since the difference between these two positions regarding orbital coefficients in the LUMO and atomic charge densities is not large enough to warrant such a high selectivity on C-2 carbon atom, at least on model compounds of types C and D. We suspect that coordination of a metal ion as a Lewis acid with the oxirane oxygen preceding the nucleophilic attack of the base may be the cause. In order to simulate metal ion coordination at the oxirane oxygen in the simplest possible way, the approach of a proton to the oxiranic oxygen of α,β-epoxy-γ-butyrolactone (12) was simulated with the MOPAC program. An intermediate was obtained at a O···H distance of 0.96 Å. Full geometry minimization on this intermediate was carried out and the final results denoted a molecule having an almost symmetrical oxirane ring. The atomic orbital contributions to the calculated LUMO of this cationic intermediate showed that the most reactive center toward a soft nucleophile will be the C-2 atom,[14] while the C-3 position is still the hardest carbon atom (charge control; Figure 1).

In summary, we conclude that a consistent explanation for the mode of addition of a base to conjugated oxiranes can be obtained by performing theoretical diagnosis based on the LUMO electron densities and charge distribution that result from molecular orbital calculations on simple model compounds on a semiempirical level like MNDO. It may be noted that the HSAB theory alone failed to correctly interpret the behavior of type B compounds toward ring opening with soft bases. The intervention of metal ion coordination seems to be important in the regioselectivity of the 1,2-addition in α,β-epoxy esters or lactones, as deduced from MNDO calculation on the simplest possible model.

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Registry No. 1, 930-22-3; 2, 765-34-4; 3, 111410-09-4; 4, 4538-50-5; 12, 111410-10-7.

Supplementary Material Available: Full computer print out for the MNDO calculations on compounds 1-4 and 12 (43 pages). Ordering information is given on any current masthead page.

(14) IUPAC numbering was not maintained, to keep consistency with in Table I compounds.
(15) Molecular orbital representation obtained by PSI/77 program: Jorgensen, W. L. QCPE program 340.

Application of Mechanistic and Transition-State Indicators to *endo*- and *exo*-2-Norbornyl Arenesulfonates. Definition of a New Mechanistic Indicator

Samuel P. McManus,*† Maurice R. Smith, Jean M. Shankweiler, and Robert V. Hoffman*‡

Departments of Chemistry, The University of Alabama in Huntsville, Huntsville, Alabama 35899, and New Mexico State University, Las Cruces, New Mexico 88003

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We have mechanistically classified *endo*- and *exo*-2-norbornyl arenesulfonates by using two common probes: the effect on rate of added thiourea and rate correlation in aqueous ethanol and trifluoroethanol. Interestingly, the exo isomer is improperly classified by each of these probes because of medium-dependent ion-pair return. In search of better mechanistic indicators, pseudo-first-order solvolytic rates and products have been determined for a series of *endo*- and *exo*-2-norbornyl arenesulfonates. Using these and literature data, we have compared these substrates with others by plotting α-deuterium isotope effects against β_{1g}^{Me} values determined for a series of arenesulfonates in the same or a similar solvent. The use of this type of plot as a heuristic method for distinguishing k_s and k_Δ substrates is discussed. Finally, our product studies are consistent with the involvement of solvent-separated ion pairs in the solvolysis of 2-norbornyl arenesulfonates. Different alcohol–ether product ratios for the isomeric esters is consistent with dual pathways for product formation with the endo substrates.

The quite different solvolytic behavior of isomeric 2-norbornyl halides and esters has attracted considerable attention and sparked controversy.[1,2] A prime contributor to the controversy is the unfortunate fact that most mechanistic indicators are too imprecise to deal with the reactivity of substrates that show any complexity; clearly the 2-norbornyl substrates are not simple. Although there is no longer a controversy,[2] an unequivocal method for mechanistic characterization of substrates that are *weakly* solvent assisted (k_s substrates), *weakly* neighboring group assisted (k_Δ substrates), and nucleophilicially unassisted (k_c substrates) would still be welcome.[3] In this paper we evaluate *exo*- and *endo*-2-norbornyl arenesulfonates with the use of common probes that are readily applicable to most substrates, and we discuss the results in terms of the solvolytic mechanisms and transition states. Our data further illustrates the problems with quantifying these substrates by qualitative probes.

Results and Discussion

Mechanistic Characterization. Three distinct mechanisms have been identified for solvolysis reactions:[3] backside nucleophilic assistance by the solvent is important with the greatest number of substrates, called k_s substrates; another group of substrates (k_Δ substrates) undergoes

† Address correspondence to this author at the University of Alabama in Huntsville.
‡ Address correspondence to this author at the New Mexico State University.

(1) Reviews: Grob, C. A. *Acc. Chem. Res.* **1983**, *16*, 426. Brown, H. C. *Ibid.* **1983**, *16*, 432. Olah, G. A.; Surya Prakash, G. K.; Saunders, M. *Ibid.* **1983**, *16*, 440. Brown, H. C. *The Nonclassical Ion Problem*; with comments by Schleyer, P. v. R.; Plenum Press: New York, 1977.
(2) Walling, C. *Acc. Chem. Res.* **1983**, *16*, 448.
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Table I. Solvolysis of *endo*- and *exo*-2-Norbornyl Tosylate in the Presence of Variable Amounts of Thiourea

isomer	solvent[a]	T, °C	thiourea, M	10^4k, s^{-1}	k_{rel}
endo[b]	50E	50	0	1.41	1.0
			0.1	1.51	1.07
			0.2	1.58	1.12
exo[c]	60E	25	0	15.2	1.0
			0.1	16.8	1.11
			0.2	18.4	1.21
			0.5	22.9	1.51
	80E	25	0	2.58	1.0
			0.1	2.76	1.07
			0.2	2.98	1.16
			0.5	3.81	1.48

[a] Solvents (v/v) 50E, 60E, and 80E are 50%, 60%, and 80% ethanol, respectively. [b] Data from ref 5. [c] One determination at each concentration.

solvolytic displacement with intramolecular assistance from n, π, or σ electrons; the third class of substrates (k_c substrates) relies on inductive stabilization by the carbon skeleton. In principle each of these mechanistic types can occur competitively; however, one or two processes are generally more energetically favorable for a given substrate.

Detection of Nucleophilic Solvent Assistance. The Thiourea Probe. Of the methods put forth to detect nucleophilic solvent participation in solvolytic processes, many are too qualitative to be of real value in assigning mechanism.[4] Two methods have proven to be especially useful in solvolytic studies: the affect of added neutral nucleophiles on rate[5] and the trifluoroethanol (TFE)–ethanol (EtOH) probe.[6] The observation of an effect on the solvolytic rate of adding nucleophiles to a reaction relates to Ingold's original description of S_N1 and S_N2 processes. Rates of S_N1 displacement reactions are independent of added nucleophiles while S_N2 processes have rates that are dependent on the concentration of added nucleophiles. However, experimental evaluation of the rate dependence on added nucleophiles is not always straightforward. If anions are used as the added nucleophile, variable salt effects may occur and give results that are difficult to analyze. We recently proposed the general use of thiourea as a relatively nonperturbing nucleophile for mechanistic characterization.[5] When thiourea produces a rate acceleration, nucleophilic assistance of leaving-group displacement is indicated. Substrates that undergo solvolysis with external ion pair return are anomalous. When anomalous cases have been found, demonstration of a common ion effect and rate–product correlations have allowed a proper analysis of the data.[5]

Substrates that show no rate acceleration with added thiourea are interpreted to be undergoing solvolytic displacement without nucleophilic assistance (k_c substrates), or they are neighboring group assisted (k_Δ substrates). Application of the thiourea probe to k_c or k_Δ substrates typically reveals slightly depressed rates with added thiourea.[5]

The pseudo-first-order rates of solvolysis of *endo*- and *exo*-2-norbornyl tosylates in aqueous ethanol with varying amounts of added thiourea are shown in Table I and the data are plotted in Figure 1. The data show a clear acceleration by thiourea in each case. With the endo derivative the acceleration is evidence for a weak nucleophilically assisted process.[5] This conclusion is warranted by considering the thiourea results in combination with other data. For example, a small amount of inversion is found in the products from solvolysis of optically active *endo*-2-norbornyl brosylate, e.g. 13% inversion in aqueous acetone, 7% in acetic acid, and 3% in formic acid.[7] Also, the endo isomer is known to give no internal or external ion pair return, and their is no common ion effect on its solvolytic rate. Therefore, by the thiourea probe, *endo*-2-norbornyl tosylate is a weak k_s substrate. From a consideration of other data,[4,7] one must conclude either that the k_s pathway for this substrate partitions to backside displacement products and solvent-separated ion pairs or that the energies of the k_s and k_c pathways are similar and hence compete.

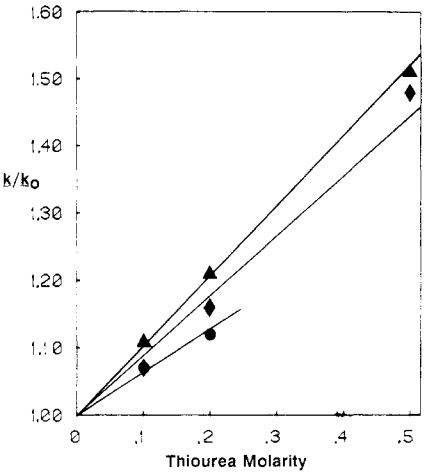

Figure 1. Effect of thiourea on pseudo-first-order rate constants for reaction of *endo*-2-norbornyl tosylate in 50% aqueous EtOH (●) and *exo*-2-norbornyl tosylate in 60% aqueous EtOH (▲) and 80% aqueous EtOH (◆).

The solvolytic behavior of the exo isomer in the presence of thiourea is more complicated. We observe acceleration, in fact slightly more than with the endo isomer, in two concentrations of aqueous ethanol. This finding is not what one observes with any other k_Δ substrate.[5] There were two k_c (S_N1) substrates (benzyhydryl and *p*-methoxybenzyl) in our recent study[5] that showed acceleration by thiourea. In each case, ion-pair return was suggested as the reason why the probe fails to properly predict mechanism in these cases. Unlike the endo isomer, *exo*-2-norbornyl substrates do suffer ion-pair return. For example, with optically active *exo*-2-norbornyl brosylate, the polarimetric rate exceeds the titrimetric rate by 1.4 in aqueous acetone, by 2.94 in ethanol, and by 4.6 in acetic acid.[7] In fact, key pieces of evidence that Winstein used to suggest the existence of a stabilized, bridged ion structure for the 2-norbornyl cation were the ease with which optically active *exo*-2-norbornyl brosylate undergoes racemization and the formation of substitution products which are only exo (retained stereochemistry) and racemic.[7] Apparently, thiourea is competing with ion-pair return and hence affecting the rate. This would seem reasonable since the return is solvent dependent.

The Trifluoroethanol–Ethanol Probe. The TFE–EtOH probe has been shown to be useful in mechanistically characterizing a wide variety of substrates.[6] This probe is based on the observation that the addition of water to EtOH causes a large gradual increase in ionizing

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(5) McManus, S. P.; Neamati-Mazraeh, N.; Karaman, R.; Harris, J. M. *J. Org. Chem.* **1986**, *51*, 4876.
(6) Raber, D. J.; Neal, W. C., Jr.; Dukes, M. D.; Harris, J. M.; Mount, D. L. *J. Am. Chem. Soc.* **1978**, *100*, 8137. Harris, J. M.; Mount, D. L.; Smith, M. R.; Neal, W. C., Jr.; Dukes, M. D.; Raber, D. J. *Ibid.* **1978**, *100*, 8147.
(7) Winstein, S.; Trifan, D. *J. Am. Chem. Soc.* **1949**, *71*, 2953. Winstein, S.; Trifan, D. *Ibid.* **1952**, *74*, 1147, 1154. Winstein, S.; Clippinger, E.; Howe, R.; Vogelfanger, E. *Ibid.* **1965**, *87*.

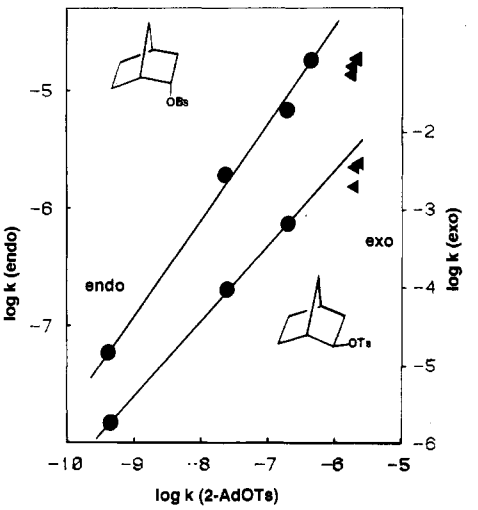

Figure 2. Plot of rates of isomeric norbornyl arenesulfonates versus 2-adamantyl tosylate in aqueous TFE(▲) and aqueous EtOH (●).

power without markedly affecting nucleophilicity, while addition of water to TFE markedly increases the resulting solvent's nucleophilicity while leaving the ionizing power nearly constant. Thus substrates that undergo nucleophilically solvent-assisted displacement (k_s substrates) show a depressed reactivity in TFE, leading to different correlation lines when log k is plotted against Y for solvolysis in aqueous EtOH and in aqueous TFE.

Raber and Harris applied the TFE–EtOH probe to *endo*-2-norbornyl brosylate and *exo*-2-norbornyl tosylate, plotting log k for the norbornyl arenesulfonates versus rates for 1-adamantyl bromide (Y_{Br}).[4,6] Their analysis of the data led them to conclude that *exo*-2-norbornyl was k_c or k_Δ while the *endo*-2-norbornyl isomer is a borderline k_s–k_c substrate. Unfortunately, it was not known at that time that, for valid TFE–EtOH correlations, use of Y values for the leaving group under consideration is necessary.[8] We have reevaluated the norbornyl arenesulfonates by plotting the published arenesulfonate rate data versus 2-adamantyl tosylate rates (Y_{OTs}), Figure 2. Like Raber and Harris, we conclude that the *endo*-2-norbornyl brosylate data is best interpreted as a k_s substrate.

The exo isomer again presents an interpretational problem. Raber and Harris obtained one correlation line for the aqueous TFE and aqueous EtOH data for *exo*-2-norbornyl tosylate plotted against 1-adamantyl bromide (Y_{Br}). However, when using Y_{OTs} (to compare with tosylates), we get what is apparently two correlation lines; that is, when plotted against Y_{OTs}, the rate data for solvolysis of *exo*-2-norbornyl tosylate in aqueous TFE gives a different slope (m = 2.87, r = 0.682) from the aqueous EtOH data (m = 0.958, r = 0.9999). Data points for solvolysis in aqueous TFE fall below the line drawn through the aqueous EtOH data. Of course, it is possible to draw one correlation line through the data (m = 0.860, r = 0.9943), but two correlation lines are visually evident (Figure 2). Since there is a wealth of evidence against *exo*-2-norbornyl derivatives being k_s substrates, we must conclude that the TFE–EtOH probe incorrectly predicts for *exo*-2-norbornyl tosylate.

We recently reported that the TFE–EtOH probe fails for mustard chlorohydrin, giving a similar plot to that for *exo*-norbornyl, but one that is considerably more distorted.[9] Mustard chlorohydrin is a k_Δ substrate that undergoes solvolysis with neighboring sulfur participation, yet its TFE–EtOH plot predicts it to be a k_s substrate. At that time we put forth two reasons that would account for the failure of the TFE–EtOH plot to properly characterize the mustard hydrolysis intermediate. First, we acknowledged that solvent-dependent ion pair return could lead to the observed behavior. For example, the nucleophilicity of 97% aqueous TFE is considerably less than that of 40% aqueous EtOH although these solvents have similar ionizing powers (Y values). On a relative basis, the leaving group, Cl^- in the case of mustard chlorohydrin, would be more likely to give significant return in 97% aqueous TFE than in 40% aqueous EtOH.

A second reason we put forth to possibly explain why the TFE–EtOH probe fails with mustard chlorohydrin relates to electrophilic differences between the mustard derivative and the model against which it is plotted (Y_{Cl} values are obtained from 1-adamantyl chloride rates). We have shown elsewhere that mustard model substrates and 1-adamantyl chloride have different susceptibilities to electrophilicity.[10] Thus as the electrophilicity of the solvent is increased, it is possible for the neighboring sulfur group to become encumbered by electrophilic solvation, hence producing a lower rate than anticipated.

Considering these two failure modes with the norbornyl substrate, one clearly is favored. Electrophilic solvation of the neighboring σ bond in the norbornyl substrate does not seem to be a plausible failure mode. On the other hand, as pointed out above, *exo*-2-norbornyl arenesulfonates are well known to suffer ion-pair return upon solvolysis. Such return is solvent dependent as judged from kinetics measurements with optically active substrates in different solvents. Therefore, the failure of the TFE–EtOH probe to properly predict the mechanism here is assigned to the ion pair return problem; that is, we believe that *exo*-2-norbornyl ion pair return varies with solvent nucleophilicity; hence, the rates in TFE are depressed.

Transition-State (TS) Characterization. A Linear Free Energy Relationship (LFER) Approach. If the norbornyl isomers are mechanistically different, as many indicators predict, their TSs should be different, and there should be indicators for the differences. The departure of the leaving group is related to the overall structural change, which for a particular leaving group is controlled by stabilization of the electron deficiency of carbon in the activated complex. From the Hammond postulate it follows that the amount of bond breaking to the leaving group is indicative of the presence and magnitude of the various modes of carbocation stabilization.[11] Strongly stabilizing features result in TSs characterized as early, with lower amounts of bond breaking. Weakly stabilizing features result in TSs characterized as late, which have more bond cleavage to the leaving group. It is thus reasonable that the extent of leaving group loss can provide valuable insight into structural changes occurring at the TS.[12]

Leaving group rate ratios (tosylate/chloride, tosylate/bromide, and bromide/chloride) have been used to eval-

(8) McLennan, D. J.; Martin, P. L. *J. Chem. Soc., Perkin Trans. 2* **1982**, 1091.

(9) McManus, S. P.; Neamati-Mazraeh, N.; Hovanes, B. A.; Paley, M. S.; Harris, J. M. *J. Am. Chem. Soc.* **1985**, *107*, 3393.

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(11) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

(12) For a review of the use of Hammett rho values as an index of TS character, see: McLennan, D. J. *Tetrahedron* **1978**, *34*, 2331.

Table II. Pseudo-First-Order Rates and Products of Solvolysis of 2-Norbornyl Arenesulfonates in 80% Aqueous Ethanol (v/v) at 31.2 °C

substrate	X	10^4k, s^{-1}	ROEt/ROH[a]
endo-2-norbornyl *p*-X-benzenesulfonate			
	OMe	0.00559 ± 0.00001	0.89 ± 0.01
	Me	0.00815 ± 0.00020	0.91 ± 0.03
	F	0.0234 ± 0.0006	0.92 ± 0.05
	Cl	0.0376 ± 0.0007	0.99 ± 0.08
	Br	0.0385 ± 0.0001	1.01 ± 0.07
	NO_2	0.294 ± 0.014	1.05 ± 0.04
exo-2-norbornyl *p*-X-benzenesulfonate			
	OMe	2.88 ± 0.05	0.66 ± 0.08
	Me	4.47 ± 0.02	0.79 ± 0.03
	F	16.3 ± 0.2	0.81 ± 0.02
	Cl	24.8 ± 0.2	0.86 ± 0.07
	Br	26.1 ± 0.4	0.90 ± 0.07
	NO_2	173 ± 3	0.98 ± 0.02

[a] ROEt/ROH is the percent ether divided by the percent alcohol found by GLC analysis of reactions run at 55 °C for 48 h with 0.1M arenesulfonate solutions in 80% (v/v) aqueous ethanol with a 2,6-lutidine buffer. For the plot in Figure 4, k_E/k_W = ROEt/ROH × $[H_2O]/[EtOH]$.

uate transition state (TS) charge development.[13,14] Brown and Schleyer and co-workers showed that some unusually high-rate ratios were affected by steric factors; hence interpretation of the meaning of these rate ratios must take into account steric contributions.[15] Owing to the low reactivity of the endo derivative and the potential for different steric factors on the ratios, we have not attempted to evaluate tosylate/chloride or tosylate/bromide rate ratios for the isomeric norbornyl substrates. However, we believe a significant amount of information about TS structure is available from leaving group ratios and have evaluated these with the use of arenesulfonates where, within a series, the steric factors are unchanged and where results can be treated by LFERs.

The most commonly used LFER for studying reaction mechanisms in general is the Hammett treatment.[16] Recently, two of us reported a method that permits the extent of carbon–leaving group bond breaking to be evaluated quantitatively for arenesulfonate leaving groups.[17] The method is based on a Brønsted-type LFER, where rate data are plotted versus equilibrium constants for methyl transfer between arenesulfonates, which Lewis and his colleagues have determined.[18] The slopes of these plots, β_{lg}^{Me}, represent the extent of bond cleavage to leaving group at the TS. The advantage of this approach is that the methyl-transfer equilibrium provides a good model reaction for ionization from carbon of arenesulfonate leaving groups. Thus β_{lg}^{Me} values range between the limits of 0 and 1 and represent no and complete loss of arenesulfonate, respectively, at the TS. Not surprisingly, β_{lg}^{Me} values correlate well with Hammett ρ values.[19]

Table III. Comparison of β Values and Deuterium Isotope Effects for Arenesulfonate Displacement in Substitution Reactions in 80% Aqueous Ethanol (80E)

$ROSO_2Ar$, R	mechanistic type	α-*d* (solvent)	β_{lg}^{Me} (°C)
methyl	k_s	0.98 (MeOH)[a]	0.45 (50)[b]
ethyl	k_s	1.02 (MeOH)[c]	0.44 (50)[b]
2-propyl	k_s	1.098 (80E)[d]	0.50 (50)[b]
allyl	k_s	1.074 (80E)[e,f]	0.51 (50)[g]
endo-2-norbornyl	k_s–k_c	1.193 (80E)[h]	0.56 (31.2)[i]
exo-2-norbornyl	k_Δ	1.124 (80E)[h]	0.57 (3.12)[i]
2-adamantyl	k_Δ–k_c	1.149 (80E)[j]	0.57 (75)[k]
cyclobutyl	k_Δ	1.10 (AQDG)[l]	0.55 (50)[m,n]
2-(phenylthio)ethyl	k_Δ	1.064 (EtOH)[o]	0.44 (25)[m,o]

[a] Johnson, R. R.; Lewis, E. S. *Proc. Chem. Soc., (London)* **1958**, 52. See also: Llewellan, J. A.; Robertson, R. E.; Scott, J. M. *Can. J. Chem.* **1960**, *38*.222. [b] Robertson, R. E. *Can. J. Chem.* **1953**, *31*, 589. [c] Lewis, E. S.; Brown, J. C; Herndon, W. C. *Can. J. Chem.* **1961**, *39*, 954. See also: Keffek, K. T.; Llewellan, J. A.; Robertson, R. E. *Can. J. Chem.* **1960**, *38*, 1505 and 2171. [d] Shiner, V. J., Jr.; Fisher, R. D.; Dowd, W. *J. Am. Chem. Soc.* **1969**, *91*, 7748. [e] This α-*d* is for benzyl tosylate in 80E and is expected to be similar to allyl. [f] Shiner, V. J., Jr.; Rapp, M. W.; Pinnick, H. R., Jr. *J. Am Chem. Soc.* **1970**, *92*, 232. [g] Reference 20. [h] Reference 25. [i] This work, see Table II. [j] Harris, J. M.; Hall, J. M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1971**, *93*, 2551. [k] Calculated from the correlation between for $2\text{-AdOSO}_2\text{Ar}$ solvolysis in 100E and 70E and solvent Z or Y values; data, respectively, from: Kevill, D. N.; Kolwyck, K. C.; Shold, D.. M.; Kim, C.-B. *J. Am. Chem. Soc.* **1973**, *95*, 6022 and Harris, J. M.; Becker, A.; Fagan, J. F.; Walden, F. A. *Ibid.* **1974**, *96*, 4484. [l] AQDG is 60% aqueous diglyme; data from Goricnik, B.; Majerski, Z.; Borcic, S.; Sunko, D. E. *J. Org. Chem.* **1973**, *38*, 1881. [m] Interpolated from the data in EtOH on the basis of the solvent effect on the methyl, ethyl, allyl, and 2-propyl derivatives. [n] Data from reference 23. [o] Reference 14.

Since there is a significant solvent effect on the magnitude of Hammett ρ values for arenesulfonate leaving groups in solvolysis,[20] it is necessary for comparisons of this kind to be confined to a single solvent. We decided to correlate the rates of the arenesulfonates of *endo*- and *exo*-2-norbornyl arenesulfonates in 80% aqueous ethanol because we were able to measure all the derivatives at a single, low temperature. Also, since a large variety of solvolytic studies of arenesulfonate esters have been carried out in that solvent, comparisons with other substrates are possible. The pseudo-first-order rates of the isomeric norbornyl arenesulfonates, determined conductimetrically, are shown in Table II. With use of pK^{Me} values of Hoffman and Shankweiler,[17] the β_{lg}^{Me} values for the series were calculated. In Table III we have summarized the β values that we calculated for these and several other systems for which appropriate rate data exists. Together, these substrates represent various mechanistic types.

For different mechanistic types, the isomeric norbornyl substrates have surprisingly similar charge separations in their TSs as measured by β_{lg}^{Me}. Interestingly, they are similar to the 2-adamantyl arenesulfonate values, which are also high. This is taken to be indicative of substantial charge separation at the TS. 1-Adamantyl arenesulfonates, which are pure k_c substrates, have not been studied in this solvent; however, in pure ethanol, 1- and 2-adamantyl arenesulfonates have similar β_{lg}^{Me} values, 0.60 and 0.61, respectively.[14] High values for the adamantyl esters are expected since these substrates are well known to be essentially limiting S_N1 types although they are mechanis-

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(14) McManus, S. P.; Sedaghat-Herati, M. R.; Cronise, R. J., IV; Neamati-Mazraeh, N.; Harris, J. M., manuscript in preparation.
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(16) See ref 12 and, for more general references, see: March, J. *Advanced Organic Chemistry*, 3rd ed.; New York: Wiley, 1985; pp 242–250.
(17) Hoffman, R. V.; Shankweiler, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 5536.
(18) Lewis, E. S.; Douglas, T. A.; McLaughlin, M. L. In *Nucleophilicity*; ACS Advances in Chemistry Series No. 215; American Chemical Society: Washington D.C., 1987; Chaper 3.

(19) When plotted against one another, β and ρ values give high correlation coefficients; however, because of the lack of a complete set of methyl arenesulfonate equilibrium data, several pK^{Me} values have been derived from Hammett σ values, thus enforcing a correlation; cf. ref 17 and 18.
(20) Kevill, D. N.; Rissmann, T. J. *J. Org. Chem.* **1985**, *50*, 3062.

tically different, being k_c and k_c–k_Δ substrates, respectively.[21,22] At the other mechanistic extreme, i.e. substrates undergoing the purest form of backside solvent displacement,[3] are methyl and ethyl, which have low β values and, presumably, early TSs. Allyl and 2-propyl, both k_s substrates in ethanol, have intermediate β_{lg}^{Me} values consistent with an intermediate amount of TS bond extention and hence charge on the leaving group.

We recently studied (in 100% ethanol) a series of substrates, $PhSCH_2CH_2OSO_2Ar$, which react with neighboring sulfur participation.[14] That series gave a very low β_{lg}^{Me} value (equal to ethyl arenesulfonates). Cyclobutyl arenesulfonates, which have also been studied in ethanol, were included in the comparison group. A high β_{lg}^{Me} value (similar to that for 2-adamantyl) is found for the cyclobutyl arenesulfonates, which have been suggested to undergo solvolysis with neighboring carbon assistance, a k_Δ process, to give the more stable cyclopropylcarbinyl cation intermediate.[23] Since we have β values for methyl, ethyl, allyl, and isopropyl in both 80% and 100% ethanol, we are able to extrapolate the β values of the (phenylthio)ethyl and cyclobutyl arenesulfonates (known for 100% ethanol) to 80% ethanol. From the combined data, we conclude that substrates of all three mechanistic classes *may* have similar, large charge separations. At the same time, a k_Δ substrate with a strong internal nucleophile like the sulfur neighboring group may have a small TS charge on the leaving group similar to pure k_s substrates such as methyl and ethyl. Clearly, then, substrates undergoing solvolysis with neighboring carbon assistance have quite different TS charge separations than substrates that have stronger participating groups such as sulfur. However, β_{lg}^{Me} values alone are not the key to understanding the TS. In the next section we compare these results to those of another TS predictor, α-deuterium isotope effects.

α-Deuterium Isotope Effects.[24] The process of solvolytic unimolecular ionization (S_N1-type TS, k_c substrate) results in geometrical distortion from the original sp^3 geometry to a new TS geometry which is approaching sp^2. Secondary deuterium isotope effects at this position are the result of such flattening, and the magnitude of the α-k_H/k_D (α-*d*) is indicative of the extent of flattening in the activated complex. If the solvolysis occurs with backside nucleophilic solvent assistance (S_N2-type TS, k_s substrate), the geometry change is quite different as the TS is reached. Hence the α-*d* is quite different for the two substrate types.[24]

A serious interpretational problem lies in distinguishing k_Δ substrates from either k_s or k_c substrates using α-*d*'s. This problem results from the fact that neighboring group assisted reactions are internal S_N2 reactions; hence they bear a resemblance to k_s processes. On the other hand, with very weak internal nucleophiles, e.g. carbon, the processes may become borderline S_N1–S_N2-like processes and hence bear stronger resemblance to k_c substrates. For example, α-*d* values for 2-adamantyl sulfonate esters are known to be highly solvent and temperature dependent, approaching the upper limit for isotope effects.[24] The high values were thought to be consistent with a k_c mechanism. Recent evidence that 2-adamantyl substrates undergo solvolysis with neighboring carbon participation (a k_Δ substrate)[22] seems to question the value of Δ-*d*'s as tools for mechanistic assignment. The use of α-*d*'s for the 2-norbornyl isomers has also been controversial.[1,25] We show below that the combined use of α-*d*'s and β_{lg}^{Me} values promises to clarify the interpretational problems.

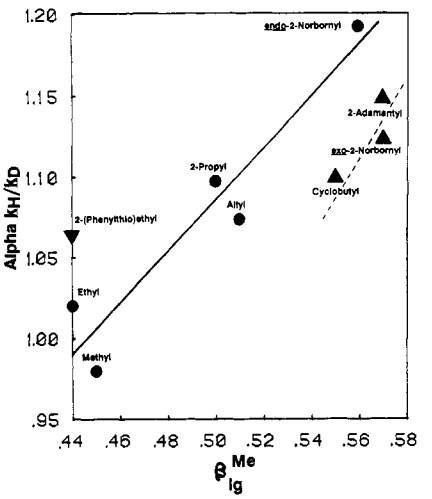

Figure 3. Plot of α-deuterium isotope effect versus β values for solvolysis of arenesulfonates in 80% aqueous EtOH.

To the extent that secondary isotope effects can be taken as a measure of geometrical changes at the TS, it is of interest to determine whether the extent of bond breaking to the leaving group, as measured by β_{lg}^{Me}, is related to the change in geometry of the α carbon. Fortunately, α-*d*'s for the substrates in Table III have been determined either in 80% aqueous ethanol or in a similar solvent. We have included these values in Table III. The interpretation of the data for *exo*-2-norbornyl is not straight forward because of ion pair return to unrearranged and rearranged substrate. Nevertheless, this problem has been treated by others[25] and has resulted in the acceptance of the value shown in Table III.

When α-*d*'s are plotted against β_{lg}^{Me} (Figure 3), a remarkable feature is that the data points for the five known k_s substrates give a good linear correlation, $r = 0.949$.[26] The line drawn through the five points is a linear regression line fitted to data following eq 1. The linear relationship between k_H/k_D and β_{lg}^{Me} in Figure 3 lends strong support to the notion that there is a smooth change in the degree of nucleophilic involvement of solvent at the transition state with different substrate types.[27]

$$k_H/k_D = 0.292 + 1.59\beta_{lg}^{Me} \quad (1)$$

A question that we and the referees have raised relates to the significance of the fit for this line. There are data points for non-k_s substrates that fall further off the line than any of the k_s substrates. Clearly, experimental error

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(26) For five data points, this value of r indicates a greater than 98% probability that the points are linearly related; cf. Young, H. D. *The Statistical Treatment of Experimental Data*; McGraw-Hill: New York, 1962; p 164.

(27) See ref 3 and the following: Winstein, S.; Grunwald, E.; Jones, H. W. *J. Am. Chem. Soc.* **1951**, *73*, 2700. Jencks, W. P. *Chem. Soc. Rev.* **1981**, *10*, 345.

and special steric or other geometric features contribute to some scatter in the plot. Nevertheless, we contend that the poor correlation of cyclobutyl, *exo*-2-norbornyl, and 2-adamantyl may be because they react by a different mechanism. These exceptional substrates are clearly not k_s substrates. There is concensus that *exo*-2-norbornyl and cyclobutyl are k_Δ substrates.[1,2,23] The 2-adamantyl substrate may be more debatable. For years 2-adamantyl derivatives have been considered to be model k_c substrates.[3,6,21] However, there is compelling recent evidence from the laboratories of le Nobel and Grob that reveals that special electronic effects may be operative in solvolyses of 2-adamantyl derivatives.[22] Le Nobel has argued that the evidence is consistent with carbon participation, while Grob prefers to call it inductivity. For our purposes here, it is not important what we term the effect. What is important to note is that the data point for each of the non-k_s substrates is off the k_s line by more than we think experimental or extrapolational errors allow. For example, to correlate, 2-adamantyl (the closest to the line of the three non-k_s substrates) would have to have an α-*d* of 1.20 rather than 1.15 or a β of 0.54 rather than 0.57. We do not think the errors are this great.

Why do k_s substrates and the k_Δ substrates (or k_Δ–k_c in the case of 2-adamantyl) not follow the same correlation? Actually, we do not have sufficient information to properly answer this question but there are precedents on which to base a reasonable response. Bordwell's studies of S_N2 displacement reactions of a variety of nucleophiles in DMSO provided Brønsted plots for several families of nucleophiles which, when treated as families, are linear over a wide range of pK units.[28] Also, it was found that correlations were sensitive to the identity of the nucleophilic atom (at a constant pK value). Thus there is reason to suggest that α-*d*'s for S_N2-type processes should be a function of the identity of the entering nucleophile. A reasonable explanation of the correlation for k_s substrates in Figure 3 follows: all are experiencing displacement by a solvent with oxygen as the nucleophilic atom. Substrates that react with neighboring group participation are experiencing displacement by a different nucleophile, the C–C σ bond or the thioether's sulfur atom. Of course, the increased strain of an intramolecular versus an intermolecular process may contribute to the poor correlation by the k_Δ substrates with the k_s substrates. There is also evidence indicating that α-*d*'s are sensitive to the identity of the nucleophile.[24]

In light of the above discussion, it is interesting to suggest that substrates having carbon participation may give a correlation as a second family. Despite having only three points, we have drawn a dotted line through these points (Figure 3) to illustrate this possible relationship. The correlation coefficient for the three points (r = 0.860) is indicative of a modest relationship. We think that it is significant that the data point for the 2-(phenylthio)ethyl arenesulfonates, which react with strong participation from the neighboring sulfur group, lies *above* the k_s line. Following our line of reasoning developed above, this would be consistent with there being families of nucleophiles with the stronger ones (with early TSs) giving correlations to the left and weaker one (with late TSs) giving correlation lines to the right. It is also possible to suggest that all k_Δ substrates follow a separate correlation with a much different slope than the k_s substrates. The study of additional substrates will show if correlations of families of nucleophiles or of families of reaction types occurs. Despite the lack of a good explanation for the underlying basis of these correlations, we believe that plots of α-*d* versus β_{lg}^{Me} show promise as a heuristic device useful in assigning mechanism. Clearly, the available data shows that 2-adamantyl and *exo*-2-norbornyl have transition states which are different than the *endo*-2-norbornyl TS.

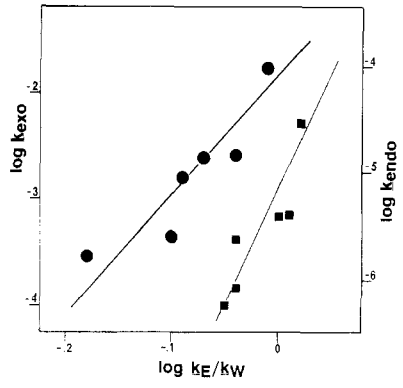

Figure 4. Stability–selectivity plot for *exo*- (●) and *endo*- (■) 2-norbornyl arenesulfonates.

In summary, we conclude that these various indicators suggest that solvolytic TSs may be quite variable within a mechanistic class, yet the indicators within that class are related and, when taken together, may be useful in discussing loose versus tight transition states. In this connection it is interesting to note that a high α-*d* value was previously taken as evidence that participation may be absent.[29] Clearly, these complementary probes promise to give us a better overall perspective on mechanism. Nevertheless, far more substrate types need to be studied before the scope and limitations of these probes can be assessed.

Nature of the Solvolysis Intermediates. Product Studies. It is well known that both *endo*- and *exo*-2-norbornyl arenesulfonates give only exo products of substitution. Winstein and co-workers concluded that the solvolytic pathway of exo esters involves return from tight ion pairs, but products form by solvent capture during collapse of solvent-separated ion pairs.[7] The results from the endo series have been explained as involving a partitioning of an initial tight ion pair to k_s product and the solvent-separated ion pairs (the same as that formed from the exo isomer), which collapse to product.[7] Since we had the series of arenesulfonates in hand, a product study seemed worthwhile. Therefore, the products of aqueous enthanolysis were determined by GLC, Table II. Each series gives a linear stability–selectivity correlation,[30] (Figure 4).

Since free cations give constant selectivities,[31] our product studies show that, if involved at all, free cations are not the only intermediate leading to product in either case. More specifically, others have shown that free cations show $k_E/k_W > 1$ and constant.[32] Thus, our observation of $k_E/k_W < 1$ and increasing is consistent with the involvement of solvent-separated ion pairs with different stabilities, depending on the counterion. The involvement of some free cation cannot be ruled out. The finding of

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(32) Ritchie, C. D. *Acc. Chem. Res.* **1972**, *5*, 342.

a higher selectivity for water is also consistent with solvent-separated ion pairs. This selectivity pattern has been often treated before, e.g., with 1- and 2-adamantyl substrates.[33] In this case as in others, there appears to be a preference for water molecules in the solvent-separated ion pairs, thus leading to a greater preference for water in the products. With the endo series, the data is affected by the k_s component, which does not involve solvent-separated ion pairs but involves backside attack by solvent. In that instance, ethanol may be preferred over water although steric factors make predicting a selectivity difficult.[34] These product studies are generally consistent with the mechanistic picture that has emerged from kinetic and other product studies.

The proposition that the endo derivatives are weak k_s substrates has not been universally accepted. The two main reasons for an alternate view are (i) typical k_s products are not dominant (only ca. 10% of the products are from backside attack) and (ii) *endo*-2-norbornyl substrates do not readily undergo S_N2 substitution reactions in the presence of good nucleophiles.[1,4] However, we believe that there is a considerable difference between a pure S_N2 TS in a nonhydroxylic solvent and solvolytic TSs in hydroxylic solvents. As revealed by our beta value and by the α-*d*, the solvolytic TS state for the endo sulfonate esters is late. This means that the backside of the developing carbocation is opened up for nucleophilic solvation and attack by the solvent. However, as Winstein proposed,[7] there is a merger of the k_s and k_c processes, leading to products from both pathways.

Summary

A number of mechanistic probes have been applied to the isomeric 2-norbornyl substrates in order to find support to mechanistically characterize their solvolyses. A number of differences in the behavior of the isomeric substrates can be detected, which can be explained by the now abundant data. However, we show that two normally reliable mechanistic indicators, the thiourea probe and the TFE–EtOH probe, fail for the exo isomer, presumably because of ion-pair return, which is solvent dependent. A linear correlation is found when α-deuterium isotope effects are plotted against β_{1g}^{Me} values determined for series of arenesulfonates in the same or a similar solvent. Since k_Δ substrates do not follow the same correlation, this type of plot may be a useful heuristic method for distinguishing k_s and k_Δ substrates. Finally, our product studies are consistent with the involvement of solvent-separated ion pairs in the solvolysis of 2-norbornyl arenesulfonates. Different alcohol–ether product ratios for the isomeric esters is consistent with the projection of different mechanisms and with the endo derivatives as k_s substrates that have a competing k_c component.

Experimental Section

General Procedures. Melting points are uncorrected. Infrared spectra were determined on a Beckman Acculab I spectrometer, the NMR spectra were determined on a Bruker HFX-90 spectrometer with tetramethylsilane as the internal standard, the refractive indexes were measured on a Bausch and Lomb Abbe 3L refractometer, the optical rotations were determined on a Rudolph Model 80 polarimeter, the product analyses were determined on a Varian Aerograph Series 1800 gas chromatograph with TC cells, and the conductivity was measured on a YSI Model 31 conductivity bridge with 60-Hz current. The conductivity cell employed 1-cm^2 platinum electrodes, separated by 1 cm, with a cell constant of 0.324 cm^{-1} at 25 °C. Anhydrous ethanol was obtained in the normal way.[35]

Materials. ***endo*-Bicyclo[2.2.1]heptan-2-ol (*endo*-norborneol)**, mp 144–145 °C (lit.[36] mp 148–149 °C), and ***exo*-bicyclo[2.2.1]heptan-2-ol (*exo*-norborneol)**, mp 124–126 °C (lit.[37] mp 124–126 °C), were purified prior to use. Sulfonate esters were prepared in dry pyridine with purified sulfonyl chlorides following the tosylate procedure.[38] The esters have the following characteristic properties and spectral data.[39] ***endo*-2-Norbornyl *p*-bromobenzenesulfonate**: mp 58–60 °C (lit.[7,40] mp 60.6–63 °C); NMR ($CDCl_3$) δ 7.72 (m, 4 H, Ar *H*), 4.83 (m, 1 H, C*H*OSO_2), 2.39 (br s, 1 H), 2.20 (br s, 1 H), 1.47 (br m, 8 H). ***endo*-2-Norbornyl *p*-methoxybenzenesulfonate**: colorless oil; $n^{22.5}{}_D$ 1.5370; NMR ($CDCl_3$) δ 7.81 (d, 2 H, J = 9 Hz), 6.98 (d, 2 H, J = 9 Hz), 4.76 (m, 1 H), 3.84 (s, 3 H), 2.33 (br s, 1 H), 2.16 (br s, 1 H), 1.49 (br m, 8 H). ***endo*-2-Norbornyl *p*-toluenesulfonate**: colorless oil; $n^{22.5}{}_D$ 1.5328; NMR ($CDCl_3$) δ 7.72 (d, 2 H, J = 8 Hz), 7.09 (m, 2 H, J = 8 Hz), 4.74 (br m, 1 H), 2.37 (s, 3 H, CH_3), 2.31 (br s, 1 H), 2.12 (br s, 1 H), 1.42 (br m, 8 H). ***endo*-2-Norbornyl *p*-fluorobenzenesulfonate**: colorless oil; $n^{22.5}{}_D$ 1.5192; NMR ($CDCl_3$) δ 7.91 (m, 2 H), 7.18 (m, 2 H), 4.80 (br m, 1 H), 2.33 (br s, 1 H), 2.16 (br s, 1 H), 1.44 (br m, 8 H). ***endo*-2-Norbornyl *p*-chlorobenzenesulfonate**: beige crystals; mp 49–51 °C; NMR ($CDCl_3$) δ 7.84 (d, 2 H, J = 8 Hz), 7.51 (d, 2 H, J = 8 Hz), 4.83 (br m, 1 H), 2.37 (br s, 1 H), 2.18 (br s, 1 H), 1.47 (br m, H). ***endo*-2-Norbornyl *p*-nitrobenzenesulfonate**: mp 90.5–92 °C; NMR ($CDCl_3$) δ 8.13 (d, 2 H, J = 9 Hz), 7.87 (d, 2 H, J = 8 Hz), 4.93 (br s, 1 H), 2.44 (br s, 1 H), 2.22 (br s, 1 H), 1.44 (br m, 8 H). ***exo*-2-Norbornyl *p*-toluenesulfonate**, mp 52–54 °C (lit.[37] mp 52–54 °C); NMR ($CDCl_3$) δ 7.78 (d, 2 H, J = 8 Hz), 7.30 (d, 2 H, J = 8 Hz), 4.47 (br m, 1 H), 2.43 (s, 3 H, CH_3), 2.39 (br s, 1 H), 2.26 (br s, 1 H), 1.32 (br m, 8 H). ***exo*-2-Norbornyl *p*-methoxybenzenesulfonate**; colorless oil; $n^{22.5}{}_D$ 1.5326; NMR ($CDCl_3$) δ 7.83 (d, 2 H, J = 8 Hz), 6.96 (d, 2 H, J = 8 Hz), 4.38 (br m, 1 H), 3.82 (s, 3 H, CH_3) 2.31 (br s, 1 H), 2.19 (br s, 1 H), 1.24 (br m, 8 H). ***exo*-2-Norbornyl *p*-fluorobenzenesulfonate**: colorless oil; $n^{22.5}{}_D$ 1.5155; NMR ($CDCl_3$) δ 7.91 (m, 2 H), 7.17 (m, 2 H), 4.46 (br m, 1 H), 2.37 (br s, 1 H), 2.26 (br s, 1 H), 1.37 (br m, 8 H). ***exo*-2-Norbornyl *p*-chlorobenzenesulfonate**: beige crystals; mp 43–45 °C; NMR ($CDCl_3$) δ 7.78 (d, 2 H, J = 8 Hz), 7.22 (d, 2 H, J = 8 Hz), 4.48 (br m, 1 H), 2.39 (br s, 1 H), 2.28 (br s, 2 H), 1.42 (br m, 8 H). ***exo*-2-Norbornyl *p*-bromobenzenesulfonate**: mp 54–56 °C (lit.[7] mp 55.3–57 °C); NMR ($CDCl_3$) δ 7.67 (m, 4 H), 4.49 (br m, 1 H), 2.38 (br s, 1 H), 2.28 (br s, 1 H), 1.40 (br m, 8 H). ***exo*-Norbornyl *p*-nitrobenzenesulfonate**: yellow crystals, mp 67–69 °C; NMR ($CDCl_3$) δ 8.14 (d, 2 H, J = 8 Hz), 7.84 (d, 2 H, J = 8 Hz), 4.57 (br m, 1 H), 2.38 (br s, 1 H), 2.22 (br s, 1 H), 1.39 (br m, 8 H).

Kinetic Methods. With use of temperature preconditioned solvents and glassware, solutions of substrates (ca. 5 × 10^{-3} M) were prepared by weighing a given sulfonate ester (60–80 mg) into a 100-mL flask and adding 80% aqueous ethanol (v/v) (50 mL). The low solubility of the *p*-nitro derivatives required a change; the alcohol solution was saturated by vigorous shaking and then decanting through a glass wool plugged funnel. For the faster reactions, the filled conductivity cell was temperature conditioned for at least 90 s before conductivity measurements were begun. In all cases, rate constants were computed by the LSKIN computer method using experimental infinity values. For the slower reactions, infinity values were obtained after heating the solutions to 60 °C until the measured conductivity value stabilized.

Product Analysis. Solutions (10 mL each) of *exo*- and *endo*-2-norbornyl *p*-substituted-benzenesulfonates were prepared

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(35) See: Fieser, L. F. *Experiments in Organic Chemistry*; D.C. Heath: Boston, 1957; pp 285.
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(37) Bartlett, P. D.; Giddings, W. P. *J. Am. Chem. Soc.* **1960**, *82*, 1240.
(38) R. S. Tipson, *J. Org. Chem.* **1944**, *9*, 238. See: Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; Wiley Interscience: New York, 1968; vol. 1, p 1180.
(39) Each new compound was fully characterized with IR, NMR, and when sufficiently stable, elemental analysis. Details of the experimental procedures and additional characterizational data are avaiiable, see: Smith, M. R., Ph.D. Dissertation, University of Alabama, 1978.
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with 80% ethanol to a strength of 0.1 M. 2,6-Lutidine (0.15 g) was added to each reaction mixture to prevent acid-catalyzed reactions. The solutions were heated for 48 h at 55 °C and then analyzed by GLC with 5% Carbowax 20M on 90–100 mesh ABS (6′ × $^1/_4$″ column) at 115 °C with a helium carrier (0.67 mL/s). Retention times of the solvolysis products and the other reaction components were found to be as follows by the use of pure samples of each component: ethanol, 46 s; water, 72 s; *exo*-2-norbornyl ethyl ether, 112 s; 2,6-lutidine, 160 s; norbornylene, 200 s; and *exo*-norborneol, 533 s. *exo*-2-Norbornyl ethyl ether was prepared by the ethanolysis of *exo*-2-norbornyl *p*-bromobenzenesulfonate in anhydrous ethanol. It was shown that the Carbowax column would give complete separations of mixtures of *endo*- and *exo*-norborneol and that the products were stable to the reaction conditions.

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Registry No. *endo*-2-Norbornyl *p*-toluenesulfonate, 840-90-4; *exo*-2-norbornyl *p*-toluenesulfonate, 959-42-2; *endo*-2-norbornyl *p*-methoxybenzenesulfonate, 111025-81-1; *exo*-2-norbornyl *p*-methoxybenzenesulfonate, 68488-93-7; *endo*-2-norbornyl *p*-fluorobenzenesulfonate, 111005-78-8; *exo*-2-norbornyl *p*-fluorobenzenesulfonate, 111005-80-2; *endo*-2-norbornyl *p*-chlorobenzenesulfonate, 111005-79-9; *exo*-2-norbornyl *p*-chlorobenzenesulfonate, 111005-81-3; *endo*-2-norbornyl *p*-bromobenzenesulfonate, 840-89-1; *exo*-2-norbornyl *p*-bromobenzenesulfonate, 840-88-0; *endo*-2-norbornyl *p*-nitrobenzenesulfonate, 25716-02-3; *exo*-2-norbornyl *p*-nitrobenzenesulfonate, 111005-82-4.

Photochemistry of Polyhaloarenes. 7. Photodechlorination of Pentachlorobenzene in the Presence of Sodium Borohydride

Peter K. Freeman* and N. Ramnath

Department of Chemistry, Oregon State University, Corvallis, Oregon 97331

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The mechanism of photodechlorination of pentachlorobenzene (1) in acetonitrile has been examined. The quantum yield of reaction (Φ_r) has been found to vary with the concentration of 1. A charge-transfer intermediate formed from the triplet excited state of 1 is proposed to explain the observations. Φ_r increases with added $NaBH_4$ and $1/\Phi_r$ varies directly with the inverse of the concentration of the electron-transfer reagent. The regiochemistry, deuterium isotope effects, tracer studies, and quenching analyses are consistent with an electron-transfer process.

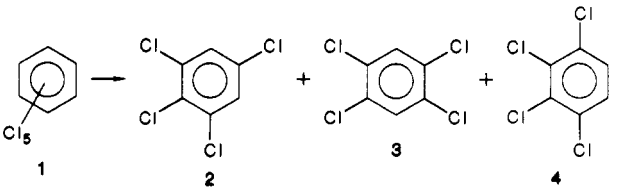
The photochemistry of aromatic halides has been actively investigated, in part, due to their role as environmental pollutants. Attention has been focused on ways to increase their photolability,[1] as a means of their efficient conversion to less toxic substrates, especially in view of the fact that they display significantly enhanced photolability in the presence of electron-transfer agents such as amines[2-5] and dienes.[5]

Increased photolability of chlorobenzene in the presence of sodium borohydride has also been reported by Barltrop and co-workers.[6] A mechanism proposed to explain their observations, however, does not explain the observations reported more recently by Epling[7] for the sodium borohydride mediated photodehalogenation of some chlorotoluenes and polychlorobiphenyls. An understanding of the mechanistic pathway of borohydride-enhanced photodechlorination is important, especially due to its potential in the destruction of polyhaloaromatics.

Pentachlorobenzene (1) was chosen as a model for our mechanistic studies because it is a significant environmental pollutant, and in an earlier study in this laboratory, the photochemistry of this compound was studied, and factors influencing the regiochemistry of its dechlorination were investigated in detail.[4] The nature of the intermediates has been shown to influence the regioselectivity,[4] and we hoped that comparison would reveal the nature of the intermediates and the mechanism pertaining to borohydride-mediated photodechlorinations.

Results

Irradiation of pentachlorobenzene (1) in acetonitrile in the 254-nm range leads to photofragmentation of the C–Cl bonds. At the low conversions maintained (15–20%) for 1, the primary products are the three tetrachloro benzenes 2–4 as shown below. A larger percentage of conversion



1 2 3 4

of 1 leads to the loss of more than one chlorine atom to form tri- and disubstituted chlorobenzenes. The quantum yield of reaction with respect to moles of 1 reacted increased with increasing concentration of 1 over the range 0.005–0.07 M (Table I). Figure 1 shows the variation of the inverse of quantum yield of disappearance of 1 with respect to the inverse of its concentration.

Irradiation of 1 in 94% aqueous acetonitrile and 4 equiv of sodium borohydride led to a significant increase in the rate of photodechlorination. The quantum yield also increased with increasing equivalents of sodium borohydride

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