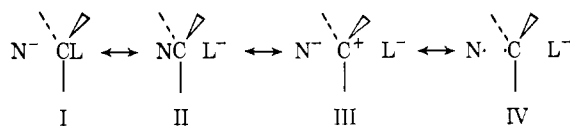


The second consideration is a two-path reaction, an electron-transfer process in competition with a favored SN2 process. Since the reaction involves complete inversion, the classical mechanism has a ΔG^\ddagger of at least 2.7 kcal/mol lower.¹⁴ This model is incomplete in that it does not attempt to explain anomalous behavior discussed below.

Finally, the reaction can be formulated as proceeding through an intermediate that is a resonance hybrid of forms including a one-electron transfer.



N is the nucleophile, L is the leaving group, forms I, II, and III are contributions from a two-electron bond formation, and IV is the contribution from a one-electron transfer. An analogous formulation has been used for proton transfer to aromatic radical anions and accounts for the rate dependence upon both the reduction potential and the localization energy.¹⁵ The extension of this concept to nucleophilic reactions has significant value in that the successful two-term rate equation includes a term for basicity and one for the reduction potential of the nucleophile.^{16,17} Similarly, the model can account for the observation that both electron-withdrawing and electron-donating groups increase the rate of nucleophilic substitution in meta- and para-substituted benzyl halides.¹⁸ Additional systems that include polar forms as well as the expected one-electron form are polarographic reductions¹⁹ and relative reactivities of free radicals.²⁰

Our results and rate data for other nucleophilic substitution reactions suggest that electron transfer contributes to these reactions and that one-electron forms should be included along with the generally accepted two-electron forms.

(14) In this explanation, the highly sensitive probe of spin trapping detects the presence of a small amount (<0.01%) of reaction from reduction of the nosylate.

(15) S. Hayano and M. Fujihira, *Bull. Chem. Soc. Jap.*, **44**, 2046 (1971).

(16) J. O. Edwards and R. G. Pearson, *J. Amer. Chem. Soc.*, **84**, 16 (1962).

(17) R. E. Davis, *J. Amer. Chem. Soc.*, **87**, 3010 (1965).

(18) (a) J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1962, p 172. (b) Electron-withdrawing substituents in both the meta and para positions are known to stabilize benzyl radicals; see ref 19 and L. W. Menapace and H. G. Kuivila, *J. Amer. Chem. Soc.*, **86**, 3047 (1964).

(19) A. Streitwieser, Jr., and C. Perrin, *J. Amer. Chem. Soc.*, **86**, 4938 (1964).

(20) See ref 9, p 135 ff.

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Rate Constants for Spin Trapping *tert*-Butoxy Radicals as Studied by Electron Spin Resonance

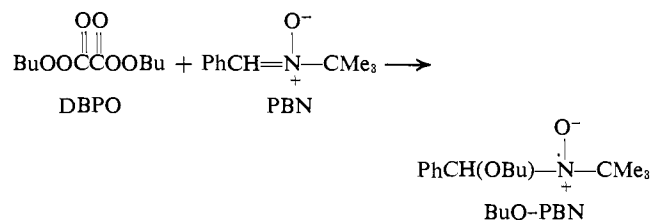
Sir:

It has recently been shown that certain free radicals can be quantitatively detected¹ by the method of spin

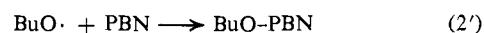
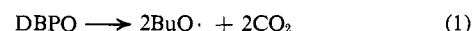
trapping.² Thus the thermal decomposition of benzoyl peroxide can be followed by trapping all of the benzoyloxy radicals produced by using phenyl *N*-*tert*-butyl nitron (PBN) in benzene at ambient temperatures. Since the rate of production of the spin adduct α -benzoyloxybenzyl *tert*-butyl nitroxide is first order in benzoyl peroxide and zero order in PBN, spin trapping appears to provide a useful method for counting short-lived reactive free radicals (spin counting¹).

The spin trapping technique could become more useful if absolute rate constants for trapping radicals were available. We previously reported two estimates of the absolute rate constant for trapping benzoyloxy radicals.¹ One of these was based on DeTar's estimates of certain rate constants. Subsequent work on trapping phenyl radicals allows us to improve these estimates and these results will be described in a following communication. In this paper we report on a study of the rate constant for trapping *tert*-butoxy radicals produced by thermal decomposition of di-*tert*-butyl peroxalate.

Di-*tert*-butyl peroxalate (DBPO) decomposes in the presence of PBN to produce the *tert*-butoxy spin adduct (BuO-PBN). The hyperfine splitting con-



stants in benzene at room temperature are: $a^{\text{N}} = 14.22$, $a_{\beta}^{\text{H}} = 1.95$ G. The reaction is first order in DBPO and zero order in PBN over the range of concentrations studied: [DBPO] = 0.001–0.1 M, [PBN] = 0.02–0.2 M. If the following mechanism is assumed, $d[\text{BuO-PBN}]/dt = 2k_1[\text{DBPO}]$ (see eq 1 and 2').



Rate constants obtained by a method previously described¹ compare well with the values of Bartlett, *et al.*:³ e.g. at 35° $k_1 = 6.8 \times 10^{-5} \text{ sec}^{-1}$ by spin counting and $7.1 \times 10^{-5} \text{ sec}^{-1}$ by observing the disappearance of DBPO by ir.³ An Arrhenius plot of the data obtained by esr over a 16° temperature range (23–39°) gives an energy of activation of 30 kcal/mol. Bartlett, *et al.*, report 26 kcal/mol. All the data available give a value of 27 kcal/mol.

Since the absolute rate constant for hydrogen atom abstraction by *tert*-butoxy radicals from toluene and cyclohexane is known,⁴ it should be possible to obtain the absolute rate constant for spin trapping *tert*-butoxy radicals by simultaneously monitoring the build-up of the *tert*-butoxy and the alkyl radical spin

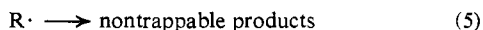
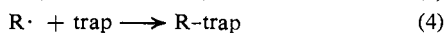
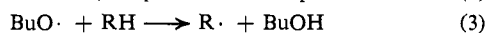
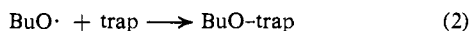
(1) E. G. Janzen, C. A. Evans, and Y. Nishi, *J. Amer. Chem. Soc.*, **94**, 8236 (1972).

(2) E. G. Janzen, *Accounts Chem. Res.*, **4**, 31 (1971).

(3) P. D. Bartlett, E. P. Benzing, and R. E. Pincock, *J. Amer. Chem. Soc.*, **82**, 1762 (1960).

(4) (a) see J. A. Howard, *Advan. Free Rad. Chem.*, **4**, 49 (1971); (b) K. U. Ingold, "Free Radicals," J. K. Kochi, Ed., Vol. 1, Wiley, New York, N. Y., 1973, p 74.

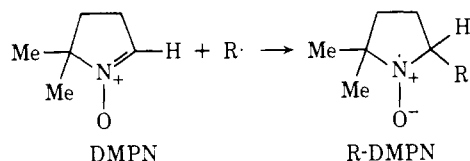
adducts produced in the following competitive reactions



Assuming steady-state conditions

$$\frac{d[\text{BuO-trap}]/dt}{d[\text{R-trap}]/dt} = \frac{k_2[\text{trap}]}{k_3[\text{RH}]} + \text{constant}$$

Such experiments appear to be successful with PBN using cyclohexane as the hydrocarbon but the overlap of the spin adduct spectra is serious. Because of this problem the cyclic spin trap, 5,5-dimethylpyrroline 1-oxide (DMPN, as in dimethylpyrrolidine "nitron" which produces pyrrolidine nitroxide spin adducts), was chosen for these competition experiments. In general the oxy radical spin adduct spectra differ greatly from the alkyl radical spin adduct spectra.⁵ Thus, for



the *tert*-butoxy and cyclohexyl spin adducts of DMPN: BuO-DMPN, $a^{\text{N}} = 13.11$, $a_{\beta}^{\text{H}} = 7.93$, $a_{\gamma}^{\text{H}} = 1.97$ (1 H); cyclohexyl-DMPN, $a^{\text{N}} = 13.88$, $a_{\beta}^{\text{H}} = 20.86$ G. The same type of kinetics are observed with DBPO in cyclohexane with DMPN as found for PBN. Thus

$$\frac{d[\text{BuO-DMPN}]/dt}{d[\text{cyclohexyl-DMPN}]/dt} = \frac{k_2'[\text{DMPN}]}{k_3[\text{RH}]} + \text{constant}$$

The ratio of the rate constants k_2'/k_3 was found to be 4340 at $[\text{DMPN}] = 0.0015 M$ at 25° . Assuming $k_3 = 1 \times 10^5 M^{-1} \text{sec}^{-1}$ for cyclohexane,⁶ the absolute rate constant of trapping *tert*-butoxy radicals by DMPN at 25° is $5 \times 10^8 M^{-1} \text{sec}^{-1}$.

In order to obtain absolute rate constants for trapping *tert*-butoxy radicals by other traps a mixture of DMPN and some other trap was allowed to compete for *tert*-butoxy radicals and the ratio of the concentrations of the two spin adducts monitored as a function of time. Thus

$$\frac{d[\text{BuO-trap}]/dt}{d[\text{BuO-DMPN}]/dt} = \frac{k_2[\text{trap}]}{k_2'[\text{DMPN}]}$$

The rate constant ratios for a number of traps are given in Table I. Using the value $k_2' = 5 \times 10^8 M^{-1} \text{sec}^{-1}$ for trapping *tert*-butoxy radicals by DMPN absolute rate constants are estimated for a number of nitrones and *tert*-nitrosobutane.

The absolute rate constant for trapping *tert*-butoxy radicals by PBN is about $100 \times$ smaller than that found for the unsubstituted *N-tert*-butyl nitron.⁹ However, the absolute rate constant for the latter is comparable to that found for DMPN.¹⁰ Substituents have a small

(5) E. G. Janzen and J. I-P. Liu, *J. Magn. Resonance*, **9**, 510 (1973); E. G. Janzen, C. A. Evans, and J. I-P. Liu, *ibid.*, **9**, 513 (1973).

(6) Howard⁴ has concluded that the hydrogen abstraction by *tert*-butoxy radicals from cyclohexane is close to the mean value estimated by Carlsson and Ingold⁷ and by Walling and Kurkov,⁸ namely $1 \times 10^6 M^{-1} \text{sec}^{-1}$ at ambient temperatures.

(7) D. J. Carlsson and K. U. Ingold, *J. Amer. Chem. Soc.*, **89**, 4885 (1967).

(8) C. Walling and V. P. Kurkov, *J. Amer. Chem. Soc.*, **89**, 4895 (1967).

(9) Spin trapping with *N-tert*-butyl nitron was first reported by G. R. Chalfont, M. J. Perkins, and A. Horsfield, *J. Amer. Chem. Soc.*, **90**, 7141 (1968).

(10) The absolute rate constant for trapping *tert*-butoxy by 2-phenyl-

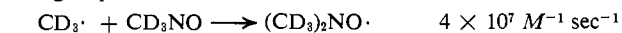
Table I. Absolute Rate Constants for Spin Trapping *tert*-Butoxy Radicals by Various Spin Traps^a

Trap	k_2/k_2''	$10^{-6}k_2, M^{-1} \text{sec}^{-1}$
$\text{CH}_2=\text{N}^+(\text{O}^-)\text{CMe}_3$	0.5-1	300-500
$\text{C}_6\text{H}_5\text{CH}=\text{N}^+(\text{O}^-)\text{CMe}_3$ (PBN)	0.011	5.5
<i>p</i> -NO ₂ PBN	0.018	9.0
<i>p</i> -ClPBN	0.013	6.5
<i>p</i> -CH ₃ PBN	0.0068	3.4
<i>p</i> -CH ₃ OPBN	0.011	5.5
	1	500
	0.042	9
$\text{Me}_3\text{CN}=\text{O}$	0.0030	1.5

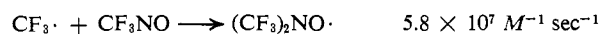
^a In benzene at 25° .

effect on the rate of trapping *tert*-butoxy radicals by PBN. The substituent effect on the rate of addition of benzyloxy radicals to PBN is larger ($\rho = 0.5$).¹

Trapping of *tert*-butoxy radicals by *tert*-nitrosobutane is about $1.5 \times 10^6 M^{-1} \text{sec}^{-1}$. Recently Perkins and Roberts¹¹ have reported the absolute rate constant for the addition of *tert*-butoxycarbonyl radicals to *tert*-nitrosobutane ($1.1 \times 10^6 M^{-1} \text{sec}^{-1}$ in di-*tert*-butyl peroxide at 40°). These authors also estimate that the absolute rate constant for the addition of methyl radicals to nitrosobenzene is 10^6 - $10^7 M^{-1} \text{sec}^{-1}$ at 65° based on Szwarc's methyl affinity data in the gas phase.¹² More recent absolute rate constants of radical additions to nitroso compounds are available in the gas phase.¹³



$$1.4 \times 10^7 M^{-1} \text{sec}^{-1}$$



The absolute rate constants for spin trapping appear to fall between 1×10^6 and $5 \times 10^8 M^{-1} \text{sec}^{-1}$ at room temperature depending on the trap used and to a lesser extent on the radical trapped.

5,5-dimethylpyrroline *N*-oxide (2-phenyl-DMPN) is about $40 \times$ slower than for DMPN (results of Robert L. Eggers in these laboratories).

(11) M. J. Perkins and B. P. Roberts, *J. Chem. Soc., Chem. Commun.*, 173 (1973).

(12) W. J. Heilman, A. Rembaum, and M. Szwarc, *J. Chem. Soc.*, 1127 (1957).

(13) A. Maschke, B. S. Shapiro, and F. W. Lampe, *J. Amer. Chem. Soc.*, **86**, 1929 (1964); H-S. Tan and F. W. Lampe, *J. Phys. Chem.*, **76**, 3303 (1972); **77**, 1335 (1973).

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Pyrolysis of

N,N,N-Trimethyl-3-homoadamantylammonium Hydroxide and *N,N*-Dimethyl-3-aminohomoadamantane *N*-Oxide. Evidence for Bridgehead Homoadamantene

Sir:

Since the pyrolysis¹ of aliphatic quaternary ammonium hydroxides² and amine oxides has been used

(1) A. C. Cope and E. R. Trumbull, *Org. React.*, **11**, 317 (1960).

(2) J. A. Chong and J. R. Wiseman, *J. Amer. Chem. Soc.*, **94**, 8627 (1972), and references cited therein.