Table III. Derived Temperature-Dependence Parameters[a] for the Hydrolysis of Ethyl Bromide and *sec*-Propyl Methanesulfonate

substrate	eq no.	A	B	C	D	$\Omega \times 10^7$	$(\Sigma\Delta k^2)n \times 10^7$
CH_3CH_2Br	2	−20182.8 ±235.1	−23.5054 ±0.727	186.848 ±4.980		5.87	
	7	−18735.5 ±1365.4	48.1172 ±4.3594	−7134.24 ±1280.54	23.4374 ±4.1389	1.71	3.12
	7	−11601.3 ±85.8	24.6798 ±0.2231	7134.24 ±1280.54	−23.4374 ±4.1389	1.88	
$(CH_3)_2CHOSO_3CH_3$	2	−16214.1 ±163.7	−16.012 ±0.577	137.079 ±3.859		2.70	
	7	−15472.7 ±995.9	46.1573 ±3.9808	−4298.91 ±907.11	17.1536 ±3.6285	1.35	1.92
	7	−11173.7 ±89.7	29.0038 ±0.2650	4298.91 ±907.11	−17.1536 ±3.6285	1.71	

[a] The number of significant figures quoted for A, B, C, and D (eq 7) and A, B, and C (eq 2) is that required to reproduce the reported rate constants to a precision which is comparable to the reported errors of the rate data. The number of digits generally exceeds those justified by the errors from the Wentworth algorithm.

treatment. The main point at issue is whether or not the mechanism

$$RX \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{intermediate} \xrightarrow{k_3} \text{products} \tag{3}$$

along with the related steady state expression

$$k_{\text{obsd}} = \frac{k_1 k_3}{k_2 + k_3} = \frac{k_1}{1 + \alpha} \tag{4}$$

where $\alpha = k_2/k_3$, will accomodate the k–T data for ethyl bromide and *sec*-propyl methanesulfonate by assuming a simple Arrhenius temperature dependence for the two quantities k_1 and α, such that

$$k_1 = \exp(A/T + B) \tag{5}$$

$$\alpha = \exp(C/T + D) \tag{6}$$

Speculation as to the precise nature of the intermediate in eq 3 is not our concern here; rather, we wish to compare how well the k–T data fit eq 2 with the fit for a combination of eq 4–6, namely,

$$k_{\text{obsd}} = \exp(A/T + B)/[1 + \exp(C/T + D)] \tag{7}$$

Equation 7 requires a nonlinear regression of the k–T data, and the algorithm reported by Wentworth[6] provides a suitable tool for such an enterprise. The same algorithm can be used for eq 2, although traditionally this calculation has been accomplished by a linear least-squares technique. Since the Wentworth regression is weighted, minor differences related to eq 2 are apparent between the nonlinear and linear calculations, but these are not significant in the present context. Since the Valentiner and Albery–Robinson fits require three and four parameters, respectively, the Gauss criterion for goodness of fit (Ω)

$$\Omega = [\Sigma\delta^2/(n - p)]^{1/2} \tag{8}$$

is used to assess the relative merits of eq 7 and 2 where $\delta = k_{\text{obsd}} - k_{\text{calcd}}$, n = number of (k–T) pairs, with $p = 3$ (A, B, and C) for the Valentiner equation and $p = 4$ (A, B, C, and D) for the Albery–Robinson expression.

The data in Tables I and II show the Albery–Robinson equation to be distinctly superior for both substrates. It is of interest to note that the Albery–Robinson equation gives rise to two numerical fits (see Table III). These are mathematically equivalent but chemically different when A, B, C, and D are given physical significance (see also Moore[7]).

The present results lend further support to our previous conclusions based on an alternative treatment of the k–T data for ethyl bromide and *sec*-propyl methanesulfonate.[4] Again we emphasize that the Albery–Robinson approach assumes real $\Delta C_p^{\ddagger}$ terms to be absent in relation to the k_1 and α quantities. This assumption is probably incorrect, but modification of eq 5 and 6 to accomodate real heat capacity terms would require a six-parameter nonlinear fit. Since the residuals relating the four-parameter nonlinear fits are already small (see Tables I and II) and are less than the sum of the estimated errors on the experimental k values, it appears pointless to include real $\Delta C_p^{\ddagger}$ terms in eq 5 and 6. Thus the present results are indicative rather than definitive as to the existence of intermediates in these reactions. The evidence presented here should nevertheless prove useful in future mechanistic discussions related to these and numerous other displacement reactions which demonstrate a similar non-Arrhenius temperature dependence.

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Neutral Products from Nucleophilic Substitution in the Gas Phase. Displacement of Water from Protonated Secondary Alcohols[1]

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Many textbooks present second-order nucleophilic substitution as a reaction that exemplifies the use of stereochemical studies to infer transition-state geometry. Inversion of configuration occurs not only in solution but also for anionic S_N2 reactions (displacement of Br^- by Cl^- on a neutral molecule) in the gas phase.[2] Recently, Speranza and Angelini[3] have described γ-radiolysis studies that suggest backside displacement also predominates in a cationic S_N2 reaction in the gas phase (displacement of HCl by H_2O on protonated methylchlorocyclohexanes). These latter results show only a 2:1 ratio of diastereomers, however, and were run under conditions (e.g., reactants at atmospheric pressure) where the effects of competing pathways and reactions on surfaces are not controlled.

$$ROH + ROH_2^+ \xrightarrow{-H_2O} R_2OH^+ \tag{1}$$

$$R_2OH^+ \xrightarrow{NX_3} R_2O \tag{2}$$

We wish to report the stereochemistry of a cationic S_N2 displacement on a protonated alcohol (reaction 1) under conditions where the effects of competing pathways may be assessed. Over

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(1) Portions of this work were presented at the 28th annual meeting of the American Society for Mass Spectrometry, New York, May 26, 1980.

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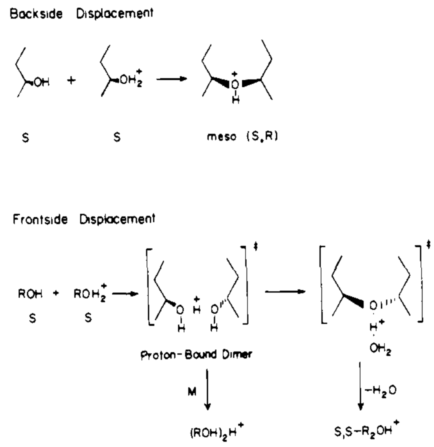
Scheme I



the past few years, we have been engaged in a study of gas-phase cation chemistry through examination of neutral products from ionic reactions at pressures below 10^{-3} torr. We generate ions by electron impact in a specially constructed electron bombardment flow (EBFlow) reactor and collect all products in a liquid-nitrogen cooled trap.[4-8] Subsequent gas chromatographic analysis enables us to differentiate isomeric products, and we have reported studies of molecular ion decompositions,[4,5] ion–molecule reactions,[6,7] and cation rearrangements.[8] This communication presents new evidence for backside displacement in reaction 1.

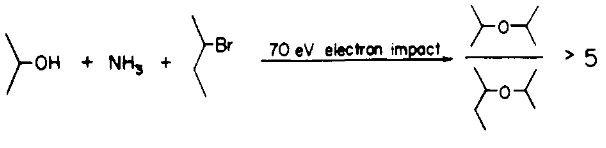
The stereochemistry of reaction 1 is inferred from the distribution of isomeric neutral ethers, R_2O, recovered from reaction 2. Beauchamp and Caserio have reported ICR studies of reaction 1 for R = *sec*-butyl, by using electron bombardment of 2-butanol.[9] Fragment ions generated by electron impact collide with neutral alcohol molecules and react to yield protonated parent ions, ROH_2^+, which subsequently react with other molecules of the neutral alcohol. Proton-bound dimer, $(ROH)_2H^+$, and protonated ether, R_2OH^+, are among products observed by ICR. If backside attack is the preferred pathway, then optically active 2-butanol should produce the meso isomer of di-*sec*-butyl ether, as shown in Scheme I.

Beauchamp, Caserio, and McMahon report,[10] however, that *tert*-butyl alcohol also undergoes reaction 1. This result is hard to reconcile with a backside displacement mechanism and has led to the hypothesis of a frontside displacement mechanism. In this pathway, as shown in Scheme I, a vibrationally excited proton-bound dimer is formed, which undergoes rearrangement to expel water. If optically active 2-butanol reacts with its protonated parent ion via this pathway, then a chiral diastereomer of di-*sec*-butyl ether results.

$$R^+ + ROH \rightarrow R_2OH^+ \quad (3)$$

$$ROH_2^+ + NX_3 \rightarrow RNX_3^+ \xrightarrow{ROH} R_2O + ROX \quad (4)$$

We find that 70-eV electron bombardment of optically active 2-butanol (5×10^{-4} torr) in the presence of amine base (2×10^{-4} torr) produces di-*sec*-butyl ether, which is observed at the part per 10^4 level in GLPC analyses of the radiolysis products. Since all reactions were run in the presence of amines, which should efficiently neutralize acidic species in condensed phases, we conclude that the recovered di-*sec*-butyl ether does not come from proton-catalyzed reactions on surfaces or in the cold trap of the EBFlow reactor. But more than one reaction yields the ether in the EBFlow reactor, and our interpretation of the data depends upon several control experiments. First, the observed products do not come from filament pyrolysis, since lowering the electron energy below ionization threshold causes the product yield to disappear. Secondly, we rule out reaction 3 as a possible alternative on the basis of the following experiment: 70-eV electron bombardment of 5×10^{-4}-torr isopropyl alcohol plus 2×10^{-4}-torr NH_3 plus 2×10^{-4}-torr 2-bromobutane (an excellent source of C_4H_9 cations[5,11]) yields diisopropyl ether, but only a relatively small quantity of isopropyl *sec*-butyl ether, as shown in reaction 5. The



(5)

isopropyl *sec*-butyl ether that is seen can be largely attributed to a reaction that occurs among the reactants simply upon standing.[12] Another conceivable alternative, (reaction 4) has also been ruled out. When isopropyl alcohol is subjected to 70-eV electron bombardment in the presence of 2-butylamine, only diisopropyl ether (and no isopropyl *sec*-butyl ether) is detected.

Apart from reaction 1, the most plausible source of di-*sec*-butyl ether is via proton-bound dimers and oligomers. The contribution of this pathway was gauged by varying the amine base in the EBFlow experiment. A relatively weak base, such as NH_3 (whose gas-phase basicity, 196 kcal/mol, is about the same as that of dibutyl ether[13]), will deprotonate R_2OH^+ or proton-bound dimers inefficiently. Therefore, cluster ions containing 2-butanol can form and grow, producing aggregates that resemble solution microenvironments and in which S_N1 pathways are accessible.

Strong bases (e.g., tripropylamine, whose gas-phase basicity = 226 kcal/mol[13]) should deprotonate all oxygen-protonated species with virtually unit efficiency. Ion clusters containing 2-butanol will be intercepted before they can form, and their contribution to the recovered product will be diminished. Our experimental data confirm this expectation: radiolyses of pure (+)- or pure (−)-2-butanol with NH_3 afford both diastereomers in virtually equal yields, meso/*d,l* = 1.2 (standard deviation = 0.2), while radiolyses in the presence of tripropylamine yield much more of the achiral isomer, meso/*d,l* = 6.4 (standard deviation = 1.5).[14]

Reaction 1 therefore does not occur via a frontside displacement mechanism. No 2-*tert*-butoxybutane is observed among the reaction products; hence, extensive rearrangement cannot be taking place. We feel justified in concluding that reaction 1 produces the meso ether from a simple backside displacement stereospecifically in the gas phase. Neutral product studies of the gas-phase S_N2 with halide nucleophiles have been reported by other investigators,[2,15] and, where stereochemical studies have been performed,[2] this reaction is also stereospecific. Thus, the anionic S_N2 and cationic S_N2 both appear to proceed via the same mechanism in the gas phase as they do in solution.

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