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Received August 7, 1974

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.

deuterium.) The highest occupied molecular orbital in donors like Me_2S is predominantly a nonbonding orbital on the heteroatom; however, this orbital has a contribution which is bonding in the β C–H stretching mode which is the most important in determining β-deuterium secondary isotope effects. For example, measurements of the detailed spectra of dimethyl sulfide and $(CD_3)_2S$ show the deuterated compound to have a higher ionization potential by about 230 cal/mol.[22] If this difference were fully realized at the transition state, the isotope effect on ET reaction of Me_2S would be predicted to be 1.39 at 80°. Thus the ET reactions listed in Table II probably have early transition states.[7]

We conclude that the dichotomy we have proposed is supported by isotope effect theory. Although more examples need to be studied, it appears that an isotope effect test does divide these reactions into SN2 and ET types and that this test can be used to probe whether radicals produced in donor–acceptor reactions arise from an ET mechanism.

Acknowledgment. This research was supported in part by the National Science Foundation, Grant GP38051X1. W.H.H., Jr., was an N.D.E.A. Fellow from 1970 to 1973 and an LSU dissertation Year Fellow Sept 1973–July 1974. We acknowledge helpful discussions with Professor Kendall N. Houk and Dr. Phillip Mollere.

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(10) Reactions cannot be divided into SN2 and ET types on the basis of their responsiveness to measures of solvent polarity such as dielectric constant or *Z*; see note 12 in ref 6e. The rates of SN2 reactions of the type studied here usually do not depend on solvent polarity.[8e,i] These ET reactions also usually show little dependence on solvent polarity, perhaps because they have very early TS's with little charge development.[7] Furthermore, radical production would be expected to depend on many solvent parameters. In particular, these solvent characteristics must be considered: viscosity,[11] complex formation between radicals (or ground states) and solvents,[12] the H bonding ability of solvents,[13] internal pressure,[14] and polarity.[15] Thus, effects of solvent polarity alone will only be discernible in a closely controlled series of solvents.

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(20) The observed isotope effect (IE) of an SN2 reaction in which the product-forming step involves the abstraction of a β-hydrogen atom of the nucleophile (eq 1) may contain a contribution from a primary IE. For eq

$$(CH_3)_2S + XOOY \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (CH_3)_2\dot{S}OY + XO^- \xrightarrow{k_d} CH_3S(OY){=}CH_2 + XOH \quad (1)$$

1, $k_{obsd} = k_1k_d/(k_{-1} + k_d)$. If k_{-1} is smaller than k_d, then k_{obsd} equals k_1, and the observed IE will be that on k_1. However, if k_{-1} is larger than k_d, then $k_{obsd} = k_1k_d/k_{-1}$, and the observed IE will contain a contribution from a primary IE on k_d. Therefore, the contribution from a primary IE to that observed will depend on k_d/k_{-1}. For example, in the reaction of phenylmethyl-d_3 sulfoxide with acetic anhydride, k_d is smaller than k_{-1} and the observed IE for this SN2 reaction is 2.9.[21] In the reaction of Me_2S with BPO, an inverse IE is observed, indicative that $k_d \gg k_{-1}$. The SN2 displacement of Me_2S on TBP should also have an inverse IE, and, since we observe a normal IE for this reaction, it must have an ET mechanism.

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Received August 7, 1974

Surface Modified Mass Spectrometry

Sir:

The addition of a collision gas to the analyzer of a mass spectrometer causes ion-molecule reactions.[1] These processes, which occur at relative kinetic energies in the kilovolt range, are a valuable source of data on thermochemistry and ion structure and a useful adjunct to analytical mass spectrometry.[2,3]

We now report that it is possible to substitute a surface for the collision gas and so to effect processes which are analogous to high energy ion-molecule reactions. Thus, a surface-induced reaction has been observed corresponding to the process of collision-induced dissociation (CID), in which the ion converts translational to internal energy in the ion-molecule reaction and subsequently fragments. For an ion AB^+ and a surface S, this surface-induced dissociation (SID) is given as

$$AB^+ + S \longrightarrow AB^{+*}$$
$$AB^{+*} \longrightarrow A^+ + B$$