Solvent reorganization for hydrolysis with hydrogen participation¹

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A study of the rates of hydrolysis of 3-Me-2-butyl bromide and methanesulfonate in water leads to values of ΔC_p^* of -80 and -40 cal deg⁻¹ mole⁻¹, respectively. The product was about 85–95 % *t*-pentanol, the remainder being olefin. The value of ΔC_p^* for the solvolysis of the methanesulfonate in D_2O was -44 cal deg⁻¹ mole⁻¹. The kinetic solvent isotope effect (k.s.i.e.) for the latter was unusually low (k.s.i.e. = 1.047 at 5 °C and 1.025 at 25 °C). Deuteration at C-3 led to a reduction in the rate of hydrolysis by a factor of about 2.25. This is consistent with an activation process involving "hydrogen participation" as previously reported by Winstein and Takahashi for solvolysis of the corresponding tosylate in acetic acid. In contrast to the latter work the reaction in water appears to be uncomplicated tosylate in acetic acid. In contrast to the latter work, the reaction in water appears to be uncomplicated.

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Introduction

In extending our examination of solvent reorganization accompanying the hydrolysis of solutes giving evidence of neighboring group participation (1), we report here the results of such a study involving hydrogen participation for the hydrolysis of 3-methyl-2 butyl methanesulfonate in H_2O and D_2O and the corresponding bromide in H₂O. Evidence for hydrogen participation for the solvolysis of this latter compound in acetic acid was discussed previously by Winstein and Takahashi (2), although they regarded the participation of hydrogen under their conditions as somewhat marginal. Because of this estimate, a question was raised as to the effect a change in solvent would have on the mechanism. Acetic acid is not a good ionizing solvent and is a weak nucleophile, while water is a good ionizing solvent and a fair nucleophile. At the time the work was initiated there was some uncertainty as to whether secondary halides hydrolyzed in water by an $S_N I$, S_N2 , or mixed mechanism. If the mechanism were S_N1, the better ionizing solvent would render hydrogen participation less important than in acetic acid; if $S_N 2$, then the $\Delta C_p \neq$ value should reflect this fact. Our criterion at that time was that $\Delta C_p \neq$ for hydrolytic displacement of a halide by an S_N^2 mechanism would have a value of about -55 cal deg⁻¹ mole⁻¹, while for reaction by an $S_N 1$ mechanism the corresponding value would be -80 cal deg⁻¹ mole⁻¹. As a result of this study and related work we now recognize that this latter criterion involves an oversimplification and probably a misconception as well.

Experimental

3-Methyl-2-butyl Methanesulfonate

This compound was prepared by the method of Tipson (3) from pure methylisopropylcarbinol and purified by double distillation under reduced pressure (0.1 mm Hg) with a bath at 60-65 °C: n_D^{25} 1.4305; neutralization equivalent 165.1, Calcd. 166.2.

Anal. Calcd. for C₆H₁₄O₃S: C, 43.33; H, 8.49. Found: C, 43.19; H, 8.30.

The sample proved to be kinetically pure from estimation of solvolvtic behavior in water.

3-Methyl-2-butyl Bromide

This compound was prepared by the method used by Cason and Corrcia (4) for synthesizing 3-bromopentane, with slight modification. The crude product was purified by the method of Bailey and Hirsch (5). A mixture of 300 ml of dimethyl sulfoxide, 33.3 g (0.323 mole) NaBr, and 62.4 g (0.258 mole) of 3-methyl-2-butyl p-toluenesulfonate was stirred at room temperature for 64 h. The reaction mixture was distilled directly under reduced pressure (ca. 15 mm Hg; bath, 55-65 $^{\circ}$ C) and distillate boiling between 32-39 $^{\circ}$ C (50 mm Hg) collected. The distillate was stirred with 30 ml water at room temperature for 2 h. The water layer was extracted once with 50 ml ether, the combined ether extract and organic layer being shaken with 50 ml concentrated HCl for 2 min. The ethereal solution was washed with ice-water, then with cold saturated NaHCO3 solution, twice with H2O, and then dried over CaCl₂. Two distillations gave 6.0 g (12 %) of pure material: b.p. 39–40° (55 mm) (lit. (5) b.p. 49.8–51.0° (75 mm)); n_D^{24} 1.4452.

Anal. Calcd. for C₅H₁₁Br: C, 39.75; H, 7.34; Br, 52.91. Found: C, 39.71; H, 7.17; Br, 52.82.

Vapor phase chromatography (v.p.c.) of the sample gave but 1 peak, using a 20 wt. % polypropylene oxide on Chromosorb W column with a He flow rate of 60 cc/min. Retention time was 37.5 min. The compound was shown to be kinetically pure by the use of a large scale Guggenheim plot (6).

Solvent

H₂O was distilled and passed through an ion exchange column containing Fisher Rexyn-1-300. D₂O was obtained from Merck, Sharpe, and Dohme or Atomic Energy Commission of Canada. This was redistilled

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	Solvolysis	Product yield (%)		
Substrate	(°C)	2-Me-2-butene	t-Pentanol	
3-Me-2-Bu-mesylate	2	5.4	94.6	
	22	6.3	93.7	
3-Me-2-Bu-bromide	35	6.7	93.3	
	51	16.6	83.4	

TABLE I	
Products of hydrolysis in water (CaCO ₃)	present)

from sodium, then from $NaDSO_4$ through a scaled-down Stuart–Wormwell still (7) where the hot vapors and condensate contacted only quartz.

Analysis of Products

The analysis of products was done by vapor phase chromatography and also by direct titration of the olefin produced. A mixture of 0.6-0.7 mmole of the compound, 5 ml of water, and sufficient precipitated calcium carbonate to neutralize the acid were placed together with a small magnetic stirring bar in a sealed tube and allowed to react for 20 half-lives. The sealed tubes were thoroughly cooled in an ice bath prior to opening for analysis. Analyses were done in quadruplicate.

Olefin Determination

The content of the olefin in the solvolysis products was determined by an iodometric back titration of the excess bromine (8). To the solvolytic mixture was added 2.5 cc of carbon tetrachloride and 5 cc of water. The resulting mixture was kept at $0 \,^{\circ}$ C for 10 min. Two cc of a 0.2 N solution of bromine in carbon tetrachloride was then added to the mixture, which was kept at $0 \,^{\circ}$ C for another 10 min with occasional shaking.

The mixture was titrated, after addition of 2.5 cc of 20% potassium iodide solution, with 0.1 N standard sodium thiosulfate, using starch as an indicator. The yield of olefin was calculated by averaging the results for 3 separate solvolysis mixtures.

Vapor Phase Chromatography

A Poropack Q (80-100 mesh) column was used at 120° for olefin separation and 180° for the alcohols. The kind and amounts of solvolytic products are listed in Table I.

In the absence of calcium carbonate, the olefin yield increased by about 10% in the case of the methanesulfonate, some 1,2 as well as 2,3 isomer being found (v.p.c.), with a corresponding decrease in alcohol. This was regarded as an artifact, and since it became apparent that the reaction probably followed an S_{N1} mechanism, the question of product was not pursued. The fact that the products found for hydrolysis in water were simpler than those reported by Winstein and Tagahashi (2) is not surprising if allowance is made for the difference in solvent properties.

Kinetics

Rates were determined by a conductance method, in stirred Queen type cells (9) using either a conventional

bridge (10) or, in the later part of the work, our Auto-RAM system (11). Temperature control and measurement, and calculations were the same as previously reported (11).

Results and Discussion

Average rate data for the hydrolysis of the methanesulfonate in H_2O and D_2O are given in Table II; corresponding data for the hydrolysis of the bromide in H_2O are given in Table III.

The temperature dependence of the rate in each case was fitted by a least-mean-square method to an equation of the form

$$[1] \quad \log_{10} k = \frac{A}{T} + B \log T + C$$

The corresponding equations are as follows

3-Methyl-2-butyl bromide in H_2O

$$[2] \quad \log_{10} k = \frac{-10628.888}{T}$$

 $-40.03150 \log T + 130.60409$

3-Methyl-2-butyl mesylate in H₂O

[3]
$$\log_{10} k = \frac{-7030.13779}{T}$$

- 18.89552 log T + 67.64076

3-Methyl-2-butyl mesylate in D₂O

$$[4] \quad \log_{10} k = \frac{-7300.50548}{T}$$

 $-20.99025 \log T + 73.72049$

Quasi-thermodynamic parameters (10) characterizing the reactions based on transition state assumptions and on the approximation that $d\Delta C_p^{\pm}/dT = 0$ are given in Table IV. It is recognized that the latter approximation is least Average rate data for the hydrolysis of 3-methyl-2-butyl methanesulfonate in H_2O and D_2O

H ₂ O				D_2O	
$10^4 k (s^{-1})$			$10^4 k (s^{-1})$		
(°C)	Obsd.	Calcd.*	(°C)	Obsd.	Calcd.*
$\begin{array}{c} 1.163\\ 1.651\\ 3.897\\ 5.891\\ 7.936\\ 10.421\\ 15.454\\ 18.338\\ 20.590\\ 21.923\\ 23.398\\ 25.502\\ (25.000) \end{array}$	$\begin{array}{c} 0.8745 \pm 0.0020 \\ 0.9381 \pm 0.0020 \\ 1.296 \pm 0.001 \\ 1.721 \pm 0.002 \\ 2.282 \pm 0.003 \\ 3.193 \pm 0.006 \\ 6.229 \pm 0^{\dagger} \\ 8.986 \pm 0.013 \\ 11.87 \pm 0^{\dagger} \\ 13.98 \pm 0.010 \\ 16.73 \pm 0.033 \\ 21.45 \pm 0.010 \end{array}$	$\begin{array}{c} 0.8736\\ 0.9380\\ 1.297\\ 1.719\\ 2.284\\ 3.203\\ 6.216\\ 8.973\\ 11.87\\ 14.00\\ 16.72\\ 21.49\\ 20.22 \end{array}$	3.797 5.012 7.112 8.365 12.409 14.287 21.879 24.808 (25.000)	$\begin{array}{c} 1.289 \pm 0 \ddagger \\ 1.472 \pm 0.001 \\ 1.977 \pm 0.001 \\ 2.364 \pm 0.002 \\ 4.064 \pm 0.001 \\ 5.203 \pm 0.006 \\ 13.53 \pm 0.013 \\ 19.34 \pm 0.038 \end{array}$	1.240 1.474 1.980 2.355 4.066 5.205 13.56 19.30 19.75

*Equation [1]. †Two cells gave identical results. ‡Four cells gave identical results.

TABLE III

Average* rate data for the hydrolysis of 3-methyl-2-butyl bromide in H₂O

	$10^4 k (s^{-1})$					
(°C)	Obsd.	Calcd.				
22.746	0.5756 ± 0.0010	0.5758				
24.812	0.7740 ± 0.0014	0.7734				
25.00	—	0.793				
27.011	1.053 ± 0.001	1.052				
29.109	1.399 ± 0.004	1.402				
31.161	1.845 ± 0.001	1.845				
33.020	2.357 ± 0.004	2.356				
33.023	2.359 ± 0.003	2.358				
35.692	3.321 ± 0.008	3.322				
38.820	4.912 ± 0.011	4.913				
41.611	6.892 ± 0.011	6.896				
41.623	6.911 ± 0.023	6.905				
44.686	9.921 ± 0.020	9.913				
46.744	12.58 ± 0.04	12.57				
48.748	15.77 ± 0.003	15.76				
49.822	17.71 ± 0.02	17.75				
50.784	19.72 ± 0.04	19.74				
50.787	19.77 ± 0.02	19.75				

*Average of 4 determinations.

important about the center of the experimental temperature range.

Winstein and Takahashi (2) have discussed the mechanism of solvolysis of 3-methyl-2-butyl tosylate in acetic acid in terms of two independent processes, (a) anchimerically unassisted solvolysis and (b) a mechanism in which the tertiary hydrogen provides neighboring group assistance. Evidence based on a comparison of $k_{\rm H}/k_{\rm D}$ for the solvolysis of the corresponding methanesul-

fonate (MeS) in water indicates a similar anchimeric assistance occurs in the present study. An approximate value of the rate of solvolysis of $(CH_3)_2$ CDCH(MeS)CH₃ at 25.5° is 1.04 × 10⁻³ s^{-1} for 91% D; the corresponding value for the protium compound is $2.145 \times 10^{-3} \text{ s}^{-1}$. These values lead to about the same value of the $k_{\rm H}/k_{\rm D}$ ratio for the methanesulfonate as was found for the solvolysis of the tosylate in two solvents (Table V). Having due regard for the fact that the methanesulfonate is a somewhat poorer leaving group than the tosylate $(k_{Tos}/k_{MeS} = 3.4)$ at 25 °C for solvolytic displacement from isopropyl (10)), it will be apparent from Table V that the degree of anchimeric assistance is just about the same for hydrolysis in water as for the tosylate under much poorer ionizing conditions but possibly conditions favoring such interaction. It would appear that the products of hydrolysis in water are simpler than for reaction in acetic acid, the major product being the tertiary alcohol (Table I). This is consistent with a transition state involving hydrogen participation and the transfer of the tertiary H to C-2 with attack of a water molecule on C-3 to yield the tertiary alcohol, subsequent to the transition state.

The fact that accurate rates, a very low k.s.i.e. (below), and about the same value of ΔC_p^{\dagger} was obtained in D_2O as in H_2O confirm that in this reaction the "neighboring hydrogen" was not exchanging with the solvent in the activation process. However, two facts in connection with the

Quasi-thermodynamic values for the hydrolysis of 3-methyl-2-butyl X							
X	Medium	Temperature (°C)	$\frac{\Delta H^{\ddagger}}{(\text{cal mole}^{-1})}$	$\frac{\Delta S^{*}}{(\text{cal deg}^{-1} \text{ mole}^{-1})}$	$\frac{\Delta C_{p}^{*}}{(\text{cal deg}^{-1} \text{ mole}^{-1})}$		
Br ⁻	H ₂ O	25 50	24.313 23.014	4.27 -2.288	82±1		
-O-S-Me	H ₂ O	25 50	20.371 19.383	- 2.513 - 5.69	40±3		
O -O-S-Me O	D2O	25	20.376	-2.57	44±3		

TABLE IV
asi-thermodynamic values for the hydrolysis of 3-methyl-2-butyl

ГA	BĽ	E	V

Comparison of $k_{\rm H}/k_{\rm D}$ values for the solvolysis of 3-methyl-2-butyl X

X-		Tomporatura	$k_{ m H}/k_{ m D}$		
	Solvent	(°C)	Experimental	Estimated*	
MeS (91 % D)†	H ₂ O	10.42	2.04	2 25	
Tos Tos	80% EtOH AcOH	25 25	2.05 2.26	2.14 2.26	

*For 100% deuteration. †The loss of deuterium occurred during the synthesis since exchange under solvolytic conditions would have made rate determination unreliable and was not expected in any case (12). However, the presence of 9% of the protonated impurity would increase the rate by a small but indeterminate degree depending on the extent of the reaction prior to time t = 0. The ratio given is therefore a lower limit.

solvolytic studies in D_2O remain unexplained. The kinetic solvent isotope effect for the solvolysis of the methanesulfonate (from smoothed data, eqs. [3], [4]) was found to be 1.047 at 5.00 °C and 1.024 at 25.00 °C. These values are somewhat lower than those previously found for the solvolysis of the sulfonates (average value 1.09)⁴. In addition, we were unable to find conditions which would give reproducible rates for the solvolysis of the 3-methyl-2-Br-butane in D_2O ; in the majority of attempts the change in resistance with time did not appear to conform to a first order relationship. None of these difficulties was apparent in our results in H₂O for either the bromide or the methanesulfonate, or for the latter in D₂O. The possibility of exchange of deuterium in the case of 3-methyl-2-butyl bromide was recognized as a possibility but not proven.

The argument that the solvolytic displacement of X from 3-methyl-2-butyl X, in water, occurs by a single mechanism has been used previously (14, 15) and may be summarized as follows. If solvolysis occurs by two mechanisms, it is improbable that each will have the same temperature coefficient, hence the one having the higher coefficient will become successively more important as the temperature increases. This trend will add a positive component to ΔC_p^{\dagger} and the resultant ΔC_p^{\dagger} will be less negative than "normal". Clearly such a criterion depends on our ability to define the limits of normality for the type of reaction under consideration. This positive effect on ΔC_p^{\dagger} is quite different from that resulting from impurities. Thus, the presence of a faster reacting impurity in the case of crotyl chloride resulted in a spurious value of ΔC_p^{+} of $-130 \text{ cal deg}^{-1} \text{ mole}^{-1}$ (14). The 91% deuterated mesylate, in the present study, gave an apparent $\Delta C_p^{+} < -100$ cal deg⁻¹ mole⁻¹, compared to a real value of about -45 cal deg^{-1} $mole^{-1}$.

⁴Robertson and Laughton (13) reported a value of k.s.i.e. = 1.046 for the hydrolysis of neopentyl methanesulfonate. It is probable that this reaction is accompanied by rearrangement but this possibility was not confirmed.

Compound	$\frac{\Delta C_{p}^{+}}{(\text{cal deg}^{-1})}$	Reference	Compound	ΔC_p^{\dagger} (cal deg ⁻¹ mole ⁻¹)	Reference
3-Me-2-butyl bromide	-80	This work	t-Butyl chloride	- 83	18
3-Br-2-Me-2-butanol	-77	1	2,2-Dichloropropane	- 75	19
2-Cl-ethyl methyl sulfide	- 71	1	<i>trans</i> -γ-Methyl allyl chloride	- 82	15
4-Br-butyl methyl ether	- 46	1	2,2-Dibromopropane	81	19
α-Br-isobutyrate	- 78	17	Isopropyl bromide Cyclohexyl bromide Cyclopentyl bromide	59 59 68	20 10 10

Т	ABLE	VI			
Comparison of ΔC_n^*	values	for	hydrolysis	in	water

These latter results illustrate the sensitivity of ΔC_{p}^{*} to certain types of reactive impurities. No evidence of such an impurity was detected in the protium compounds, hence the large negative value of ΔC_p^{+} (-80 cal deg⁻¹ mole⁻¹) for the solvolysis of 3-methyl-2-butyl bromide in water was taken as evidence of extensive solvent reorganization in the activation process and similar to values found for molecules reacting by an S_N1 mechanism (Table VI). Values of ΔC_p^{*} for the hydrolysis of the secondary halides, isopropyl, cyclohexyl, and cyclopentyl bromides are included. From this comparison it is clear that the ΔC_p^{\dagger} value found here for the hydrolysis of the 3-Me-2-butyl bromide is more negative than the corresponding value found for some secondary bromides and in the same range as values found for halides which probably react unambiguously by an S_N1 mechanism. Following the argument given above, and in contrast with the conclusion reached by Winstein and Takahashi (2) for the solvolysis of the corresponding tosylate in acetic acid, it seems unlikely that the solvolysis of this halide occurs in water by mixed kinetics. The same conclusion seems equally likely for the mechanism of solvolysis of the corresponding methanesulfonate where $\Delta C_p^{*} = -40 \pm 3$ cal deg⁻¹ mole⁻¹ for solvolysis in water. The corresponding value for solvolysis in D_2O is -44 \pm 3 cal deg⁻¹ mole⁻¹.

These latter values lie very close to those for the hydrolysis of isopropyl benzenesulfonate and methanesulfonate. If anchimeric assistance predicates solvent reorganization associated with an S_N mechanism in the hydrolysis of the bromide, it is even more likely to do so with the solvolysis of the sulfonates. This seemingly inevitable conclusion raises an anomaly. In previous papers we have accounted for the more negative values of ΔC_n^{\dagger} which characterize the S_N1 displacement of halides from tertiary carbon in terms of the requirement for additional solvent reorganization about the quasi-cation (10). It seemed logical that the same reasoning apply to the value of -80 cal deg⁻¹ mole⁻¹ found for the displacement of the bromide in this study, compared to a value of about -50 which characterizes displacement from primary halides and -60 for secondary halides. Why then should there be no corresponding difference between the value of ΔC_p^{+} for the hydrolysis of methyl methanesul-fonate (-35 cal deg⁻¹ mole⁻¹) and that for isopropyl methanesulfonate $(-35 \text{ cal deg}^{-1})$ mole⁻¹), or for 3-Me-2-butyl methanesulfonate $(\Delta C_p^{+} = -44 \text{ cal deg}^{-1} \text{ mole}^{-1})$? One possible suggestion is that the presence of the sulfonic group localizes the breakdown of water structure, an interpretation which is consistent at least with the reduced kinetic solvent isotope effects which characterize the hydrolysis of this series of compounds (16). The similarity in the products (Table I) for the hydrolysis of bromides and methanesulfonates is consistent with the creation of some common intermediate which can react with adjacent water molecules. Neither reason provides a necessary and sufficient condition to explain the difference in ΔC_p^{+} . Intuitively we feel that if the bromide reacts by an S_NI mechanism, as seems likely on the above evidence, then the methanesulfonate does so as well. This leaves the lack of sensitivity of ΔC_p^{+} to an expected change in mechanism of solvolysis in the sulfonate series

an open question. This conclusion led to а reconsideration of our criterion (admittedly based on a limited number of examples) that the hydrolysis of halides reacting by an S_N1 mechanism (Table VI) is normally characterized by much more negative values of ΔC_p^{+} than those reacting by an unambiguous S_N2 mechanism. Quite aside from the problem raised above with respect to the ΔC_p^{+} for the hydrolysis of the secondary sulfonates, there are the intermediate values of ΔC_p^{\dagger} already noted for the unassisted solvolysis of secondary halides. For the purposes of this paper, we note that the ΔC_p^{\dagger} value determined for the 3-methyl-2-butyl bromide here implies extensive solvent reorganization at the transition state characteristic of those halides reacting by an S_N1 mechanism. The more general problem will be dealt with in a forthcoming paper (21).

Some years ago, Hoffmann proposed that the value of the rate ratio $k_{\rm Tos}/k_{\rm Br}$ be used as a criterion of mechanism, though he omitted to specify the limits which define any particular mechanism (22). In the presence of a strong nucleophile and a poor ionizing medium, this ratio may be less than unity. Under good ionizing conditions and with favorable structure, values greater than 1000 are found. The ratio obtained here for $k_{\rm Mes}/k_{\rm Br} = 25.5$, which is equivalent to $k_{\rm Tos}/k_{\rm Br} = 53$, i.e., about 1/2 the value given for displacement from isopropyl, but well above the value of the ratio (17–5) which characterizes the hydrolysis of primary compounds in water.

Whatever the quantitative utility of this ratio in terms of mechanistic distinction, there is undoubted value to be gained from examining the probable reasons for variation in this ratio and relating these to other criteria of mechanism. Hoffmann notes that the value of the $k_{\text{Tos}}/k_{\text{Br}}$ ratio for gas phase dehydrohalogenation follow a similar pattern to that found for solvolysis, the difference being that the activation energies in solution are reduced by about 1/2 and there is some indication that the spread of the values may be reduced as well. In the gas phase, the ratio apparently reflects the ability of an R-group to support the partial or total loss of an electron, coupled to the relative advantage the "electronically versatile" tosylate has over bromide to accommodate the complementary acquisition of charge. This intrinsic difference revealed in the gas phase experiments provides a quantitative

answer to the curious fact that while ΔS^{\dagger} for a series of sulfonates showed a wider change for $(\Delta S^{\dagger}_{isopropyl} - \Delta S^{\dagger}_{ethyl})$ than for the correspond-ing halides, the ΔC_p^{\dagger} values showed just the opposite tendency (20). Thus, $(\Delta S^{\dagger}_{isopropyl} - \Delta S^{\dagger}_{ethyl})$ ΔS^{\pm}_{ethyl} for the hydrolysis of mesylate is 8.3 e.u., and for bromide is 4.6 e.u. The corresponding values⁵ for $(\Delta S_1^{\dagger} - \Delta S_{etbyl}^{\dagger})$ from the present study are 6.6 e.u. for the mesylate and 3.68 e.u. for the bromide. In both systems, the value of ΔC_p^{\dagger} for the hydrolysis of the sulfonates are about the same, while the value of the $\Delta\Delta C_p^{\pm}$ for the bromides are, respectively, -10 and -32 cal deg⁻¹ mole⁻¹. We know of no reason to question the assumption that ΔC_p^{*} is a more sensitive indicator of solvent reorganization than ΔS^{\pm} , at least for hydrolysis in water. Hence, the above comparison points to the existence of important factors, other than solvent reorganization, which contribute to ΔS^{\dagger} . For solutes which react by an S_N1 mechanism, these factors seem to be related to the ease with which the solute becomes thermally activated. In this connection, it is probable that the nature of the solvent as well as the solute is significant in determining ΔS^{*} , but a detailed study designed to relate the properties of the solute to variations in ΔS^{\dagger} has yet to be made. An indication of the possibility of individual difference may be gained from a consideration of the variation in k_{Tos}/k_{Br} reported by Hoffmann (22) for the solvolysis of the 2-pentyl compounds: k_{Tos}/k_{Br} has the values 498 in formic acid, 105 in water, 73 in ethanol. For the neophyl series (PhMe₂CCH₂X) the corresponding values are 14 - 106. The corresponding Y + 3 values (23) which purport to measure the relative ionizing power of the solvent are 5.05, 6.49, and 0.97; the lack of correlation with the latter solvent property is obvious. Hoffmann suggests that these anomalies and others he discusses may be related to a desolvation of the nonclassical carbonium ion formed in the transition state. Our interpretation would be to attribute the difference to variations in the charge distribution which determines the initiation of exothermic solvation or of more specific interaction with the quasi-cation, individually. This is implied in Hoffmann's postulate that "the faster an $S_N 1$ (E₁) reaction, the more ionic its transition state". This statement is consistent with the requirement that the more

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 $^{{}^{5}\}Delta S_{1}^{*}$ is for 3-Me-2-butyl methanesulfonate.

diffuse the charge, the higher the charge level required on the ion as a whole to exceed solventsolvent interaction, and to result in secondary solvent-cation interaction leading to the completion of the reaction. The fact that those structures which release electrons better, solvolyze faster was established early in the work of Ingold and his co-workers (24) and is related to the inherent hypothetical ΔF_{g}^{*} (22). A graded series of increasingly reactive structures would probably show a parallel increase in ΔS_g^{+} , as we have already noted.

We disagree with Hoffmann's conclusion that the more polar solvent necessarily favors the more polar transition state. It is a recognized fact that a reactant with structural characteristics which favor an S_N1 mechanism will show a very strong rate dependence on the ionizing properties of the solvent. Water is a better ionizing solvent than acetic acid, but the values of the k_{Tos}/k_{Br} ratio are higher in the latter. The relation of charge level to ionizing properties cannot be resolved by a simple hypothesis because at the transition state not only solvation properties, but also nucleophilic properties of the solvent are involved, as well as charge distribution and steric considerations of the quasication. The tosyl group undoubtedly disperses charge better than the bromide, thus facilitating both the S_N1 and $S_N 2$ mechanism. In the $S_N 2$ displacement of the sulfonic group from a primary carbon, the spare electrons on the oxygen provide available sites for solvent interaction; thus nucleophilic displacement is achieved with less requirement for overlap, an inference supported by the relative α -deuterium isotope effects (25).

From these observations, we are led to conclude that while the k_{Tos}/k_{Br} ratio forms an interesting basis for inspection, it should be regarded as a supplementary indication of possible mechanistic difference, the common lot of most comparable tests.

It would be simple to conclude on the basis of the above evidence that hydrogen participation in the hydrolysis of 3-Me-2-butyl bromide is characterized by solvent reorganization characteristic

of an S_Nl mechanism. Neighboring group participation has been shown previously to result in reduced (as well as enhanced) values of the kinetic solvent isotope effect (26). The example reported here may be regarded as a further example of the same phenomenon. Obviously, to draw attention to such similarity is not equivalent to providing a satisfactory explanation, and further work will be required in this area.

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