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Received November 26, 1974

Radical Production from the Interaction of Closed Shell Molecules. II. The Reaction of Organic Sulfides with *tert*-Butyl Peroxybenzoates[1]

Sir:

In recent years it has become clear that a number of the reactions in which nucleophiles react with substrates to give substitution products actually proceed by a chain mechanism involving radicals and radical ions.[2] In this context, the reactions of nucleophiles (donors) with peroxidic substrates provide a lode of rich variety for study; these reactions can involve either an SN2 reaction (eq 1) or an electron transfer (ET) process (eq 2). Many peroxide-nucleophile reactions which involve an SN2 mechanism are known,[3] but very few ET reactions of peroxides have been proposed.

$$\mathrm{D + XOOY \xrightarrow{S_N2} [D^{+}\!\!-\!OX + {}^{-}OY] \longrightarrow \longrightarrow} \text{ ultimate products} \tag{1}$$

$$\mathrm{D + XOOY \xrightarrow{ET} [D\cdot^{+} + \cdot OX + {}^{-}OY] \longrightarrow \longrightarrow} \text{ similar or identical products} \tag{2}$$

Recently ET reactions have been postulated for the interaction of diphenylhydroxylamine with benzoyl peroxide (BPO)[4a] and alkyllithium and Grignard reagents with alkyl peroxides.[4b] In these systems, the leakage of radicals from a seemingly nonradical reaction has been interpreted as an important clue that an ET mechanism is involved.

Distinguishing between SN2 and ET paths is subtle and can be very difficult. For example, in 1950 Horner[5] postulated that the rapid radical production which results from the reaction of dimethylaniline (DMA) with BPO results from an ET mechanism. In 1957 in his book, Walling[6] dismissed this possibility and proposed that the DMA-BPO reaction is a normal SN2 process, and that radicals arise from the homolysis of the ammonium salt, $\mathrm{BzO^{-}\,{}^{+}NMe_2Ph}$, which is the first intermediate in the ionic displacement process.[7,8] Horner later partially recanted[9] and suggested that *both* ET and an SN2 reaction (followed by homolysis) are responsible for the radical production observed. Despite the fact that research published by several groups in recent years appears to support Horner's original ET mechanism,[10] most of the critical reviews of the DMA-BPO system ignore ET and continue to formulate the DMA-BPO reaction as an SN2 process.[11] Clearly, ET reactions of peroxides are not at all easy to establish, and further studies are needed.

We previously reported on the reaction of sulfides with benzoyl peroxide, a process which does *not* produce radicals.[3e] We now describe the superficially similar reaction of sulfides with *tert*-butyl peroxybenzoates (TBP's) which *does* lead to radicals and for which we propose an ET mechanism.[12] This system is of interest in comparison both with the BPO system and also with *ortho*-mercapto-substituted TBP, studied by Martin, *et al.*[13,14]

The rate of decomposition of TBP in sulfide solutions can be written as in eq I where k_H is the rate constant for homolysis and k_S and k'_S are the second-order and pseudo-first-order rate constants for the sulfide-TBP reaction. The fraction of the bimolecular, assisted process that leads to radicals is calculated by comparing the rates of peroxide and scavenger disappearance. (The TBP disappearance was monitored using the peroxide infrared band at 1758 $\mathrm{cm^{-1}}$; styrene[3e] or galvinoxyl in limiting[15] or excess[16] concentration were used as scavengers.)

$$\frac{-d[\mathrm{TBP}]}{dt} = k_{\mathrm{H}}[\mathrm{TBP}] + k_{\mathrm{S}}[\mathrm{R_2S}][\mathrm{TBP}] = (k_{\mathrm{H}} + k'_{\mathrm{S}})[\mathrm{TBP}] \tag{I}$$

Table I gives the data; the last three columns give the per cent radical production. Despite the lack of precision in these small values,[17,18] it is clear that the interaction of sulfides with TBP derivatives does produce radicals. Conservatively, averaging all the data in the last three columns, 2.3 ± 1.5% of the bimolecular interactions produce radicals.[19]

It is important to establish that the radicals we observe do not arise from homolysis of an intermediate produced in an SN2 process. It is clear that species such as $\mathrm{BzOS^{+}Me_2}$ or $\mathrm{BzOS(Me){=}CH_2}$,[20] which can be formed from TBP + $\mathrm{Me_2S}$ by SN2 processes, do not produce radicals since the BPO-$\mathrm{Me_2S}$ system does not form radicals.[3e,21] Homolysis of t-$\mathrm{BuOS^{+}Me_2}$ was excluded by showing that $\mathrm{MeOS^{+}Me_2}$, synthesized independently,[22] initiates the polymerization of styrene too slowly to be responsible for radical production in the $\mathrm{Me_2S}$-BPO system.

The products (gas chromatographic analysis) from reaction of 1 *M* dimethyl sulfide with TBP at 80° in $\mathrm{CCl_4}$ containing 0.2 *M* styrene (to eliminate induced decomposition) are 90% t-$\mathrm{C_4H_9OH}$, 96% $\mathrm{CH_3SCH_2OCOC_6H_5}$ (BOMS),[3e,23,24] six unidentified compounds in less than 1% yield, and no DMSO, $\mathrm{PhCO_2H}$, or *tert*-butyl benzoate. Without styrene the products are 90% t-$\mathrm{C_4H_9OH}$, 40–50% $\mathrm{C_6H_5CO_2H}$, and 50–60% BOMS.

Equations 2a, 2b, and 3 present a generalized mechanism

Table I. The Reaction of Dialkyl and Aryl Alkyl Sulfides with Substituted *tert*-Butyl Peroxybenzoates[a]

Substituent[b]	$10^7\ k_H$,[c] $\mathrm{sec^{-1}}$	$10^7\ k'_S$,[d] $\mathrm{sec^{-1}}$	Assisted path,[d,e] %	Radicals from assisted path, %[h]		
				Styrene	Lim[f] Gal	Excess[f] Gal
p-$\mathrm{CH_3O}$	10	89	90	3.5	3.5	
H	8.8	146	94	2.9	0.6	
p-Cl	4.2	334	99	0.7	0.6	
p-$\mathrm{NO_2}$	2.9	1550	100	2.3	0.9	3.5
3,5-$\mathrm{(NO_2)_2}$	1.1	13400	100			4.7
Rho[g]	−0.29 ± 0.05	+1.34 ± 0.03				

[a] At 80° in $\mathrm{CCl_4}$. [b] In perester. [c] Unimolecular homolysis, extrapolated from higher temperatures; 0.2 *M* styrene present to reduce induced decomposition. [d] In 1 *M* methyl sulfide in $\mathrm{CCl_4}$. [e] Per cent of total reaction which is bimolecular. $100k'_s/(k_H + k'_S)$. [f] Limiting or excess galvinoxyl. [g] Hammett ρ value. [h] Calculated as the ratio of the rates of scavenger disappearance in $\mathrm{R_2S}$-containing solutions (corrected for scavenger loss due to first-order homolysis) to scavenger disappearance in non-sulfide solutions, divided by the ratio of the rates of TBP disappearance in sulfide solutions to non-sulfide solutions.[1b,3e,13a]

for the interaction of a donor, D, with a peroxide by an ET mechanism.[2a,e,j,12] (Equation 2a) In many cases, formation

$$D + XOOY \longrightarrow D\cdot^{+} + XOOY\cdot^{-} \qquad (2a)$$

$$XOOY\cdot^{-} \longrightarrow XO\cdot + YO^{-} \qquad (2b)$$

$$XO\cdot + YO^{-} + D\cdot^{+} \longrightarrow \left\{\begin{matrix} D^{+}\!\!-\!OX + YO^{-} \\ \text{or} \\ D^{\cdot}\!\!-\!OY + XO^{\cdot} \end{matrix}\right\} \longrightarrow \longrightarrow \text{products} \qquad (3)$$

of a loose complex[2k,25,26] probably precedes reaction. The rate determining step probably is electron transfer,[2k,l] and the transition state for this step may be similar to a charge-transfer complex with the resonance structures: $(D,XOOY) \leftrightarrow (D\cdot^{+}, XOOY\cdot^{-})$.[27] (Equation 2b) It is likely that bond scission is not synchronous with electron transfer in most cases.[28] (Equation 3) Reaction of $XO\cdot$ or YO^{-} (or $XO\text{-}OY\cdot^{-}$) with $D\cdot^{+}$ leads to substitution products which can be identical with those which would have been produced by an SN2 reaction.[2,3e] The D^{+}-OX + YO^{-} pair may undergo ligand exchange,[24] attack by YO^{-} to give products,[3c,3d,6,29] or ylide production as in eq 4.[3e,24] The $D^{\cdot}$-OY + $XO\cdot$ pair

$$Me_2S^{+}\!-\!OBz + t\text{-}BuO^{-} \longrightarrow \underset{\mathbf{1}}{CH_3S(OBz){=}CH_2} + t\text{-}BuOH \qquad (4)$$

may also undergo similar reactions. Radical or radical ion combinations or disproportionations, for example, as in eq 3 or 5a and b, explain the reduced yields of radicals from these systems.

$$Me_2S\cdot^{+} + BzO^{-} + t\text{-}BuO\cdot \longrightarrow \mathbf{1} + t\text{-}BuOH \qquad (5a)$$

$$Me_2S\cdot^{+} + BzO\cdot + t\text{-}BuO^{-} \longrightarrow \mathbf{1} + t\text{-}BuOH \qquad (5b)$$

Although eq 2a, 2b, and 3 ascribe all products to the ET path, the possibility cannot be excluded that some of the reaction occurs by a competitive and independent SN2 process, eq 1.[30] Isotope effect studies, however, show that a major pathway is ET.[8]

It is worthwhile to compare the TBP-$PhSCH_3$ reaction and the intramolecular reaction of o-CH_3S substituted TBP.[13] Unsubstituted TBP, in 10 *M* $PhSCH_3$ where every perester is adjacent to a sulfide molecule,[31] decomposes 270 times slower at 80° than the o-CH_3S substituted TBP. The external case gives about 2% radicals, whereas the internal case gives more than 50%.[13a]

In contrast to TBP, the BPO-sulfide reaction does not give radicals.[3e] Here the assisted path is faster (Me_2S reacts 10^4 faster with BPO than TBP); this more facile assisted process involves SN2 rather than ET, probably because of the superior leaving group in BPO relative to TBP.

Acknowledgment. This research was supported in part by the National Science Foundation, Grant GP 38051X1. W.H.H., Jr., was an N.D.E.A. Fellow from 1970 to 1973 and an LSU Dissertation Year Fellow Sept 1973 to July 1974.

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Radical Production from the Interaction of Closed Shell Molecules. III. An Isotope Effect Test for Distinguishing SN2 from Electron Transfer (ET) Reactions[1]

Sir:

Recent studies from a large number of laboratories[2] have demonstrated that nucleophiles can react with a variety of substrates either by an SN2 or by an electron transfer (ET) mechanism. In our continuing investigations of radical production from the interactions of closed-shell molecules,[1,3] we are studying the reactions of nucleophiles with peroxides.[4] Although these reactions can occur either by SN or ET mechanisms, as we pointed out in the preceding paper,[1b] it often is a subtle and difficult problem to establish which mechanism applies to a given system. An accelerated rate of radical production from a peroxide in the presence of the nucleophile is a *clue* that an ET reaction occurs, but is not *in itself* conclusive since homolysis of intermediates produced in SN2 processes may be faster than homolysis of the peroxidic substrate itself.[1b,5] Furthermore, as the data in Table I show,[6] neither the magnitude of the acceleration of the preoxide decomposition produced by the nucleophile[1b] nor Hammett ρ values[7,8] can be used to distinguish SN and ET reaction types. In addition, the nature of the reaction products,[6e,9] and the effect of solvent polarity also do not allow a distinction to be made.[10-15]

In contrast, isotope effects do appear to divide nucleophile-peroxide reactions into two classes. If the rate constants for the reaction of a peroxide with a nucleophile and with the β-deuterated nucleophile are contrasted (k_H/k_D), inverse isotope effects (*i.e.*, $k_H/k_D < 1$) are observed for SN2 reactions whereas the isotope effects for ET are normal ($k_H/k_D > 1$). Table II presents these data. Some of the data are not very precise, but they are adequate to distinguish inverse from normal isotope effects, which is all that is necessary.

The use of isotope effects for identifying SN2 reactions is well known. Isotope effects are smaller for SN2 than SN1 reactions because of higher vibrational frequencies for deuterium in both substrate and nucleophile at the transition state for SN2 relative to SN1.[16] These higher frequencies can be rationalized as being due to hybridization, steric, hyperconjugative, or inductive effects.[17] Computer studies correctly predict inverse or near unity isotope effects for α-deuterated substrates in SN2 reactions and normal isotope effects for SN1 reactions,[18] and inverse isotope effects are predicted and observed for SN2 reactions in which the nucleophile is deuterated in the β-position.[19,20,21]

In contrast, vibrational frequencies for β-hydrogens in the donor are loosened at the transition state in ET reactions, and normal isotope effects are observed. Weakened bonding (*i.e.*, loosened vibrational frequencies) in the transition state produces normal isotope effects; therefore, normal secondary isotope effects, $k_H/k_D > 1$, will be observed in ET reactions whenever the ionized electron is lost from an orbital which has bonding character at the β C-D bond. (Inverse isotope effects will be observed when ionization occurs from an orbital which was antibonding character at

Table I. Reactions of Peroxides with Nucleophiles (Donors)

No.	Peroxide	Donor	Acceleration[a]	ρ^b peroxide	ρ^c donor	% radical[d]	Ref
1	BPO[e]	$PhNMe_2$	3×10^4 (40°)	+1.6[f]	−2.7[g]	18[h]	6a
2	BPO	Ph_2NOH	6×10^5 (40°)	+0.8		100	2h
3	BPO	Me_2S	5×10^4 (40°)		−1.3[i]	0	6e
4	BPO	ArCH=CHAr	4×10^3 (45°)[j]	+1.2	−1.0[k]	10[j]	6f
5	BPO	$Me_2C=CMe_2$	1×10^2 (45°)			0	6g
6	TBP[l]	Me_2S	17 (80°)	+1.3	−1.7[i,m]	2	6h
7	TBP	Ph_3P	2×10^3 (80°)	+1.2		0	6i
8	*o*-MeSTBP		5×10^3 (80°)[n]		−1.3[o]	50	6j
9	2-MeS-3-*t*-BuOOCOTBP		1×10^5 (80°)[n]			50	6l
10	*o*-$Ph_2C=CHTBP$		42 (80°)[n]			80	6m
11	*o*-$Ph_2C=CHBPO$		387 (70°)[n]	+0.7	−1.8	11	6m

[a] The acceleration of the rate of peroxide disappearance in a 1.0 *M* solution of the nucleophile relative to the rate in the same solvent without nucleophile. [b] Hammett equation ρ when substituents are in the Ar group of the peroxide. [c] Substituents in the Ar group of the nucleophile. [d] Per cent of the total reaction that produces scavengeable radicals. [e] Benzoyl peroxide. [f] Reference 6b. [g] Reference 6c. [h] Reference 6d. [i] This work; nucleophile is Ar substituted $ArSCH_3$. [j] For reaction of *m*,*m*′-Br_2BPO with *trans*-*p*-*p*′-$(MeO)_2$stilbene. [k] With σ^-. [l] *tert*-Butyl peroxybenzoate. [m] For reaction with *tert*-butyl *p*-chloroperoxybenzoate. [n] Relative to unsubstituted peroxide. [o] Reference 6k.

Table II. β-Deuterium Isotope Effects for Reactions of Nucleophiles (Donors) with Substrates

Substrate	Nucleophile	Temperature (°C)	Mechanism	$k_H/k_D{}^a$	Ref
CH_3OTs	$PhN(CD_3)_2$	51.29	SN2	0.883 ± 0.008	19a
CH_3OTs	$PhP(CD_3)_2$	51.29	SN2	0.952 ± 0.002	19a
t-BuOOH	CD_3SCD_3	80	SN2	0.93 ± 0.03	6h
BPO[b]	CD_3SCD_3	40	SN2	0.88 ± 0.05	6h
BPO	Ph_2NOD	24.8	ET	1.53[c]	2h
ClO_2	$(CD_3)_3N$	25.2	ET	1.3	2g
TBP[d]	CD_3SCD_3	80	ET	1.08 ± 0.06	6h
3,5-$(NO_2)_2$TBP	CD_3SCD_3	80	ET	1.06 ± 0.03	6h

[a] Per molecule. [b] Benzoyl peroxide. [c] May be due in part to a contribution from a primary isotope effect. [d] *tert*-Butyl peroxybenzoate.