large in comparison with the standard deviations in each $\Delta H^{\ddagger}$ value, the very similar $\Delta H^{\ddagger}$ values for each pair of isomers nevertheless demonstrate that the ground-state enthalpy differences of between 2 and 5 kcal are not significantly changed[9] at the transition state and are probably somewhat increased. Since ground-state steric effects appear to be retained,[10] if not actually increased at the transition state, this indicates a lack of free rotation about the C–C bond and is more consistent with cyclic bromonium ion formation than with development of an open α-bromocarbonium ion. Product studies support this conclusion. The *cis*-diisopropylethylene yields only racemic *dl*-dibromide. Neither the *meso*-dibromide nor the acetoxy bromide, which were independently synthesized, could be detected in the products by glc. The *trans*-olefin under identical conditions gives the *meso*-dibromide as predominant product, no detectable *dl*- dibromide, some acetoxy bromide, and unidentified material. Thus both olefins add bromine predominantly, if not completely, trans.

We are currently investigating pairs of unsymmetrical olefins which are known[4,11] not to give stereospecific trans addition in acetic acid, such as alkyl-substituted styrenes, and also symmetrical alkenes, which have even larger ground-state effect differences, such as the *cis*- and *trans*-di-*tert*-butylethylenes.[12]

[9] The enthalpies of isomerization quoted in Table I refer to the pure liquid state while the activation enthalpies refer to acetic acid solution. However, it seems unlikely that the enthalpies of solution for geometrical isomers will differ by an amount greater than experimental error in the $\Delta H^{\ddagger}$ values (see H. Herzog, Ph.D. Thesis, University of Paris, 1968, and J. E. Dubois and H. Herzog, unpublished results).

[10] A referee has pointed out that in two of the three cases above, the cis isomer reacts faster than the trans, and that this could be interpreted in terms of relief of steric strain. However, it is dangerous to draw such conclusions from simple rate differences of this magnitude since these only represent about 0.5 kcal in free energy. In the case of the *cis-tert*-butylethylethylene which reacts twice as fast as the *trans*-, it is the fact that the large ground-state enthalpy difference of more than 5 kcal is at least retained at the transition state which is significant.

[11] J. H. Rolston and K. Yates, *J. Amer. Chem. Soc.*, **91**, 1469 (1969); R. C. Fahey and H. J. Schneider, *ibid.*, 90, 4429 (1968).

[12] R. D. Turner, D. E. Nettleton, Jr., and M. Perelman, *ibid.*, **80**, 1430 (1958); J. D. Rockenfeller and F. D. Rossini, *J. Phys. Chem.*, **65**, 267 (1961).

Keith Yates,* Robert S. McDonald
Department of Chemistry, University of Toronto
Toronto, Ontario, Canada

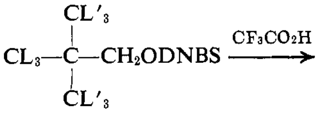
Received August 14, 1971

Lack of Methyl Participation in a Neopentyl Arylsulfonate Solvolysis

Sir:

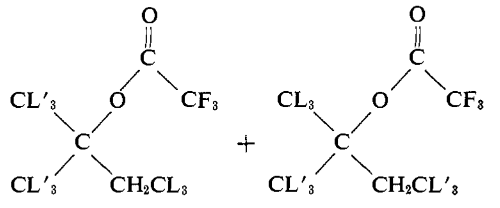
We have obtained relatively direct evidence that the methyl migration step and the rate-controlling step in the solvolysis of neopentyl 2,4-dinitrobenzenesulfonate in 97.3% trifluoroacetic acid are not the same. A further inference is that there is no methyl participation in the rate-controlling step. The method used consists of a comparison of the kinetic isotope effects produced by successive replacement of β-CH$_3$ by β-CD$_3$ with the extent of CH$_3$–CD$_3$ migration in the solvolyses of II and III.[1]

Trifluoroacetic acid was chosen as the solvent because (a) there is a pronounced accelerating effect of



$$\mathrm{CL_3{-}C(CL'_3)_2{-}CH_2ODNBS} \xrightarrow{\mathrm{CF_3CO_2H}}$$

I, CL$_3$ = CL$_3'$ = CH$_3$
II, CL$_3$ = CD$_3$; CL'$_3$ = CH$_3$
III, CL$_3$ = CH$_3$; CL'$_3$ = CD$_3$
IV, CL$_3$ = CL'$_3$ = CD$_3$



(1)

β-CH$_3$ (at 75°, $k_{\mathrm{NeoPOTs}}/k_{\mathrm{EtOTs}}$ = 480 in CF$_3$CO$_2$H and 1/1750 in EtOH)[2] which has been attributed to participation in the C–O heterolysis step, and (b) a single product, *tert*-amyl trifluoroacetate, is formed.[2] For practical reasons, 97.3% CF$_3$CO$_2$H containing 0.17 *M* CF$_3$CO$_2$Na was settled upon.[3,4] A fast leaving group also was required.[4]

First-order rate constants were determined by following the change in ultraviolet absorbance at 273 mμ of solutions *ca.* 2 × 10^{-4} *M* in substrate.[1,2] The results, Table I, show that there is no significant kinetic isotope effect. Other neopentyl derivative solvolyses also have little or no γ-*d* kinetic isotope effect.[1a,5]

Table I. First-Order Rate Constants, 10^4k (sec^{-1}), in 97.3% CF$_3$CO$_2$H-0.17 *M* CF$_3$CO$_2$Na[a,b]

Compd	30°	40°	50°
I	2.03 ± 0.02	6.32 ± 0.08[c]	18.4 ± 0.2
II		6.32 ± 0.02	
III		6.12 ± 0.06	
IV	1.99 ± 0.06	6.15 ± 0.11[c]	18.1 ± 0.1

[a] Average of three–five kinetic runs, except where indicated. [b] Average deviations listed. [c] Twelve runs.

Extents of CH$_3$ to labeled methyl migration in the samples of compounds II and III were determined by nmr, Table II. With an HA-100, 16 scans of the nmr spectrum of each solution, about 0.1 *M* in substrate, were made over the period 8–12 half-lives of the solvolysis and recorded in a Varian C-1024 time averaging computer.[6] The data were then transferred to a DEC PDP-12 computer in which the isolated γ-hydrogen

Table II. Relative Product γ-H Areas in 97.3% CF$_3$CO$_2$H-0.17 *M* CF$_3$CO$_2$Na at 40° [a,b]

I	II	III
100.24 ± 0.40	74.23 ± 1.36	41.56 ± 0.39

[a] γ-H areas of product solutions relative to a value of 100 for the Ar-H areas. [b] Standard deviations are listed.

---

[1] (a) W. M. Schubert and P. H. LeFevre, *J. Amer. Chem. Soc.*, **91**, 7746 (1969); (b) *ibid.*, in press.

[2] I. L. Reich, A. Diaz, and S. Winstein, *ibid.*, **91**, 5635 (1969).

[3] The ultraviolet spectral change in 100% CF$_3$CO$_2$H was too small for accurate rate determinations.

[4] In the time of 20 half-lives of the solvolysis of I, *tert*-amyl trifluoroacetate (0.1 *M*) in 97.3% CF$_3$CO$_2$D-0.17 *M* CF$_3$CO$_2$Na suffered less than 2% γ-D incorporation.

[5] For neopentyl methanesulfonate in water, $k_{\gamma\text{-}h_9}/k_{\gamma\text{-}d_9}$ = 1.017; M. J. Blandamer and R. E. Robertson, *Can. J. Chem.*, **42**, 2137 (1964).

[6] There was no detectable γ-hydrogen exchange over this time period, but β-hydrogen exchange was extensive.[4]

Table III. Per Cent Isotopic Composition of $(Cl_3)_3CCH_2OH$[a,b]

Sample					
$(CH_3)_2CCD_3CH_2OH$		d_3 82.9 ± 0.1	d_2 15.7 ± 0.1	d_1 0.7 ± 0.1	d_0 0.6 ± 0.1
$(CD_3)_2CCH_3CH_2OH$		d_6 66.7 ± 0.3	d_5 30.5 ± 0.2	d_4 1.0 ± 0.1	d_3 0.9 ± 0.1
$(CD_3)_3CCH_2OH$	d_9 56.3 ± 0.3	d_8 36.8 ± 0.3	d_7 2.8 ± 0.3	d_6 2.8 ± 0.3	d_5 1.3 ± 0.1

[a] Derived from average of five determinations of parent peak masses in a Consolidated Electrodynamics Model 21/103 mass spectrometer.
[b] Average deviations listed.

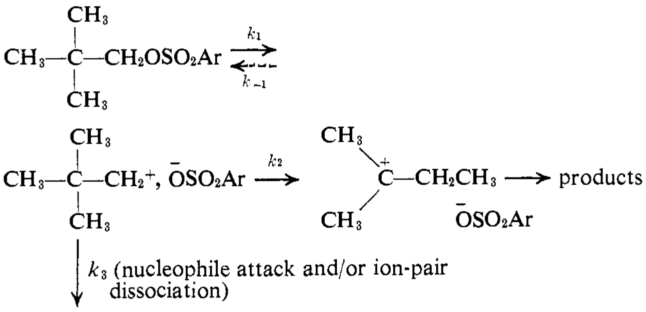
and aromatic-hydrogen areas were computed. Equation 2 expresses the relative extent of hydrogen to deuterium in the migrated groups.

$$[\gamma\text{-H}]_\infty/[\gamma\text{-D}]_\infty = \text{relative } \gamma\text{-H area}/(1.0024\text{relative ArH area} - \text{relative } \gamma\text{-H area}) \quad (2)$$

For isotopically pure II, $[\gamma\text{-H}]_\infty/[\gamma\text{-D}]_\infty$ would be directly $2k_{CH_3}{}^{CH_3,CD_3}/k_{CD_3}{}^{CH_3,CH_3}$, the ratio of rates of competitive CH_3 to CD_3 migration steps *alone*.[7] Similarly for pure III, $[\gamma\text{-H}]_\infty/[\gamma\text{-D}]_\infty$ would be directly $^1/_2 \cdot k_{CH_3}{}^{CD_3,CD_3}/k_{CD_3}{}^{CD_3,CH_3}$. However, as revealed by mass spectral analysis of the neopentyl alcohols, Table III, the sample of II was only 93.68% isotopically pure and the sample of III, 94.08%.[8] As an approximation, it was assumed that the samples behaved as a mixture of fully labeled and completely unlabeled compounds, and the appropriate nmr areas substracted from both the γ-H and Ar-H areas. This gives $k_{CH_3}{}^{CH_3,CD_3}/k_{CD_3}{}^{CH_3,CH_3} = 1.32 \pm 0.20$ and $k_{CH_3}{}^{CD_3,CD_3}/k_{CD_3}{}^{CD_3,CH_3} = 1.22 \pm 0.02$.[9] An exact treatment was based on the usual assumption of an additive effect per deuterium on the differential free energies of activation. For the sample of II, for example, set $k_{CH_3}{}^{CH_3,CH_2D}/k_{CH_2D}{}^{CH_3,CH_3} = (k_{CH_3}{}^{CH_3,CHD_2}/k_{CHD_2}{}^{CH_3,CH_3})^{1/2} = (k_{CH_3}{}^{CH_3,CD_3}/k_{CD_3}{}^{CH_3,CH_3})^{1/3} = \chi$,[1] which express the concentration of each isotopic product in terms of that of an isotopic starting material. Computer solution of the resulting cubic equations in χ gives $k_{CH_3}{}^{CH_3,CD_3}/k_{CD_3}{}^{CH_3,CH_3} = 1.31 \pm 0.20$ and $k_{CH_3}{}^{CD_3,CD_3}/k_{CD_3}{}^{CD_3,CH_3} = 1.22 \pm 0.02$.[9] Of course, each of these rate constant ratios for the migration step is not purely a migrational isotope effect (*i.e.*, one with constant nonmigrating groups) but is the product of a migrational isotope effect (CH_3 *vs.* CD_3 migrating) and the inverse of a secondary, nonmigrational isotope effect (CD_3 *vs.* CH_3 nonmigrating). Although the agreement between $k_{CH_3}{}^{CH_3,CD_3}/k_{CD_3}{}^{CH_3,CH_3}$ and $k_{CH_3}{}^{CD_3,CD_3}/k_{CD_3}{}^{CD_3,CH_3}$ is nothing to write home about, it is clear that both ratios differ significantly from unity.

Since there is no significant kinetic isotope effect but nevertheless a distinct preference for CH_3 to migrate faster than CD_3, it is concluded that the migration step probably occurs after the rate-controlling step. For the rate-controlling and migration steps to be the same would require a fortuitous cancelling or near-cancelling (bearing in mind experimental error) of the kinetic isotope effects exerted in migrating *vs.* nonmigrating groups of all three isotopic compounds. Furthermore, it can be shown that if the rate-controlling and migration steps are assumed to be the same, then the kinetic isotope effect exerted in the nonmigrating group would have to be inverse; that is, the rate increased by deuterium in the nonmigrating group. This would be unlikely since in a transition state involving synchronous methyl migration and C–O bond heterolysis, the deuterium in the nonmigrating group would lie β to a developing cationic center.

The following mechanistic scheme is consistent with both methyl migration after the rate-controlling step and the enhancement of the relative rate of neopentyl to ethyl arylsulfonate solvolysis in such solvents as trifluoroacetic acid. The scheme is an extension to primary systems of that proposed by Shiner for secondary systems, *e.g.*, 3,3-dimethyl-2-butyl *vs.* isopropyl brosylate,[10,11] and corresponds to a suggestion by Sneen.[12]



Ionization to the ion pair, step 1, would be rate controlling if rearrangement of the ion pair (and subsequent product formation) is faster than ion pair return ($k_2 > k_{-1}$). Ion pair rearrangement to tertiary cation could circumvent, *i.e.*, have a lower barrier than, nucleophile attack on the ion pair and/or dissociation of the ion pair ($k_2 < k_3$). For the ethyl compound on the other hand, nucleophile attack on the ion pair or dissociation of the ion pair could be rate controlling ($k_3 < k_{-1}$).[10,12] *I.e.*, by means of the escape hatch of ion pair rearrangement, the transition state of highest free energy along the direct path to products can be changed from that in the step of nucleophilic attack on ion pair or ion pair dissociation (ethyl compound) to that in the first step (neopentyl compound), of lower free energy. Thus acceleration would not be due to participation in the ioni-

---

(7) In the symbols $k_{CL_3}{}^{CL_3,CL'_3}/k_{CL'_3}{}^{CL_3,CL_3}$, the subscript denotes the migrating group and the superscripts denote the nonmigrating groups.

(8) In the preparation of II, 99.5% CD_3I was used, and in the preparation of III, 99.5% CD_3COCD_3.

(9) The ± figures are standard deviations and include that for the relative γ-H area of the d_0 compound.

(10) V. J. Shiner, Jr., R. D. Fisher, and W. Dowd, *J. Amer. Chem. Soc.*, 91, 7748 (1969).

(11) Solvolysis of 3,3-dimethyl-2-butyl brosylate also has only a small γ-d_9 kinetic isotope effect,[1,10] although α-*d* and β-d_3 kinetic isotope effects are substantial,[10] *i.e.*, consistent with rate-controlling formation of an unrearranged ion pair.

(12) R. A. Sneen and J. W. Larsen, *J. Amer. Chem. Soc.*, 91, 6035 (1969).

zation step, but rather to rearrangement of the ion pair *after* the ionization step.[10,12]

Acknowledgment. Support by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged, as well as an NDEA Title IV Fellowship for one of the authors (W. L. H.).

W. M. Schubert,* William L. Henson
Department of Chemistry, University of Washington
Seattle, Washington 98195
Received August 2, 1971

Infrared Spectrum of Matrix-Isolated HBO

Sir:

Boroxine ($H_3B_3O_3$), a trimer of HBO, has been observed as a product in a number of high temperature (or high energy) reactions including (a) the reaction of H_2O with elemental boron at temperatures above 1000°,[1] (b) explosive reactions of B_2H_6–O_2[2] and B_5H_9–O_2[3] mixtures at low pressures, and (c) the photolysis of $H_2B_2O_3$–B_2H_6 mixtures with radiation in the vacuum-ultraviolet.[4] These experimental results have suggested that a simple monomeric species, HBO, is a short-lived chemical intermediate. We have now identified the HBO molecule as one of the photolysis products of $H_2B_2O_3$ in a low-temperature argon matrix.

The matrix-isolation apparatus has been described.[5] Manometrically prepared gas mixtures of Ar and $H_2B_2O_3$ were metered into the vacuum system and deposited on a cooled (5°K) CsI target window. Residual pressure in the system was maintained at 5×10^{-6} Torr or lower during deposition. The photolysis source was a low-pressure (0.5 mm) Xenon lamp[6] with a LiF window. The body of lamp was extended through a sealed flange into the vacuum system to place the lamp window within 4 cm of the target window. Microwave power for the lamp was provided by a Raytheon 2450-MHz unit. Radiation reaching the target has a wavelength of 1480 Å with a half-width of about 10 Å. In a typical experiment, a gas sample containing Ar + $H_2B_2O_3$ was simultaneously deposited and photolyzed for 5 hr with a total deposition of $10\text{–}15 \times 10^{-6}$ mol of $H_2B_2O_3$. The dewar was then rotated and the absorption infrared spectrum (4000–250 cm^{-1}) was recorded on a Perkin-Elmer 521 spectrometer calibrated with NH_3 and HCl. Essentially identical spectra were obtained from the following experiments: (1) variation of the molar ratio of $Ar/H_2B_2O_3 = 250$ to a ratio of 1000, (2) photolysis during or after deposition, and (3) photolysis with a low-pressure xenon lamp or a medium-pressure mercury lamp (1849-Å radiation). Samples of $H_2B_2O_3$ with the natural isotopic composition were prepared from B_5H_9 and O_2.[7] Isotopically labeled samples, $D_2B_2O_3$, $H_2{}^{10}B_2O_3$, and $D_2{}^{10}B_2O_3$, were prepared from the appropriately labeled diborane and oxygen.[4]

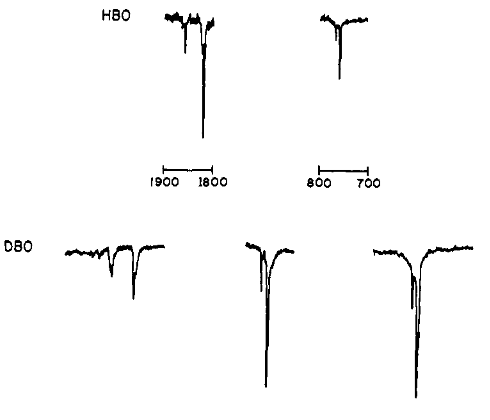


Figure 1. Infrared spectra of matrix-isolated HBO and DBO.

Products of the photolysis of $H_2B_2O_3$ in an argon matrix exhibit strong ir absorption in the region 2000–2130 cm^{-1}; moderately strong bands at 3685 and 3635 (OH stretching region), 1382 and 1425 (^{11}B–O and ^{10}B–O stretch), 1398 and 1440 cm^{-1} (^{11}B–O and ^{10}B–O stretch); a relatively broad band centered at 3367 cm^{-1} which shifts to 2505 cm^{-1} on deuterium substitution; and a group of line-like bands that will be discussed subsequently. Two of the strongest bands at 2062 and 2130 cm^{-1} that also appear when $D_2B_2O_3$ is photolyzed are readily identified with the molecule B_2O_3.[8]

In Figure 1 is shown the band structure associated with the molecule HBO and in Tables I and II are listed fundamentals and results of product rule calculations based on a linear molecule with $C_{\infty v}$ symmetry. There is very good agreement between the experimental and calculated results in Table II. Force constants calculated by assuming a simple valence force model[9] for

Table I. Frequencies (cm^{-1}) Observed for HBO in an Argon Matrix

	Isotopic species			
	H^{11}BO	H^{10}BO	D^{11}BO	D^{10}BO
ν_1	(2849)[a]	(2874)[a]	2259	2303
ν_2	754	764	606	617
ν_3	1817	1855	1648	1663

[a] Calculated.

Table II. Product Rule Calculations for HBO

Vibration species	Isotope pair X/X′	$(\nu_1\nu_3)/(\nu_1'\nu_3')$ Obsd	$(\nu_1\nu_3)/(\nu_1'\nu_3')$ Calcd	ν_2/ν_2' Obsd	ν_2/ν_2' Calcd
Σ^+	D^{10}BO/D^{11}BO	1.029	1.031		
π	H^{10}BO/H^{11}BO			1.013	1.013
π	H^{11}BO/D^{11}BO			1.244	1.243
π	D^{10}BO/D^{11}BO			1.018	1.019

---

(1) W. P. Sholette and R. F. Porter, *J. Phys. Chem.*, **67**, 177 (1963).

(2) L. Barton, F. Grimm, and R. F. Porter, *Inorg. Chem.*, **5**, 2076 (1966).

(3) G. H. Lee, W. H. Bauer, and S. E. Wiberly, *J. Phys. Chem.*, **68**, 1443 (1964).

(4) F. A. Grimm and R. F. Porter, *Inorg. Chem.*, **7**, 706 (1968).

(5) A. Kaldor and R. F. Porter, *J. Amer. Chem. Soc.*, **93**, 2140 (1971).

(6) P. G. Wilkinson and Y. Tanaka, *J. Opt. Soc. Amer.*, **45**, 344 (1955).

(7) J. F. Ditter and I. Shapiro, *J. Amer. Chem. Soc.*, **81**, 1022 (1959).

(8) A. Sommer, D. White, M. J. Linevsky, and P. E. Mann, *J. Chem. Phys.*, **38**, 87 (1963); W. Weltner, Jr., and J. R. W. Warn, *ibid.*, **37**, 292 (1962).

(9) G. Herzberg, "Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1945, p 173.