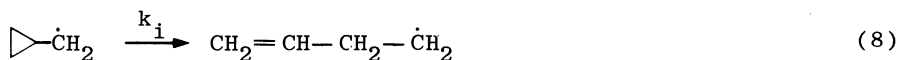
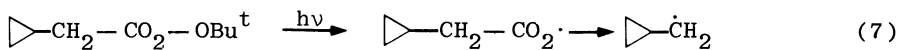
$$\log(k_c/s^{-1}) = (10.7 \pm 1.0) - (7.8 \pm 1.0)/2.3RT$$

This expression gives $k_c = 1 \times 10^5 \text{ s}^{-1}$ at 25°C (Ref. 4).

The rate constant for the ring-opening (8) of the cyclopropylmethyl radical, generated by reaction (7) in methylcyclopropane solution, has been obtained similarly (and with the same assumption about the bimolecular termination rates). Studies in the temperature range 128–153 K gave (Ref. 5):

$$\log(k_i/s^{-1}) = (12.48 \pm 0.85) - (5.94 \pm 0.57)/2.3RT$$

which gives $k_i = 1.3 \times 10^8 \text{ s}^{-1}$ at 25°C.



Aryl-rearrangements illustrated by reaction (9) have also been examined in this way (Ref. 6); radicals $\text{ArCMe}_2\text{CH}_2\cdot$ were generated from Ar-CMe_3 in DTBP by photolysis, and examples are in Table 2.

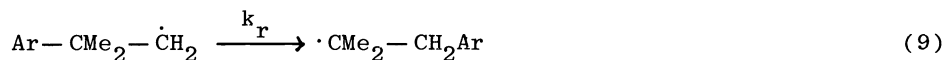
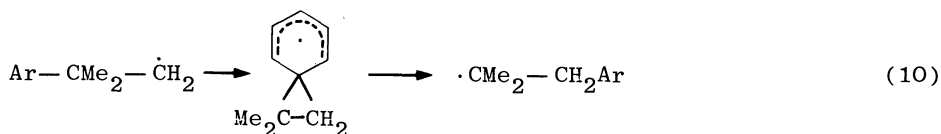


TABLE 2: Kinetic data for reaction (9)

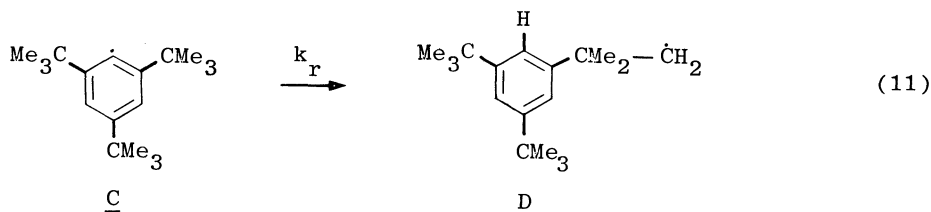
Ar	k/s ⁻¹ (25°C)	log(A/s ⁻¹)	E/kcal mol ⁻¹
Phenyl	59	11.75	13.6
2-Naphthyl	2.9 x 10 ³	11.75	11.3
4-Pyridyl	1.4 x 10 ³	11.8	11.8

The notable feature of the results is the activation of the naphthyl and pyridyl systems compared with phenyl. It has been pointed out that naphthalene and pyridine are activated in homolytic aromatic substitution at the 2- and 4-positions, respectively, implying the mediation of a delocalised cyclohexadienyl radical in the rearrangement,



as in the homolytic substitution.

The final example is perhaps the most significant. The rates of the 1,5-hydrogen shift (11) and of the 1,5-deuterium shift in the perdeuterio-*t*-butyl substituted aryl radical have been determined in the ranges -26 to -160°C and 20 to -150°C, respectively. The radical C was generated photolytically and its concentration was found to be

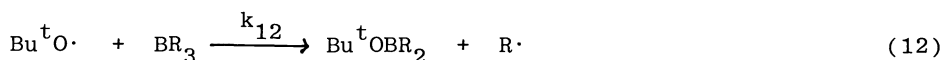


proportional to the incident light intensity and that of D to the square root of the light intensity, showing that C yields D which decays bimolecularly (i.e. termination by the coupling of the hindered C with D is negligible). Values of k_r at various temperatures were obtained by monitoring the decay of C when the light was cut off. In addition, with continuous illumination, steady-state analysis gives

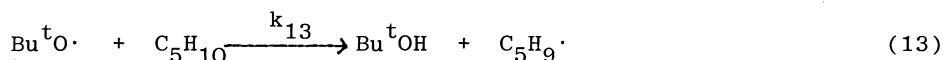
$$1/[\text{D}] = 2k_t[\text{D}]/k_r[\text{C}]$$

and since $2k_t$ was obtained independently, a check on the k_r values was available. The results provide most compelling evidence for the operation of quantum-mechanical tunnelling. Thus, the Arrhenius plots show the expected marked curvature; both the activation energy and the pre-exponential factor are significantly higher for the deuterium shift; and, most significantly, k_H/k_D is far larger than is theoretically possible for a purely classical hydrogen-shift (e.g. at -150°C it is 13,000, compared with a calculated maximum of 260) (Ref. 7).

Reactions at boron and phosphorus. The *t*-butoxyl radical reacts with boranes by the S_H^2 process:



If this reaction is in competition with another, such as the abstraction of hydrogen from cyclopentane (C_5H_{10}),

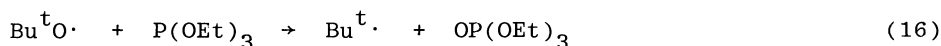
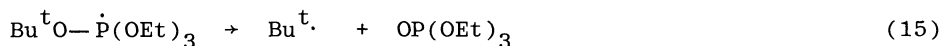
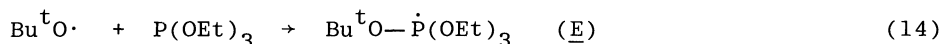


then, providing that all t-butoxyl radicals react only in these two ways, and given the reasonable assumption that the bimolecular termination rate constants involving $R\cdot$ and $C_5H_9\cdot$ are equal, it follows from steady-state analysis that

$$\frac{k_{12}[BR_3]}{k_{13}[C_5H_{10}]} = \frac{[R\cdot]}{[C_5H_9\cdot]}$$

The appropriate plot yields k_{12}/k_{13} . A value for k_{13} ($2.2 \times 10^5 M^{-1} s^{-1}$ at $40^\circ C$) has been derived from other measurements, enabling k_{12} to be determined; for example, for tributylborane k_{12} is $3 \times 10^7 M^{-1} s^{-1}$ at $30^\circ C$ (Ref. 8).

Reaction of the t-butoxyl radical at tervalent phosphorus differs from that at boron in that it results in oxygen-atom transfer [reaction (16)]. Moreover, the e.s.r. spectrum of the intermediate E can be observed, pointing to the two-step mechanism of reactions (14) and (15).



When this reaction was carried out in cyclopentane with a relatively large $[P(OEt)_3]$, the observed cyclopentyl radical concentration was small enough to allow its involvement in the kinetic analysis to be neglected, and this enabled k_{15} to be evaluated, as follows. Steady-state treatment for $Bu^t\cdot$ gives

$$1/[Bu^t\cdot] = 2k_t[Bu^t\cdot]/k_{15}[E] + 2k_t'/k_{15}$$

where k_t and k_t' refer to bimolecular reactions involving $Bu^t\cdot$ and $Bu^t\cdot + E$, respectively (in fact, the linear plots at various temperatures passed through the origin, indicating the unimportance of the latter). With $2k_t = 2 \times 10^9 M^{-1} s^{-1}$, k_{15} was evaluated as $5 \times 10^5 s^{-1}$ at $30^\circ C$.

Decrease in $[P(OEt)_3]$, so that $[C_5H_9\cdot]$ was no longer negligible, enabled k_{16} to be measured, since under these conditions

$$\frac{k_{16}[P(OEt)_3]}{k_{13}[C_5H_{10}]} = \frac{[Bu^t\cdot]}{[C_5H_9\cdot]}$$

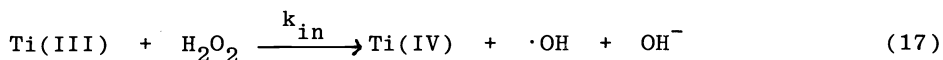
The value obtained was $1.6 \times 10^8 M^{-1} s^{-1}$ at $30^\circ C$ (Ref. 9).

FLOW SYSTEMS: REDOX TECHNIQUES

A variety of redox reactions has proved suitable, in conjunction with a relatively simple continuous-flow and mixing system, for monitoring radical concentrations by e.s.r. Typically, the two redox reagents, at flow rates in the range $1 - 5 cm^3 s^{-1}$, are mixed ca. 50 ms before passage of the combined solution through the cavity of the spectrometer. For the majority of organic radicals, for which the bimolecular termination rate constant is ca. $10^9 M^{-1} s^{-1}$, it can readily be shown that, to a close approximation, only those

radicals which are generated within the cavity are observed (Ref. 10). For example, when the observed concentration of radicals is 10^{-6}M and with $2k_t = 10^9 \text{M}^{-1} \text{s}^{-1}$, $t_{1/2}$ ($= 1/2k_t[\text{R}\cdot]$) is ca. 10^{-3}s , which is negligible compared with the time between mixing and observation; that is, radicals generated between the mixing point and the cavity are essentially all destroyed before they can be observed. As a result, kinetic analysis of the quasi-steady-state in the cavity is relatively simple.

Consider the redox reaction (17), for which k_{in} , determined by stopped-flow kinetics with measurements of ultraviolet absorption, is $590 \text{M}^{-1} \text{s}^{-1}$ in sulphuric acid at pH 1 and 25°C (Ref. 11). The hydroxyl radical is exceptionally reactive, so that the inclusion of an organic compound RH can lead to essentially complete conversion of hydroxyl radicals into radicals R \cdot . If these decay only bimolecularly, the system is described by reactions (17) - (19), and



steady-state treatment gives

$$\begin{aligned} d[\text{R}\cdot]/dt &= k_{18}[\cdot\text{OH}][\text{RH}] - 2k_t[\text{R}\cdot]^2 \\ &= k_{in}[\text{Ti(III)}]_t[\text{H}_2\text{O}_2]_t - 2k_t[\text{R}\cdot]^2 = 0 \end{aligned}$$

where the subscript t refers to the concentration in the cavity, t seconds after mixing. Now, if hydrogen peroxide is in considerable excess over titanium(III) ion, $[\text{H}_2\text{O}_2]$ remains sensibly constant and $[\text{Ti(III)}]$ decreases exponentially between the mixing point and the cavity; i.e. $[\text{Ti(III)}]_t = [\text{Ti(III)}]_0 \exp(-k_{in}[\text{H}_2\text{O}_2]_0 t)$, where subscript zero refers to the concentration at the mixing point. Therefore

$$\begin{aligned} [\text{R}\cdot]^2 &= k_{in}[\text{Ti(III)}]_t[\text{H}_2\text{O}_2]_t/2k_t \\ &= k_{in}[\text{Ti(III)}]_0[\text{H}_2\text{O}_2]_0 \exp(-k_{in}[\text{H}_2\text{O}_2]_0 t)/2k_t \end{aligned}$$

It follows, first, that for a system described by reactions (17) - (19), $[\text{R}\cdot]$ should vary linearly with $[\text{Ti(III)}]_0$, and this has been verified in many cases; as we shall see, deviations from this behaviour enable other reactions of R \cdot to be identified. Secondly, for typical conditions ($[\text{Ti(III)}]_0 = 10^{-2} \text{M}$, $[\text{H}_2\text{O}_2]_0 = 10^{-1} \text{M}$, $2k_t = 10^9 \text{M}^{-1} \text{s}^{-1}$, $t = 50 \text{ms}$), the concentration of R \cdot can be readily determined - that is, $[\text{R}\cdot] > \text{ca. } 10^{-6} \text{M}$ - provided that k_{in} is within the range ca. $1 - (2 \times 10^3) \text{M}^{-1} \text{s}^{-1}$. A wide variety of redox reactions has been found to fulfil this criterion.

Thirdly, if k_t is known, k_{in} can be determined. A simple method for evaluating it is to determine the concentration of the redox component in excess which corresponds to the maximum observed concentration of R \cdot ; for instance, for the Ti(III)- H_2O_2 reaction, differentiation of the steady-state equation shows $[\text{R}\cdot]$ is maximal when $[\text{H}_2\text{O}_2] = 1/k_{in}t$. Examples of values determined in this way are in Table 3.

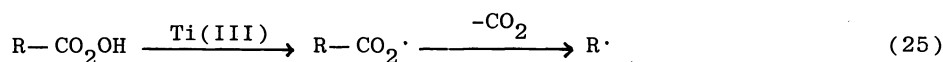
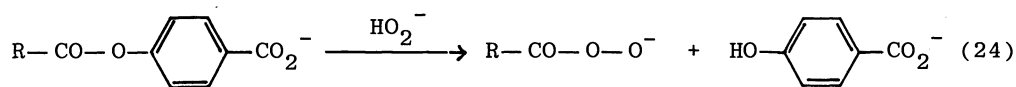
TABLE 3. Values of k_{in} for redox couples

Reaction	pH	$k/M^{-1} s^{-1}$	Ref.
$Fe(II) + H_2O_2 \rightarrow Fe(III) + \cdot OH + OH^-$	1	76	
$Ti(III) + Bu^tO_2H \rightarrow Ti(IV) + \cdot OBu^t + OH^-$	1	180	
$Ti(III) + PrO_2H \rightarrow Ti(IV) + \cdot OPr + OH^-$	1	280	12
$Ti(III) + NH_2OH \rightarrow Ti(IV) + \cdot NH_2 + OH^-$	2	6×10^5	13

The high reactivity of the hydroxyl radical makes it suitable for studying the reactions of radicals to which it gives rise when one of a variety of types of substrate is included. Reactions (20) - (23) provide examples, one of which is considered further in the sequel.



Two disadvantages of the use of the Ti(III)-H₂O₂ couple for this purpose are that the hydroxyl radical is relatively unselective, so that except with simple substrates a mixture of radicals is likely to be formed, and that it is confined to the study of radicals from compounds which have at least moderate solubility in water. These snags can be overcome by the strategy summarised in reactions (24) and (25): the water-soluble ester is treated with hydrogen peroxide at ca. pH 9, at which the peroxyacid anion is formed relatively rapidly but does not decompose fast; reaction with Ti(III) then gives RCO₂· which (unless R is unsaturated or aromatic) essentially instantaneously yields the radical R· specifically (Ref. 14).



Rates of reaction of organic radicals. The following examples illustrate the use of the redox method combined with e.s.r. in determining rate constants for three types of reaction of organic radicals (their one-electron reduction, one-electron oxidation, and hydrogen-atom abstraction) and also the scope and limitations of the method.

t-Butyl alcohol is an example of a compound of which oxidation by the Ti(III)-H₂O₂ couple can be accounted for by the kinetic analysis based on reactions (17) - (19), where R· is ·CH₂CMe₂(OH); that is, there is no significant contribution to radical termination from processes other than the bimolecular one. The same is true of the oxidation of acetone, with formation of ·CH₂COMe, in acid solution. However, when acetone is oxidised at pH 7 in the presence of EDTA, the plot of [·CH₂COMe] versus [Ti(III)]^{1/2} shows curvature consistent with destruction of the radical by the Ti(III)-EDTA complex, as in reaction (26). The results have been analysed to give k_{26} as $1.4 \times 10^7 M^{-1} s^{-1}$ (Ref. 15).



In contrast, no significant contribution to radical termination by the reduction of the radical $\cdot\text{CHMeCOEt}$ could be detected. On the other hand, when the radical $\cdot\text{CH}_2\text{CHO}$ was generated in the presence of Ti(III)-EDTA , its spectrum could not be detected; evidently its reduction is too rapid to allow $[\cdot\text{CH}_2\text{CHO}]$ to achieve the minimum detectable steady-state concentration. These results show, then, an order of ease of one-electron reduction, $\cdot\text{CH}_2\text{CHO} > \cdot\text{CH}_2\text{COME} > \cdot\text{CHMeCOEt}$, which is consistent with the known electronic influence of alkyl groups, and they also indicate the limitations of this kinetic method: the rate constant must be large enough that the appropriate reaction competes significantly with bimolecular termination but not so large that $[\text{R}\cdot]$ is too small for observation.

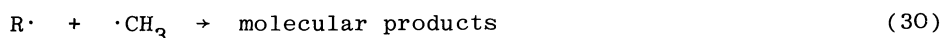
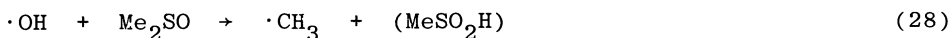
In a complementary study, rate constants have been obtained for the one-electron oxidation of organic radicals by hydrogen peroxide (Ref. 16). A competitive method was used in which radicals $\text{R}\cdot$ and $\text{R}'\cdot$ were generated by use of the $\text{Ti(III)-H}_2\text{O}_2$ couple, where one of the two radicals, $\text{R}'\cdot$, was known not to terminate to a significant extent by oxidation as compared with the bimolecular mode. Under these conditions, it can be shown that $[\text{R}'\cdot]/[\text{R}\cdot]$ should vary linearly with $[\text{Ti(III)}]_{\text{O}_2}^{\frac{1}{2}}$ with a gradient related to the rate constant for reaction (27). For example,



k_{27} for $\cdot\text{CH}_2\text{OH}$, $\cdot\text{CHMe(OEt)}$, and $\cdot\text{CH(OMe)}_2 = 2.3 \times 10^4$, 5.5×10^4 , and $1.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, respectively, at room temperature. In general, k_{27} increases with the introduction of alkyl groups or hydroxyl or alkoxy groups - that is, as the ability of R to sustain a developing positive charge is increased.

The occurrence of these one-electron transfer processes, with large rate constants in some instances, serves to warn investigators to test for the possibility of their significance before drawing conclusions from e.s.r. observations. For example, when ethanol is oxidised with the $\text{Fe(II)-H}_2\text{O}_2$ couple, the predominant radical detected is $\cdot\text{CH}_2\text{CH}_2\text{OH}$, whereas with the $\text{Ti(III)-H}_2\text{O}_2$ system it is $\cdot\text{CHMe(OH)}$. This has been taken as indicating that the hydroxyl radical is not 'free' in the former case, but in fact it is almost certainly the result of the more rapid oxidation of $\cdot\text{CHMe(OH)}$ than of $\cdot\text{CH}_2\text{CH}_2\text{OH}$ by Fe(III) ; in contrast, Ti(IV) is a weak oxidant. On the other hand, when kinetic analysis reveals that such one-electron and other processes are insignificant compared with bimolecular decay, then competitive experiments can be used to determine relative reactivities; if a compound yields two radicals, $\text{R}\cdot$ and $\text{R}'\cdot$, with rate constants k and k' , then providing that it can reasonably be assumed that the three bimolecular termination constants are the same, $[\text{R}\cdot]/[\text{R}'\cdot] = k/k'$.

Absolute rate constants for hydrogen-atom transfer can be obtained providing that the spectra of both the abstracting radical and the radical which results from abstraction can be observed. This is not so for abstraction by hydroxyl, the e.s.r. spectrum of which is not detectable in aqueous solution, but the method can be applied to abstracting agents like the methyl radical. The scheme summarised by reactions (28) - (30) is illustrative (Ref. 17).



The success of the method depends on the fact that $\cdot\text{OH}$ (from $\text{Ti(III)-H}_2\text{O}_2$) reacts with dimethyl sulphoxide with a rate constant close to the diffusion-controlled limit ($7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$), greater than those of its reactions with most other compounds; therefore, with $[\text{Me}_2\text{SO}] > [\text{RH}]$, virtually all hydroxyl radicals react with the sulphoxide. Methyl radicals then react with RH to give $\text{R}\cdot$, and, by arranging concentrations so that the observed concentration

of $R\cdot$ is much less than that of $Me\cdot$, the only significant radical-radical process for $R\cdot$ is reaction (30). Steady-state analysis then shows that

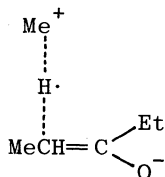
$$k_{29} = k_{30} [R\cdot] / [RH]$$

Some values for k_{29} are in Table 4. The notable feature is that the effectiveness of a substituent in activating the adjacent methylene group to

TABLE 4. Values of k for abstraction of hydrogen by methyl from the underlined CH group

RH	$10^{-3} k/M^{-1} s^{-1}$	RH	$10^{-3} k/M^{-1} s^{-1}$
<u>Me</u> CO ₂ H	0.2	Me <u>CH</u> ₂ CN	1.2
Me <u>CH</u> ₂ CO ₂ H	3.0	Me <u>CH</u> ₂ CN	4.5
Me <u>CH</u> CO ₂ H	9.0	Me <u>CH</u> ₂ COEt	14.0
MeCN	<0.3	Me <u>CH</u> ₂ CO ₂ Me	2.9

hydrogen-atom abstraction falls in the order COEt > CO₂H, CO₂Me > CN. This is different from the order of effectiveness of the group in delocalising an unpaired electron on adjacent carbon, but is the same as that for the mesomeric electron-accepting capacity of the substituents. This points to the importance of polar structures such as



in the full description of the transition state; that is, it reflects the nucleophilic character of the methyl radical.

LINE-WIDTH MEASUREMENTS

Since, from the uncertainty principle, an uncertainty in the life-time of an electron spin-state is correlated with an uncertainty in the energy of the state, it follows that, as the life-time of a radical is reduced, the line-widths of its electron spin resonance absorptions increase. The natural line-widths, governed by relaxation modes, can be very small for a free radical tumbling freely in solution (< 1 μ T), and the increase in width which occurs when the radical takes part in a rapid intermolecular process (e.g. the electron-exchange between naphthalene and its radical-anion) can be readily measured. The appropriate rate constant can be determined from the increase and the applications of the method have been reviewed (Ref. 18).

A somewhat different situation arises when a radical undergoes an intramolecular process which, while not affecting the life-time of the radical as a whole, does affect the life-time of specific molecular states such as conformations. In this case an alternation of line-widths can result. Consider the radical \cdot CH₂OH. At -125°C the spectrum exhibits two doublet-splittings for the C-H protons, consistent with the occurrence of the radical in the conformations

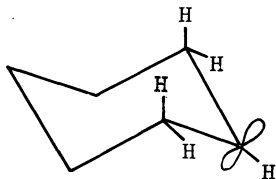


in which H^1 and H^2 are magnetically inequivalent with respect to the unpaired electron and with no, or relatively slow, interconversion. When the temperature is raised, the inner line of each doublet broadens, they then coalesce to a single broad line, and finally, by -58°C , this line sharpens to give overall a 1 : 2 : 1 triplet with equal line-widths. Broadening occurs when the rate of interconversion is of the same order as the hyperfine splitting interval for the two protons. It occurs only for the inner lines because the total spin interaction is altered only when the two protons which exchange places have opposite spins - the situation corresponding to the inner lines - whereas it is unaltered when these protons have like spin. The theory has been described (Ref. 19); line-shape analysis enables the rate of interchange to be calculated provided that the hyperfine splitting interval is known (as it is in this instance, from the spectrum at -125°C , which shows that the interval is 0.088 mT, equivalent to 1.6×10^6 Hz). The Arrhenius parameters obtained for the interconversion above are $E = 4.6 \text{ kcal mol}^{-1}$, $\log(A/s^{-1}) = 12.6$ (Ref. 20).

In the next example - the cyclohexyl radical - line-broadening is associated with the interaction of the unpaired electron with the β -protons. It arises because hyperfine splitting by such protons varies with the dihedral angle, θ , subtended by the β -C-H bond and the half-filled p orbital according to the expression

$$\underline{a}(\beta\text{-H}) = \rho(B_0 + B \cos^2\theta)$$

where B_0 and B are constants ($B_0 \ll B$) and ρ is the spin density at the tervalent carbon (which itself can be obtained from hyperfine splitting constants). The spectrum of the cyclohexyl radical at -80°C shows that the four β -protons couple as two non-equivalent pairs; the larger splitting is assumed to be that from the axial protons, for which θ is smaller than for the equatorial protons, and the result shows that interconversion of



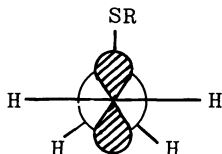
and the alternative chair is slow in terms of the e.s.r. time-scale. As the temperature is raised, line-broadening is observed, consistent with increase in the rate of chair-chair interconversion; the rate constant has been obtained at various temperatures by line-shape analysis, to give the activation energy as $4.9 \pm 0.5 \text{ kcal mol}^{-1}$ (cf. 11 kcal mol^{-1} for cyclohexane itself) (Ref. 21).

In the final example - the propyl radical - both line-broadening effects and the magnitude, and its temperature dependence, of $\underline{a}(\beta\text{-H})$ have been used to obtain information about conformation. Line-broadening corresponds to $\underline{M}_I = 0$ for the α -protons, consistent with the preferential occurrence of the conformations:



(in which H^1 and H^2 are magnetically inequivalent) and with hindrance to their interconversion. This is supported by the relatively large value for $\underline{a}(\beta\text{-H})$, which indicates that $\langle \cos^2\theta \rangle$ is relatively large; moreover, $\underline{a}(\beta\text{-H})$ decreases as the temperature is increased, again compatible with preferred conformations in which θ is small. An estimated value for the barrier to rotation of $1 - 2 \text{ kcal mol}^{-1}$ has been obtained from the temperature-dependence (Ref. 22).

In contrast, $a(\beta\text{-H})$ for the radical $\text{MeSCH}_2\text{CH}_2\cdot$ is relatively small and rises with temperature, consistent with a preferred conformation



Detailed analysis indicates that, although the radical is certainly not a symmetrically 'bridged' species, the $\beta\text{-C-S}$ bond is tipped towards the half-filled p orbital, implying the occurrence of a bonding interaction (Ref. 22).

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