

Electron Paramagnetic Resonance and the Art of Physical-Organic Chemistry¹

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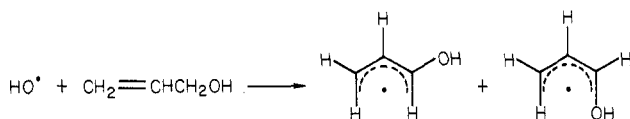
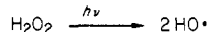
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During the past decade, electron paramagnetic resonance (EPR) spectroscopy has been developed into a remarkably powerful tool for the physical-organic chemist. Though generally simple, both in concept and in practice, a carefully designed EPR experiment can yield results which will answer some questions of considerable sophistication, questions which deal with reaction mechanisms and kinetics, as well as the structural and dynamic properties of free radicals. In this Account we will attempt to illustrate the utility and versatility of EPR spectroscopy by describing a few experiments which have been chosen mainly from work done in our own laboratory.

Basic Requirements

Given a spectrometer, the next most obvious requirement is to find a method for generating a chosen radical which is both efficient and continuous and which works at any desired temperature and uses only a small quantity of material. These conditions are somewhat stringent, but they are dictated by the fact that many radicals of interest in organic chemistry are very short-lived. Solutions to this problem came over a decade ago when several groups showed that UV photolysis of samples within the spectrometer cavity was an excellent method for radical generation.²

Livingston and Zeldes produced a series of α -hydroxyalkyl radicals by UV photolysis of hydrogen peroxide/alcohol mixtures, e.g.³

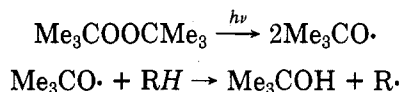


This approach was extended^{4,5} by the use of di-*tert*-butyl peroxide as the photolabile reagent, which has the

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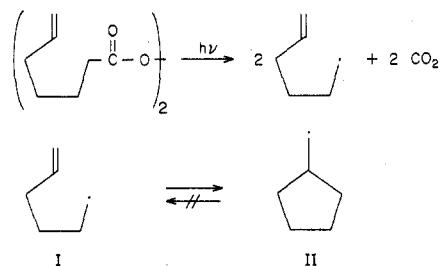
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advantage that it is miscible with most organic liquids. The *tert*-butoxyl radical produced is highly reactive in H-atom abstractions⁶ and, moreover, cannot be observed by EPR spectroscopy in solution.⁷



e.g.,² $\text{RH} = \text{Me}_3\text{CH}, \text{CCl}_3\text{H}, \text{C}_6\text{H}_5\text{CMe}_2\text{H}, \text{CH}_2\text{CH}_2\text{NH}, \text{Me}_3\text{COOH}, \text{C}_6\text{H}_5\text{OH}, \text{Me}_3\text{SiH}, (\text{EtO})_2\text{P}(\text{O})\text{H}, \text{etc.}$

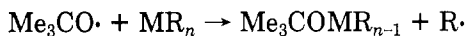
In an outstanding series of papers,^{4,8} Krusic and Kochi described several other methods for radical generation and at the same time demonstrated the potential of EPR as a mechanistic and kinetic tool. For example, they were able to observe the cyclization of the 5-hexenyl radical (I) to cyclopentylmethyl (II) during photolysis of a solution of 6-heptenoyl peroxide at -55°C .



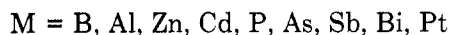
Moreover, they^{8b,d} and others⁹⁻¹³ demonstrated that the

- (1) Issued as N.R.C.C. No. 18395.
- (2) For a recent review, see: Griller, *D. Magn. Reson. Rev.* 1979, 5, 1.
- (3) Livingston, R.; Zeldes, *H. J. Chem. Phys.* 1966, 44, 1245.
- (4) Krusic, P. J.; Kochi, J. K. *J. Am. Chem. Soc.* 1968, 90, 7155. Kochi, J. K.; Krusic, P. J. *Ibid.* 1968, 90, 7157.
- (5) Hudson, A.; Hussain, H. A. *Mol. Phys.* 1969, 16, 199.
- (6) (a) Paul, H.; Small, Jr., R. D.; Scaiano, J. C. *J. Am. Chem. Soc.* 1978, 100, 4520. (b) Wong, S. K. *Ibid.* 1979, 101, 1235.
- (7) Symons, M. C. R. *J. Am. Chem. Soc.* 1969, 91, 5924.
- (8) (a) Krusic, P. J.; Kochi, J. K. *J. Am. Chem. Soc.* 1969, 91, 3938; (b) *Ibid.* 1969, 91, 3942. (c) Kochi, J. K.; Krusic, P. J. *Ibid.* 1969, 91, 3940. (d) *Ibid.* 1969, 91, 3944.
- (9) Ingold, K. U.; Roberts, B. P. "Free Radical Substitution Reactions"; Wiley: New York, 1971. Davies, A. G.; Roberts, B. P. "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, Chapter 10.
- (10) Davies, A. G.; Roberts, B. P. *Chem. Commun.* 1969, 699. Kochi, J. K.; Krusic, P. J. *Spec. Publ.-Chem. Soc.* 1970, No. 24, 147.

tert-butoxyl radical reacts at the metal centers of a variety of organometallic compounds by a bimolecular homolytic substitution, S_{H2} , process.⁹ Apart from its mechanistic significance, this reaction provides another simple route to radicals which cannot be obtained by H-atom abstraction, e.g., *n*-alkyl radicals,¹⁰ phenyl radicals,¹¹ and dialkylaminy radicals.¹²



e.g.,¹³



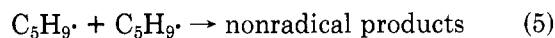
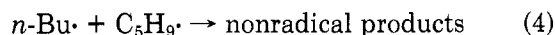
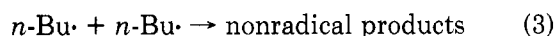
Similar S_{H2} reactions may of course also be induced by radicals other than *tert*-butoxyl.⁹

Techniques for the photolytic generation of a chosen radical over a wide range of temperatures (-170 to 300 °C) have made the EPR machine a useful instrument for the physical-organic chemist. Since there is nowadays no particular difficulty in generating a specific radical, its formation, the reactions it can undergo, and its structure can all be examined with relative ease.

Radical-Molecule Reactions

The EPR experiments described in this section have been chosen to illustrate some of the methods by which the kinetics and mechanisms of radical-molecule reactions can be examined.

Relative Rates of Reaction of *tert*-Butoxyl with Trialkylboranes. Continuous UV photolysis of a mixture of di-*tert*-butyl peroxide and tri-*n*-butylborane gives an excellent spectrum of the *n*-butyl radical.¹⁰ In the presence of an appropriate concentration of cyclopentane the spectrum of the cyclopentyl radical can also be observed.¹³ The radicals are destroyed by bimolecular processes and the overall steady-state system can be represented by eq 1-5. Since it is now well estab-



lished that the bimolecular self-reactions of all simple alkyl radicals proceed at the diffusion-controlled limit¹⁴⁻¹⁸ (which means that $k_3 = k_4 = k_5$), this scheme yields the relation

$$\frac{k_1}{k_2} = \frac{[n\text{-Bu}\cdot][\text{C}_5\text{H}_{10}]}{[\text{C}_5\text{H}_9\cdot][(n\text{-Bu})_3\text{B}]}$$

(11) Furimsky, E.; Howard, J. A.; Morton, J. R. *J. Am. Chem. Soc.* **1972**, *94*, 5932. Phenyl is too reactive to be detected directly by EPR under these conditions.

(12) Dennis, R. W.; Roberts, B. P. *J. Organometal. Chem.* **1972**, *43*, C2. Roberts, J. R.; Ingold, K. U. *J. Am. Chem. Soc.* **1973**, *95*, 3228. Some $\text{R}_2\text{N}\cdot$ can be generated by H abstraction from R_2NH using *tert*-butoxyl. Maeda, Y.; Ingold, K. U. *J. Am. Chem. Soc.* **1980**, *102*, 328.

(13) Davies, A. G.; Griller, D.; Roberts, B. P. *J. Chem. Soc. B*, **1971**, 1823.

(14) Ingold, K. U. "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, **1973**; Vol. 1, Chapter 2.

(15) Watts, G. B.; Ingold, K. U. *J. Am. Chem. Soc.* **1972**, *94*, 491.

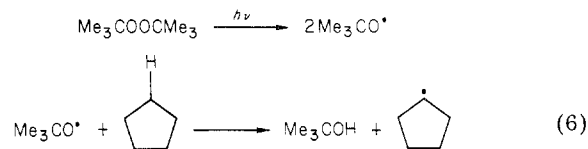
(16) Griller, D.; Ingold, K. U. *Int. J. Chem. Kinet.* **1974**, *6*, 453.

(17) Schuh, H.; Fischer, H. *Int. J. Chem. Kinet.* **1976**, *8*, 341; *Helv. Chim. Acta* **1978**, *61*, 2130, 2463.

(18) Lezni, M.; Schuh, H.; Fischer, H. *Int. J. Chem. Kinet.* **1979**, *11*, 705.

Similar experiments with other trialkylboranes and cyclopentane yield the relative rate constants for their *tert*-butoxyldealkylation.¹³ Reactivity decreases along the series $(n\text{-Bu})_3\text{B} > (i\text{-Bu})_3\text{B} > (sec\text{-Bu})_3\text{B}$, though all three boranes are more reactive than C_5H_{10} . This unusual reactivity order, in which a secondary alkyl is produced less readily than a primary alkyl, is due to steric factors, i.e., the approach of *tert*-butoxyl to the small, central boron atom becomes more difficult as the alkyl groups become more branched. It has been shown^{13,19} that the activation energy for dealkylation is greater for $(sec\text{-Bu})_3\text{B}$ than for $(n\text{-Bu})_3\text{B}$.

The relative rate constants for these S_{H2} and indeed all reactions of *tert*-butoxyl can now be put on an absolute basis thanks to a time-resolved EPR study carried out by Wong.^{6b} The experiment was, in essence, flash photolysis using EPR to detect the growth of alkyl radicals derived in a hydrogen-abstraction reaction.



Thus, k_6 was found to be $3.4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C.^{6b}

The EPR technique is particularly advantageous because it allows direct detection of simple alkyl radicals. This cannot be easily achieved by using flash photolysis with its normal optical detection because of the very short wavelengths at which alkyls absorb. For example, in a complementary laser flash photolysis experiment^{6a} using optical detection, the radical derived from benzhydrol, which absorbs strongly in the UV-visible, was used as a probe of the *tert*-butoxyl-hydrocarbon reaction. In this experiment^{6a} k_6 was found to be $8.8 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, in fair agreement with the EPR result.

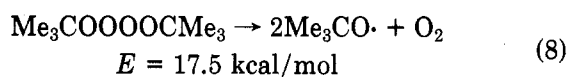
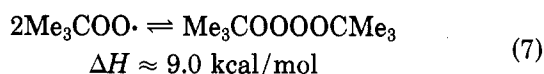
Absolute Rate Constants for *tert*-Butylperoxyl Radical-Molecule Reactions. Many of the early kinetic EPR experiments were concerned with the bimolecular self-reactions of peroxyl radicals.²⁰ A happy marriage of the EPR work with more conventional kinetic methods²¹ revealed that *tert*-alkylperoxyl radicals decay with second-order kinetics at a rate which is very much less than the diffusion-controlled limit. The radicals exist in equilibrium with a tetroxide, the irreversible decay of which is slow because it has an appreciable activation energy. The *tert*-butylperoxyl radicals decay somewhat more slowly than other *tert*-

(19) Similar behavior has been observed for *tert*-butoxyldealkylation of dialkyl selenides. See: Scaiano, J. C.; Schmid, P.; Ingold, K. U. *J. Organometal. Chem.* **1976**, *121*, C4. However, the relative ease of displacement of alkyl groups in mixed alkyl boranes by *n*-BuS· follows the usual sequence, primary < secondary < tertiary. See: Davies, A. G.; Maki, T.; Roberts, B. P.; Pelter, A.; Sharrocks, D. N. *J. Organometal. Chem.* **1974**, *82*, 301.

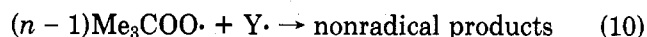
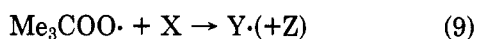
(20) Ingold, K. U. *Acc. Chem. Res.* **1969**, *2*, 1. Piette, L. M.; Landgraf, W. C. *J. Chem. Phys.* **1960**, *32*, 1107. Thomas, J. R. *J. Am. Chem. Soc.* **1963**, *85*, 591. Bersohn, M.; Thomas, J. R. *Ibid.* **1964**, *86*, 959. Ingold, K. U.; Morton, J. R. *Ibid.* **1964**, *86*, 3400. Thomas, J. R. *Ibid.* **1965**, *87*, 3935. Bartlett, P. D.; Guaraldi, G. *Ibid.* **1967**, *89*, 4799. Thomas, J. R.; Ingold, K. U. *Adv. Chem. Ser. No. 75* **1968**, 258. Adamic, K.; Howard, J. A.; Ingold, K. U. *Chem. Commun.* **1969**, 505; *Can. J. Chem.* **1969**, *47*, 3793, 3803. Bennett, J. E.; Brown, D. M.; Mile, B. *Chem. Commun.* **1969**, 504; *Trans. Faraday Soc.* **1970**, *66*, 386, 397.

(21) Blanchard, H. S.; *J. Am. Chem. Soc.* **1959**, *81*, 4548. Bartlett, P. D.; Traylor, T. G. *Ibid.* **1963**, *85*, 2407. Hiatt, R.; Clipham, J.; Visser, T. *Can. J. Chem.* **1964**, *42*, 2754. Factor, A.; Russell, C. A.; Traylor, T. G. *J. Am. Chem. Soc.* **1965**, *87*, 3692. Thomas, J. R. *Ibid.* **1967**, *89*, 4872. Howard, J. A.; Ingold, K. U.; Symonds, M. *Can. J. Chem.* **1968**, *46*, 1017. Howard, J. A.; Ingold, K. U. *Ibid.* **1968**, *46*, 2655; **1969**, *47*, 3793, 3797.

alkylperoxyls. Their overall activation energy for decay is ca. 8.5 kcal/mol. The reaction mechanism is given by



The *tert*-butylperoxyl radicals are produced either by H abstraction from Me_3COOH or by generating $\text{Me}_3\text{C}\cdot$ in an oxygen-containing solvent. At the concentrations normally used in an EPR experiment (ca. 10^{-5} – 10^{-6} M) the *tert*-butylperoxyl radicals will decay extremely slowly at temperatures below ca. -30°C unless some compound, X, is present with which they can react rapidly. In such cases, the *tert*-butylperoxyl radicals are destroyed more rapidly and the decrease in their concentration can be monitored.²² If $[\text{X}] \gg [\text{Me}_3\text{COO}\cdot]$, decay will occur with pseudo-first-order kinetics (eq 9 and 10), where $C = nk_9[\text{X}]$ and n is the



$$-d[\text{Me}_3\text{COO}\cdot]/dt = C[\text{Me}_3\text{COO}\cdot]$$

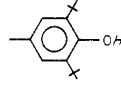
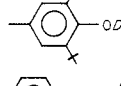
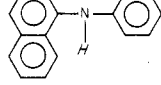
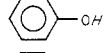
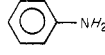
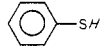
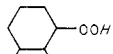
stoichiometric factor for the overall reaction. The value of n can be determined by monitoring the change in $[\text{Me}_3\text{COO}\cdot]$ upon addition of a deficiency of X. These simple techniques are of considerable value because of the technical importance of autoxidation reactions.

The technique outlined above has proved invaluable in examining the kinetics and rates of reaction of peroxyl radicals with metal chelates,²³ phosphines and phosphites,²⁴ phenols, thiophenols, and aromatic amines,^{25,26} and secondary alkyl hydroperoxides.²⁷ Most of these reactions would be difficult to study quantitatively by conventional methods at even one temperature. The EPR method can be easily applied over a wide temperature range. The derived Arrhenius parameters are often surprising. For example, it has been found that H-atom abstractions from heteroatoms generally have low activation energies and Arrhenius preexponential factors very much lower than those considered "normal" in gas kinetics (viz., $10^{8.5 \pm 0.5} \text{ M}^{-1} \text{ s}^{-1}$).²⁸ Some results for reaction 11 are given in Table I.



Reactivity in hydrogen abstractions is controlled to a large extent by the antibonding interaction between the H-donor and H-acceptor atoms, i.e., by the triplet repulsion energy in the transition state due to the oc-

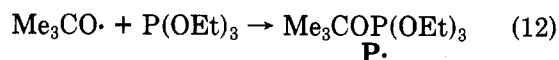
Table I
Arrhenius Parameters for Some Examples of Reaction 11

AH	E_{11} , kcal/mol	\log (A_{11}/M^{-1} s^{-1})	$k_{11}^{25^\circ}$ $\text{M}^{-1} \text{ s}^{-1} \times$ 10^{-3}	ref
	0.8	4.6	10	25
	1.4	4.2	1.5	25
	1.0	5.1	23	25
	5.2	7.2	2.4	26
	5.0	6.6	0.9	26
	1.1	4.5	5.0	26
	4.5	6.0	0.5	27

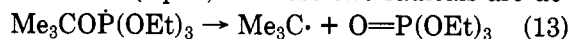
currence of parallel electron spins on these two atoms.²⁹ The "low" activation energies and "low" A factors for the above reactions arise because there is only a weak triplet repulsion between oxygen and oxygen, nitrogen, or sulfur.²⁹ The transition states are all very "tight", with little stretching of the bond being broken.

The large temperature range over which kinetic EPR studies can be carried out makes this technique the most reliable source of Arrhenius parameters for H abstractions and other radical-molecule reactions in solution.

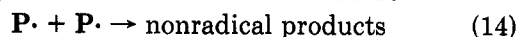
Detection of Intermediates in Reactions at Trivalent Phosphorus. A long-standing question in physical-organic chemistry was: Are tetravalent phosphorus centered radicals (phosphoranyl) formed as distinct intermediates in radical reactions at trivalent phosphorus or are they merely the transition states in such reactions? A useful approach to this problem has been provided by EPR spectroscopy.^{8,30-33} For example,^{31,32} continuous photolysis of a hydrocarbon solution containing di-*tert*-butyl peroxide and triethyl phosphite at temperatures below ca. -90°C gives the EPR spectrum of the *tert*-butoxytriethoxyphosphoranyl radical, P.



At temperatures above -90°C the *tert*-butyl radical is also present, and above -20°C it is the only radical that can be detected (eq 13). These two radicals are de-



stroyed by the bimolecular reactions 14–16.



(29) Zavitsas, A. A.; Melikian, A. A. *J. Am. Chem. Soc.* **1975**, *97*, 2757. Mahoney, L. R.; DaRooge, M. A. *Ibid.* **1975**, *97*, 4722.

(30) Kochi, J. K.; Krusic, P. J. *J. Am. Chem. Soc.* **1969**, *91*, 3944. (31) Davies, A. G.; Griller, D.; Roberts, B. P. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 738; *J. Chem. Soc., Perkin Trans. 2* **1972**, 993.

(32) Watts, G. B.; Griller, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1972**, *94*, 8784.

(33) For comprehensive reviews of phosphoranyl, see: Schipper, P.; Jansen, E. H. J. M.; Buck, H. M. *Top. Phosphorus Chem.* **1977**, *9*, 407. Roberts, B. P. *Adv. Free-Radical Chem.*, in press.

(22) Provided, of course, that X will not itself yield a *tert*-alkylperoxyl. (23) Howard, J. A.; Ohkatsu, Y.; Chenier, J. H. B.; Ingold, K. U. *Can. J. Chem.* **1973**, *51*, 1543. Howard, J. A.; Chenier, J. H. B. *Ibid.* **1976**, *54*, 382.

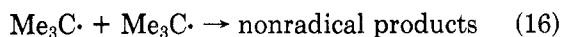
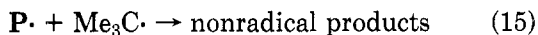
(24) Furimsky, E.; Howard, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 369.

(25) Howard, J. A.; Furimsky, E. *Can. J. Chem.* **1973**, *51*, 3738.

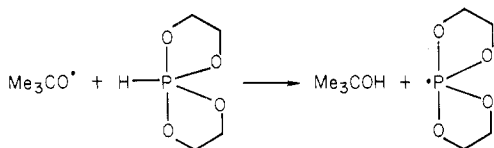
(26) Chenier, J. H. B.; Furimsky, E.; Howard, J. A. *Can. J. Chem.* **1974**, *52*, 3682.

(27) Chenier, J. H. B.; Howard, J. A. *Can. J. Chem.* **1975**, *53*, 623.

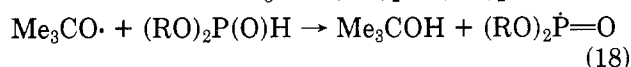
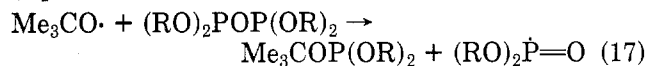
(28) So-called "normal" values have been derived almost exclusively for a carbon-centered radical abstracting hydrogen bound to carbon. See, e.g.: Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976; p 148.



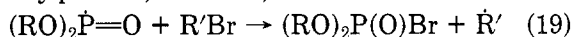
A variety of other phosphoranyl radicals have been generated both by substitution at trivalent phosphorus^{33,34} and by H abstraction from certain spirophosphoranes.³⁵



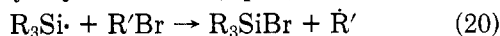
Dialkyloxyphosphonyl radicals, $(RO)_2\dot{P}O$, have also been prepared by substitution and by H abstraction³⁶ (eq 17 and 18). These radicals have been used³⁶ to



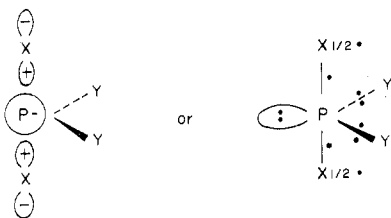
generate alkyl radicals from alkyl bromides via reaction 19. They provide, therefore, an alternative route to the



more usual bromide to alkyl radical reaction which involves trialkylsilyl radicals³⁷ (eq 20).



The EPR spectra of phosphoranyl radicals provide detailed information about their structures.^{33,38} The majority have a trigonal-bipyramidal structure with two axial and two equatorial substituents. The unpaired electron occupies a molecular orbital which can be represented as a three-center nonbonding orbital involving the axial ligand orbitals modified by mixing with the phosphorus 3s orbital in an antibonding combination, i.e.,



EPR spectroscopy has proved to be the most direct and useful method for studying the rates and possible mechanisms by which the axial and equatorial ligands exchange position.^{33,39} The role of ligand electronegativity as a factor controlling the lifetime and frag-

(34) Davies, A. G.; Griller, D.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* 1972, 2224. Griller, D.; Roberts, B. P. *Ibid.* 1973, 1339.

(35) Griller, D.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* 1973, 1416.

(36) Davies, A. G.; Griller, D.; Roberts, B. P. *J. Am. Chem. Soc.* 1972, 94, 1782.

(37) Hudson, A.; Jackson, R. A. *Chem. Commun.* 1969, 1323.

(38) See, e.g.: Davies, A. G.; Dennis, R. W.; Griller, D.; Ingold, K. U.; Roberts, B. P. *Mol. Phys.* 1973, 25, 989. Davies, A. G.; Parrott, M. J.; Roberts, B. P. *Chem. Commun.* 1974, 973. Gilbro, T.; Williams, F. J. *Am. Chem. Soc.* 1974, 96, 5032. Nishikida, K.; Williams, F. *Ibid.* 1975, 97, 5462. Colussi, A. J.; Morton, J. R.; Preston, K. F. *J. Chem. Phys.* 1975, 62, 2004.

(39) Krusic, P. J.; Meakin, P. *Chem. Phys. Lett.* 1973, 18, 347. Griller, D.; Ingold, K. U. *J. Am. Chem. Soc.* 1975, 97, 1813. Dennis, R. W.; Elson, I. H.; Roberts, B. P.; Dobbie, R. C. *J. Chem. Soc., Perkin Trans. 2* 1977, 889. Cooper, J. W.; Parrott, M. J.; Roberts, B. P. *Ibid.* 1977, 730. Hay, R. S.; Roberts, B. P. *Ibid.* 1978, 770. Nakanishi, A.; Nishikida, K.; Ben-trude, W. G. *J. Am. Chem. Soc.* 1978, 100, 6398, 6403. Roberts, B. P.; Singh, K. *Chem. Commun.* 1979, 980.

mentation behavior of phosphoranyl radicals has also been studied by EPR.⁴⁰

The techniques used to study phosphoranyl radicals have recently been applied to homolytic organosulfur chemistry and have led to the discovery of structurally analogous trivalent and pentavalent sulfur-centered radicals.⁴¹

Kinetics of a Unimolecular Radical Reaction

The observation that the *tert*-butoxytriethoxyphosphoranyl radical, $P \cdot$, decomposes to give the *tert*-butyl radical led to a simple method for measuring the rates of unimolecular radical reactions.^{31,32} If we refer back to reactions 12–16, then under conditions of steady photolysis (where the radical concentrations do not change with time) we can write

$$\frac{d[Me_3C \cdot]}{dt} = 0 = k_{13}[P \cdot] - 2k_{16}[Me_3C \cdot]^2 - 2k_{15}[P \cdot][Me_3C \cdot]$$

This can be rearranged into the form

$$\frac{1}{[Me_3C \cdot]} = \frac{2k_{16}[Me_3C \cdot]}{k_{13}[P \cdot]} + \frac{2k_{15}}{k_{13}}$$

and so a plot of $1/[Me_3C \cdot]$ vs. $[Me_3C \cdot]/[P \cdot]$ (the radical concentration being changed by varying the light intensity) gives a straight line, the slope of which is $2k_{16}/k_{13}$.^{31,32} The rate constant for the bimolecular self-reaction of *tert*-butyl, $2k_{16}$, could be measured (see below) or calculated (since it is a diffusion-controlled process).¹⁷ In this way the activation energy for reaction 13 was found to be 10.3 kcal/mol with a preexponential factor of $10^{12.95} \text{ s}^{-1}$, corresponding to $k_{13} = 5 \times 10^5 \text{ s}^{-1}$ at 30 °C.³¹

It should be clear that the same technique can be applied to obtain the rate constant for any unimolecular radical reaction provided that both the reagent radical and the product radical can be observed by EPR. The technique has been successfully used with a variety of radical scission reactions and rearrangements. The results are interesting in themselves but, more importantly, unimolecular radical reactions that proceed at known rates provide the most reliable “clocks” for measuring the rates of radical–molecule reactions. Work in this area will form the subject of a future Account.

Radical–Radical Reactions

The bimolecular self-reactions of many radicals proceed at the diffusion-controlled limit. Under typical experimental conditions these radicals can be generated at concentrations of $\leq 10^{-6} \text{ M}$ in the EPR spectrometer. When the light is shut off, ca. 50% of the radicals are destroyed within 1–2 ms. A special technique which allows many identical radical decays to be collected and

(40) Davies, A. G.; Dennis, R. W.; Griller, D.; Roberts, B. P. *J. Organometal. Chem.* 1972, 42, C47.

(41) See, e.g.: Morton, J. R.; Preston, K. F. *J. Chem. Phys.* 1973, 58, 2657. Chapman, J. S.; Cooper, J. W.; Roberts, B. P. *J. Chem. Soc., Chem. Commun.* 1976, 835. Gilbert, B. C.; Kirk, C. M.; Norman, R. O. C.; Laue, H. A. H. *J. Chem. Soc., Perkin Trans. 2* 1977, 497. Gara, W. B.; Roberts, B. P. *Ibid.* 1977, 1708. Gara, W. B.; Roberts, B. P.; Gilbert, B. C. *J. Chem. Res., Synop.* 1977, 152. Gilbert, B. C.; Kirk, C. M.; Norman, R. O. C. *Ibid.* 1977, 173. Cooper, J. W.; Roberts, B. P. *Chem. Commun.* 1977, 228. Gara, W. B.; Roberts, B. P. *J. Organometal. Chem.* 1977, 135, C20. Gara, W. B.; Roberts, B. P.; Kirk, C. M.; Gilbert, B. C.; Norman, R. O. C. *J. Magn. Reson.* 1977, 27, 509.

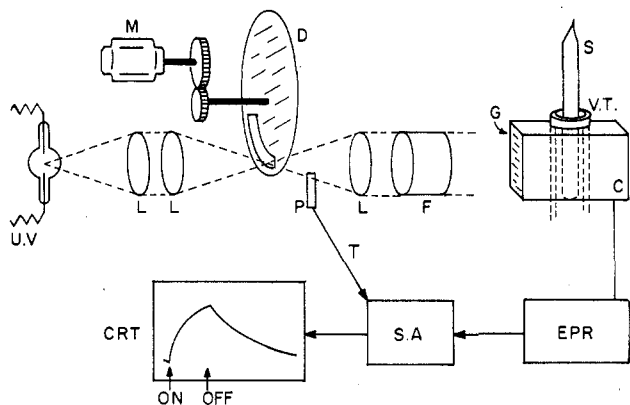
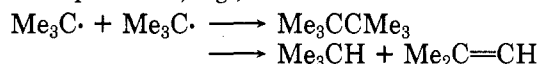


Figure 1. Experimental arrangement for fast kinetics by EPR: C, cavity of spectrometer; CRT, cathode ray tube displaying the collected decay signals (averaged) and showing the light-on and light-off positions; D, sectored metal disk; EPR, spectrometer's detector, amplifier, etc.; F, filter to remove infrared and visible radiation; G, 50% transmittance grid; L, quartz lenses; M, 1800-rpm synchronous motor; P, photocell; S, sample; S.A., signal averager; T, trigger pulse to initiate signal collection with each light flash; UV, 500-W high-pressure mercury lamp; V.T., variable temperature Dewar insert.

"averaged" so as to improve the signal to noise is used to follow such fast reactions. This technique was originally pioneered by Fessenden⁴² and by Weiner and Hammond.⁴³ The equipment is shown diagrammatically in Figure 1. The UV light is brought to a focus outside the EPR cavity, and there it is mechanically chopped by a rotating sectored metal disk. When the light falls on the sample to generate the radicals it also falls on a photocell which provides a trigger pulse. This is fed to the signal averager and initiates signal collection. Several thousand light pulses are generally required to obtain a smooth decay trace.

This kind of equipment has been used extensively to study the bimolecular self-reactions of many classes of free radicals. The vast majority react at, or near, the diffusion-controlled limit—which means that the rate constant is ca. $4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in typical solvents at ambient temperatures. This is true both for carbon-centered radicals, e.g., $\text{Me}\cdot$,¹⁵ $\text{Me}_3\text{CCH}_2\cdot$,¹⁵ $\text{C}_6\text{H}_5\text{CH}_2\cdot$,¹⁸ $\text{Me}_3\text{C}\cdot$,^{15,17} $\text{Et}_3\text{C}\cdot$,¹⁵ and $\text{HC}(\text{CN})_2\cdot$,⁴⁴ and for heteroatom-centered radicals, e.g., $\text{Me}_3\text{Si}\cdot$,¹⁵ $\text{Me}_3\text{Sn}\cdot$,¹⁵ $\text{Et}_2\text{N}\cdot$,¹¹ $\text{Et}_2\text{NNH}\cdot$,⁴⁵ $\text{H}_2\text{NNMe}\cdot$,⁴⁶ $\text{MeONMe}\cdot$,⁴⁷ $(\text{EtO})_2\text{P}\cdot$,⁴⁸ $(\text{EtO})_2\text{P}=\text{O}\cdot$,⁴⁸ and $(\text{Me}_2\text{CH})_2\text{NS}\cdot$.⁴⁹ At the experimental temperatures employed all these radicals gave thermodynamically stable dimers and/or β -disproportionation products, e.g.,



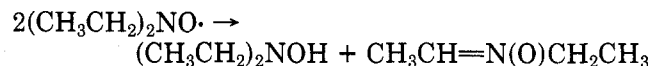
More recently Fischer, Schuh, and Lehni have used this technique to carry out a careful series of measurements on the self-reactions of *tert*-butyl¹⁷ and benzyl¹⁸ in a variety of solvents. The data obtained were sufficiently precise that they allowed discrimina-

tion between various models for radical diffusion in solution. It was also suggested that combination/disproportionation ratios are controlled by the relative orientations of radicals in the solvent cage.

The technique of modulation spectroscopy⁵⁰ has also been applied to EPR studies of radical self-reactions by Paul.^{6a,51,52} This approach is somewhat different from the time-resolved experiment described above and is, in principle, more powerful. The initiating light is modulated as a sine wave and the EPR signal is processed through a phase sensitive detector with the initiating sine wave as a reference. When the half-life of the radical becomes similar to the frequency of the sine wave, the out-of-phase signal detected becomes quite significant. Analysis of the frequency dependence of the signals yields quite sophisticated data. For example, in a system containing two different radicals it is possible to determine the rates of self-reaction and the rate of cross reaction between unlike radicals.⁵²

Radicals which do not give thermodynamically stable products generally decay rather slowly. Very often decay occurs via a thermodynamically unstable dimer with which the radicals exist in equilibrium. One example mentioned above was *tert*-butylperoxyl. At ambient temperatures this radical undergoes a relatively slow bimolecular self-reaction ($2k = 1.2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ at 30 °C). The slowness of this reaction is a consequence of the low equilibrium concentration of the tetroxide dimer (reaction 7) and the relatively high activation energy for its irreversible decomposition (reaction 8).

There are some other classes of radicals which undergo bimolecular self-reaction at rates which are slower than diffusion controlled, e.g., *sec*-alkylperoxyls.⁵³ However, among the most interesting of radicals in this category are di-*n*-alkyl nitroxides^{54,55} and acyl methyl nitroxides.⁵⁶ These radicals undergo bimolecular disproportionation reactions to give hydroxylamine and nitron,^{54,57} e.g.,⁵⁴



The reaction kinetics are characterized by abnormally low *A* factors (10^3 – $10^5 \text{ M}^{-1} \text{ s}^{-1}$) and activation energies which are sometimes less than that required for diffusion. These results have been interpreted^{54–56} in terms of a model in which the majority of radical–radical encounters do not lead to reaction because the dipole–dipole interaction between nitroxide pairs within a solvent cage is sufficient to hold them in an orientation which disfavors reaction. The common fate of most

(50) For reviews, see: Hunziker, H. E. *IBM J. Res. Develop.* 1971, 15, 10. Günthard, H. H. *Ber. Bunsenges. Phys. Chem.* 1974, 78, 1110.

(51) Paul, H. *Chem. Phys.* 1976, 15, 115; *J. Phys. Chem.* 1978, 82, 2754; *Chem. Phys.* 1979, 40, 265.

(52) Paul, H. *Int. J. Chem. Kinet.* 1979, 11, 495.

(53) Russell, G. A. *J. Am. Chem. Soc.* 1957, 79, 3871. Ingold, K. U. *Acc. Chem. Res.* 1969, 2, 1. Lindsay, D.; Howard, J. A.; Horswill, E. C.; Iton, L.; Ingold, K. U.; Cobbley, T.; Li, A. *Can. J. Chem.* 1973, 51, 870. Hiatt, R. R.; Glover, L. C.; Mosher, H. S. *J. Am. Chem. Soc.* 1975, 97, 1556.

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(42) Fessenden, R. W. *J. Phys. Chem.* 1964, 68, 1508.

(43) Weiner, S.; Hammond, G. S. *J. Am. Chem. Soc.* 1968, 90, 1659; 1969, 91, 986.

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(45) Malatesta, V.; Ingold, K. U. *J. Am. Chem. Soc.* 1974, 96, 3949.

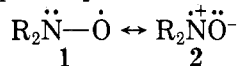
(46) Kaba, R. A.; Lunazzi, L.; Lindsay, D.; Ingold, K. U. *J. Am. Chem. Soc.* 1975, 97, 6762.

(47) Kaba, R. A.; Ingold, K. U. *J. Am. Chem. Soc.* 1976, 98, 7375.

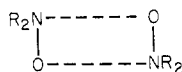
(48) Griller, D.; Roberts, B. P.; Davies, A. G.; Ingold, K. U. *J. Am. Chem. Soc.* 1974, 96, 554.

(49) Maillard, B.; Ingold, K. U. *J. Am. Chem. Soc.* 1976, 98, 521.

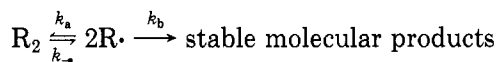
radical pairs is cage escape rather than chemical reaction. Since relatively few encounters lead to products, the free nitroxide radicals are in equilibrium with caged pairs and the measured rate constants are made up from a composite of elementary rate and equilibrium constants. The dipole moments of nitroxides are large (ca. 3 D) and suggest that canonical structures 1 and 2 are of about equal importance. Calculation⁵⁵ based



on a simple dipole interaction for a pair of nitroxides in the following arrangement are consistent with the observed^{54,55} "enthalpies" for the "monomer-dimer equilibrium".



One of the more interesting consequences of bimolecular radical decay reactions occurring under conditions where the radicals are in equilibrium with a dimer is that the measured kinetics for radical decay are frequently *first order* in radical concentration! This kinetic "booby trap" awaits the unwary whenever the concentration of the dimer is larger than the concentration of the radical. Formal kinetic derivations have been given.^{58,59} For example, for the reaction system

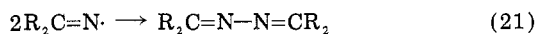


decay of $\text{R}\cdot$ will be first order if $2k_a[\text{R}\cdot]/k_{-a} > 1$ with $k_{\text{exp}} = k_b k_{-a}/2k_a$. That is, by monitoring the change in the concentration of $\text{R}\cdot$ one is effectively monitoring the change in $[\text{R}_2]$ and the dimer certainly decomposes with first-order kinetics.

First-order decay kinetics for bimolecular radical reactions have been identified for many classes of radical, e.g., certain phenoxy ($\text{ArO}\cdot$),⁵⁸ dialkyliminoxyl ($\text{R}_1\text{R}_2\text{C}=\text{NO}\cdot$),⁵⁹ 2,2-dialkylhydrazyls ($\text{R}_2\text{NNH}\cdot$),⁴⁵ and *N*-alkoxyanilinyl (RONC_6H_5)⁴⁷ radicals.

Persistent Radicals

What happens if a radical cannot undergo a disproportionation and steric factors retard dimerization? Obviously the rate of the bimolecular self-reaction must be reduced below the diffusion-controlled limit. This effect can be illustrated by the results of a kinetic EPR study of some iminyl radicals.⁶⁰ Decay is a bimolecular dimerization to the corresponding azine, but there is an impressive decrease in the rate constants as the bulk of the radical is increased (eq 21).



R	k_{21} ($\text{M}^{-1} \text{s}^{-1}$) at -35°C
CF_3	4×10^9
Me_2CH	4×10^7
1-adamantyl	5×10^4
Me_3C	4×10^2

Steric hindrance may, of course, be so great that dimerization simply cannot occur. If disproportionation is also impossible, the radicals will either not decay or,

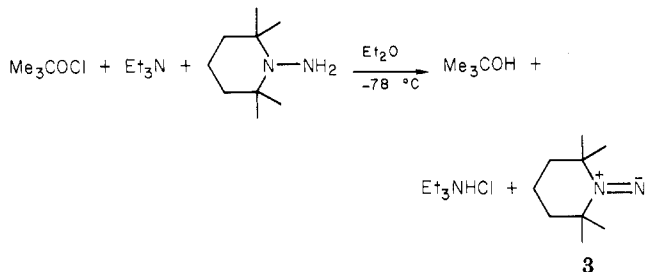
(58) Weiner, S. A.; Mahoney, L. R. *J. Am. Chem. Soc.* **1972**, *94*, 5029.

(59) Brokenshire, J. L.; Roberts, J. R.; Ingold, K. U. *J. Am. Chem. Soc.* **1972**, *94*, 7040.

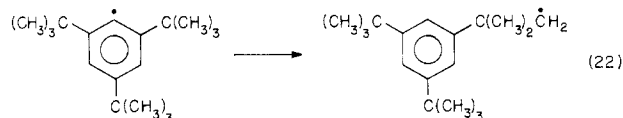
(60) Griller, D.; Mendenhall, G. D.; van Hoof, W.; Ingold, K. U. *J. Am. Chem. Soc.* **1974**, *96*, 6068.

if they do decay, it will be by some unimolecular (i.e., intramolecular) process or by reaction with some species present in their environment, e.g., the solvent or adventitious oxygen. Such radicals will be relatively long-lived. In an earlier Account⁶¹ we argued that all radicals showing *kinetic* "stability" should be referred to as *persistent* radicals. This word was chosen to contrast with *transient* radicals which are those that undergo bimolecular self-reactions at the diffusion-controlled limit. Persistent was also chosen in order that the *kinetic* "stability" of a radical could be clearly distinguished from its *thermodynamic* "stability". The latter can best be defined in terms of the *stabilization energy* of a radical. For example, benzyl is a transient radical¹⁸ for which the stabilization energy = $D[\text{C}_2\text{H}_5-\text{H}] - D[\text{C}_6\text{H}_5\text{CH}_2-\text{H}] = 13 \text{ kcal/mol}$.

Gomberg, in his original paper on triphenylmethyl,⁶² suggested that its long lifetime was probably due to steric hindrance to dimerization. In subsequent years this idea was almost forgotten and resonance stabilization was generally invoked to explain the behavior of the *stable* radical, triphenylmethyl. However, when Gomberg's original ideas were revived, the number and variety of persistent radicals underwent explosive growth.⁶³ Indeed, the concept of steric protection of a highly reactive center has even led to the synthesis of a persistent amino nitrene, **3**,⁶⁴ which in ether solution has a half-life of hours at -78°C .



The detailed mechanisms by which persistent carbon-centered radicals decay have been worked out in only a few instances, but perhaps the most fascinating story relates to the decay of certain sterically hindered phenyl radicals^{65,66} (eq 22). Decay occurs by an in-



tramolecular H-atom transfer which appears to involve extensive quantum mechanical tunneling. This process can be illustrated by the behavior of the relatively persistent 2,4,6-tri-*tert*-butylphenyl and the much more persistent 2,4,6-tri-*tert*-(perdeuteriobutyl)phenyl. Decay occurs by intramolecular H (or D) transfer from an *o*-*tert*-butyl group via a five-center cyclic transition state.

(61) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1976**, *8*, 13.

(62) Gomberg, M. *J. Am. Chem. Soc.* **1900**, *22*, 757.

(63) For a recent summary of the literature on persistent radicals, see: Griller, D.; Marriotti, P. R. *Int. J. Chem. Kinet.* **1979**, *11*, 1163.

(64) Hinsberg, W. D.; Dervan, P. B. *J. Am. Chem. Soc.* **1978**, *100*, 1608; **1979**, *101*, 6142.

(65) Brunton, G.; Griller, D.; Barclay, L. R. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 6803.

(66) Brunton, G.; Gray, J. A.; Griller, D.; Barclay, L. R. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1978**, *100*, 4197.

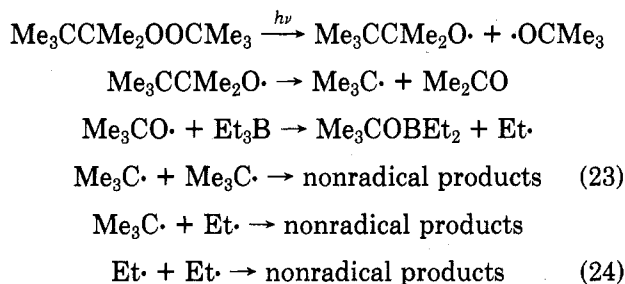
The rate constants for H transfer, k_{22}^H , and for D transfer, k_{22}^D , could be determined by direct EPR monitoring of the decay of the phenyls. In the temperature range -30 to -120 °C normal Arrhenius plots of the kinetic data give very different A factors for H and D transfer.^{65,66} Moreover, at low temperatures in solid matrixes⁶⁶ (-120 to -245 °C) k_{22}^H becomes essentially independent of temperature so that the relationship between $\log k_{22}$ and $1/T$ is nonlinear. Furthermore, the kinetic isotope effect, k_{22}^H/k_{22}^D , is greater than the "classical" maximum. (The classical maximum isotope effect is calculated by assuming that all zero-point energy in the bond is lost in the transition state). For example, at -30 °C the classical maximum isotope effect is 17 while the observed value is 80. These results and those of others⁶⁷ suggest that quantum-mechanical tunneling can be quite important in H-atom transfers.

Problem Solving

The application of EPR to physical-organic problems will be illustrated by two examples.

The *tert*-Butyl Self-Reaction. Despite evidence (derived from classical rotating-sector studies⁶⁸ and kinetic EPR¹⁵) that the bimolecular self-reaction of $\text{Me}_3\text{C}\cdot$ occurred at the diffusion-controlled limit in solution, there was a period when gas kinetic data suggested that this reaction in the gas phase was some three orders of magnitude slower than the $\text{Et}\cdot + \text{Et}\cdot$ reaction.⁶⁹ The difference was in part interpreted as being due to experimental inaccuracies in the solution data. However, a very simple EPR experiment showed quite clearly the solution data was not in error.¹⁶

Photolysis of a pentane solution of $\text{Me}_3\text{CCMe}_2\text{OOCMe}_3$ and triethylborane gave the spectra of both $\text{Me}_3\text{C}\cdot$ and $\text{Et}\cdot$.



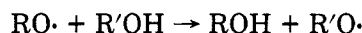
Under conditions where $[\text{Me}_3\text{C}\cdot]/[\text{Et}\cdot]$ was experimentally independent of the Et_3B concentration, all $\text{Me}_3\text{CCMe}_2\text{O}\cdot$ radicals must undergo β scission and all $\text{Me}_3\text{CO}\cdot$ must react with Et_3B . A simple kinetic treatment^{16,70} gives

$$\frac{k_{24}}{k_{23}} = \frac{[\text{Me}_3\text{C}\cdot]^2}{[\text{Et}\cdot]^2}$$

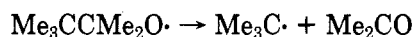
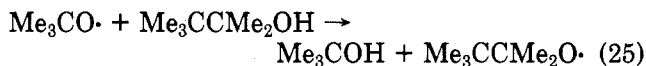
The rate constant ratio k_{24}/k_{23} was found to be 1.2 ± 0.4 in solution whereas the gas-phase value was reported to be $10^{3.3 \pm 1.5}$. We suggested that the gas-phase data were in error because $\Delta H_f(\text{Me}_3\text{C}\cdot)$ was too small by ca. 3 kcal/mol. Subsequent work in the gas phase has

shown that k_{23} is indeed nearly as fast as k_{24} and, in general, support a larger heat of formation for *tert*-butyl.⁷¹

The Alkoxy-Alcohol Reaction. The reaction



was generally regarded as being very unlikely to take place. However, its occurrence was readily demonstrated by EPR using alcohols which give alkoxy radicals that undergo rapid β scission.⁷² Thus, photolysis of di-*tert*-butyl peroxide and $\text{Me}_3\text{CCMe}_2\text{OH}$ gave $\text{Me}_3\text{C}\cdot$ (plus a primary alkyl radical via abstraction from the Me groups).



Similarly, both $(\text{Me}_3\text{C})_2\text{CHOH}$ and $(\text{Me}_3\text{C})_3\text{COH}$ gave $\text{Me}_3\text{C}\cdot$ after loss of their hydroxylic hydrogen. Reaction 25 is fast ($k_{25} \sim 3 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ at 20 °C) and has a low activation energy (~ 2.6 kcal/mol) and A factor ($\sim 10^{6.4} \text{ M}^{-1} \text{ s}^{-1}$), just like other oxyl radical H abstractions from heteroatoms (vide supra).

Recent Developments

EPR at High Pressure. The measurement of changes in hyperfine splittings (hfs) as a function of temperature is a rather popular EPR experiment. It is generally carried out at *constant pressure*, though the data have been invariably interpreted as though the experiment had been carried out at *constant volume*. This means that any effects produced by the change in solvent density with temperature have been tacitly, but firmly, ignored. To check on the validity of this tacit assumption it appeared worthwhile to measure the change in the hfs of a suitable radical as a function of temperature and pressure. The latter experiment was done in an EPR cell made from heat drawn thick-walled quartz that could withstand internal pressures of up to 2000 atm.⁷³ The radical chosen for study was di-*tert*-butyl nitroxide since the magnitude of its nitrogen hfs, a^N , has often been used to probe the "cybotactic" region, that is, the region in which solvent molecules interact directly with the solute. The change in a^N with temperature and pressure for a constant mole fraction of radical in the solvent can be described by the relation

$$\left(\frac{\partial a^N}{\partial T}\right)_P = \left(\frac{\partial a^N}{\partial T}\right)_V + \left(\frac{\partial a^N}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

i.e.,

$$A = B + CD$$

Terms A, C, and D were measured experimentally, C being obtained in the high-pressure experiment. Term B, which has usually been assumed to equal term A, was in fact zero in ethanol and cyclopentane.⁷³ The common assumption that measurements of hfs at constant

(67) For a beautiful example of tunneling also discovered by EPR, see: Hudson, R. L.; Shiotani, M.; Williams, F. *Chem. Phys. Lett.* 1977, 48, 193.

(68) Carlsson, D. J.; Ingold, K. U. *J. Am. Chem. Soc.* 1968, 90, 7047.

(69) McMillen, D. F.; Golden, D. M.; Benson, S. W. *J. Am. Chem. Soc.* 1972, 94, 4403. Hiatt, R.; Benson, S. W. *Int. J. Chem. Kinet.* 1973, 5, 385.

Konar, R. S.; Marshall, R. M.; Purnell, J. H. *Ibid.* 1973, 5, 1007.

(70) Weiner, S. A. *J. Am. Chem. Soc.* 1972, 94, 581.

(71) See, for example: Parkes, D.; Quinn, C. P. *J. Chem. Soc., Faraday Trans. 1* 1976, 72, 1953. Taylor, J. E.; Milazzo, T. S. *Int. J. Chem. Kinet.* 1978, 10, 1245. Davis, H. *Ibid.* 1979, 11, 1131. Tsang, W. *Ibid.* 1978, 10, 821. Atri, G. M.; Baldwin, R. R.; Evans, G. A.; Walker, R. W. *J. Chem. Soc., Faraday Trans. 1* 1978, 74, 366. Rossi, M.; Golden, D. M. *Int. J. Chem. Kinet.* 1979, 11, 969.

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pressure are effectively identical with measurements at constant volume is, therefore, unjustified.

EPR Measurements of Vibrational Frequencies.

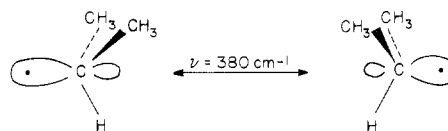
As a final example of the versatility of EPR we describe its use to measure the out-of-plane vibrational frequencies of alkyl radicals. An EPR spectrum provides an average picture of all the radicals in a sample. Most of the radicals will be in the zero-point vibrational level, but as the temperature is raised higher levels will become increasingly populated. When the out-of-plane vibration can be described by the simple harmonic oscillator approximation the average amplitude⁷⁴ of vibration will increase with temperature. This will lead to an increase in the degree of s character of the semioccupied orbital and hence to an increase in the $^{13}\text{C}_\alpha$ hfs, $a^{13}\text{C}_\alpha$. The out-of-plane vibrational frequency, ν , can be obtained together with the theoretical hfs, a_0 , for the radical rigidly held in its theoretical planar configuration, and also the constant $a_2/2F$, by measuring $a^{13}\text{C}_\alpha$ over a range of temperature and using

$$a^{13}\text{C}_\alpha(T) = a_0 + \frac{a_2 h \nu}{2F} \coth \frac{h \nu}{2kT}$$

When applied to the isopropyl radical⁷⁵ this procedure yielded $\nu = 380 \text{ cm}^{-1}$, in excellent agreement with a value of 375 cm^{-1} obtained by an infrared spectroscopic study of matrix isolated isopropyl radicals.⁷⁶ If

(74) More specifically, in the EPR experiment we are dealing with the mean-square amplitude of vibration.

(75) Griller, D.; Preston, K. F. *J. Am. Chem. Soc.* 1979, 101, 1975.



reasonable assumptions are made about geometry of isopropyl, the force constant, F , for the out-of-plane vibration can be obtained, and this in turn can be used to calculate ν for other simple alkyls.⁷² There is excellent agreement between the calculated frequencies and the frequencies measured by infrared, e.g., CH_3 , 596 vs, 617 cm^{-1} ; CD_3 , 462 vs, 463 cm^{-1} ; CH_3CH_2 , 499 vs, 541 cm^{-1} .

A similar study of $a^{13}\text{C}_\alpha$ for $\text{Me}_3\text{C}\cdot$ has shown that this radical has a minimum energy of configuration which is nonplanar.⁷⁷ Its out-of-plane vibration is best described by a double-minimum potential function.

Concluding Remarks

In this Account we have tried to show that very simple EPR experiments can provide interesting and important data. The majority of techniques described are very easy to apply and, with a few exceptions, do not require any special equipment. The versatility of EPR encourages the design of elegant and simple experiments to further the art of physical-organic chemistry.

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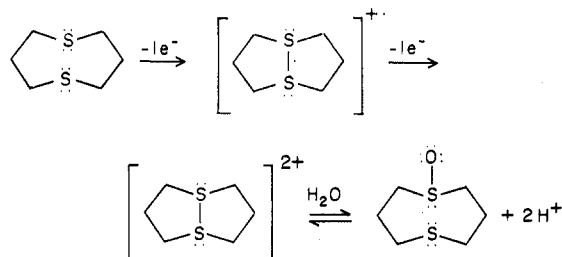
Chemistry of Aliphatic Thioether Cation Radicals and Dications

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This Account is concerned with the preparation and properties of aliphatic thioether cation radicals and dications of the type shown below. These cations can



be obtained either by a stepwise one-electron oxidation of 1,5-dithiacyclooctane (1,5-DTCO) or by an acidifi-

cation of 1,5-dithiacyclooctane 1-oxide.^{1,2} As shown, cation formation occurs with concomitant coupling of the two sulfur atoms. Most of the compounds studied have been mesocyclic (7- to 10-membered rings) dithioethers, but it appears that any appropriately substituted aliphatic thioether may be used and any group (amine, alcohol, etc.) which can function as a lone-pair donor can participate in the oxidative coupling reaction. The reason for initially choosing mesocyclic dithioethers was based on studies of transannular reactions by N. J. Leonard. In a recent Account he has described the consequences of using the trimethylene bridge as a synthetic spacer of functional groups.³

The intramolecular coupling of heteroatoms on oxidation of aliphatic dithioethers is in marked contrast to the species formed on oxidation of aromatic thio-

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