Relative Rates. Mixtures of 1 (2 mmol) and either 2 mmol of 2 or 3 were diluted with CCl₄ to 4 ml. This solution was analyzed and added to 50 ml of degassed H₂SO₄. The mixture was stirred mechanically and sampled by removal of 1-ml aliquots which were added to ice–water and extracted with an additional 1 ml of CCl₄. The CCl₄ solution was dried and analyzed by glpc (6 ft × ⅛ in. 10% Apiezon J on Chromosorb W column). Mixtures of 1 and 3 were analyzed at 90° for 8 min followed by temperature programming (32 deg min⁻¹) to 160°. Mixtures of 1 and 2 were analyzed at 90° for 8 min then programmed (8 deg min⁻¹) to 160°. N-Chlorodiisopropylamine was then added and the solution irradiated under N₂ at 15° with two sun lamps. Aliquots were periodically removed and analyzed. Norbornane conversion was computed on the percentage of norbornyl materials present as starting material and the disappearance of the other hydrocarbon measured from this by using the predetermined conversion factor. These data were then converted to relative reactivities as described by Poutsma.[31]

Ambident Behavior of Some Phenols and Alkoxy Benzenes in Antimony Pentafluoride–Fluorosulfonic Acid Mixtures[1]

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Contribution from the Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37916, and Institute Ruder Bosković, 41001 Zagreb, Yugoslavia. Received February 21, 1974

Abstract: The position of protonation of several alkyl-substituted phenols and alkoxy benzenes has been studied in several SbF₅–FSO₃H mixtures as a function of temperature. Carbon and oxygen protonation follow different acidity functions and oxygen protonation is slightly more exothermic than carbon protonation, the differences increasing as the antimony pentafluoride concentration increases. The ratio of O:C protonation is sensitive to the nature and concentration of solutes such as SO₂, H₂O, and the organic base. Because of this, it appears that measurements at nmr concentrations will be unsuitable for quantitative studies of such systems. Structural effects on the ambident behavior vary with acid concentration and are not well understood.

Hydroxy and alkoxy aromatics are one of the most thoroughly studied classes of ambident bases. These molecules can be protonated on either carbon or oxygen; the position of protonation varies in complex patterns, and the factors controlling this variation are not yet understood. If the factors influencing the ambident behavior of these molecules could be isolated and understood, these molecules might constitute a very useful probe of solvent–solute interactions in strong acid systems. To this end we have examined the behavior of a few such ambident bases in mixtures of antimony pentafluoride and fluorosulfonic acid.

There is a good review of this area,[2] but because of much recent activity it is somewhat out of date. There is also a brief discussion of the behavior of alkyl aryl ethers in Olah's review.[3] For trihydroxy compounds, carbon protonation predominates in sulfuric and perchloric acid.[4] In superacids, initial protonation of the trihydroxy and trialkoxy compounds always occurs at carbon, but a second proton can be added at either carbon or oxygen to give a dication.[5] Even with dication formation, carbon protonation predominates. Except for hydroquinone and p-dimethoxybenzene which protonate on oxygen, the dihydroxy and dialkoxy benzenes show predominantly carbon protonation.[6] Some oxygen protonation occurs with o-dimethoxybenzene.

The bases showing the most complex behavior, perhaps because they have received the most attention, are anisole and p-methylanisole. Early work with these was complicated by the fact that they sulfonate very readily.[7,8] Both of these compounds are ambident bases as shown in Scheme I and their protonation behavior in various solvents is complex.[6,9–12] In addition to these two compounds other methyl-substituted phenols and anisoles,[6,13–15] and halogen-substituted

(1) Some of this work has appeared in preliminary form: J. W. Larsen and M. Eckert-Maksić, *Tetrahedron Lett.*, 1477 (1972).

(2) D. M. Brouwer, E. L. Mackor, and C. MacLean in "Carbonium Ions," Vol. II, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N. Y., 1970.

(3) G. A. Olah, A. M. White, and D. H. O'Brien, *Chem. Rev.*, 70, 561 (1970).

(4) A. J. Kresge, Y. Chiang, and L. E. Hukka, *J. Amer. Chem. Soc.*, 93, 6161 (1971), and references therein.

(5) G. A. Olah and Y. K. Mo, *J. Amer. Chem. Soc.*, 94, 5341 (1972).

(6) G. A. Olah and Y. K. Mo, *J. Org. Chem.*, 38, 353 (1973).

(7) B. G. Ramsey, *J. Amer. Chem. Soc.*, 88, 5358 (1966).

(8) U. Svonholm and V. D. Parker, *J. Chem. Soc. Perkin Trans. 2*, 962 (1972).

(9) T. Birchall, A. N. Bourns, R. J. Gillespie, and P. J. Smith, *Can. J. Chem.*, 42, 1433 (1964).

(10) T. Birchall and R. J. Gillespie, *Can. J. Chem.*, 42, 502 (1964).

(11) D. M. Brouwer, E. L. Mackor, and C. Maclean, *Recl. Trav. Chim. Pays-Bas*, 85, 109 (1966).

(12) G. A. Olah, M. B. Comisarow, E. Nemanworth, and B. Ramsey, *J. Amer. Chem. Soc.*, 89, 5259 (1967).

(13) J. W. Larsen and M. Eckert-Maksić, *Croat. Chem. Acta*, 45, 503 (1973).

(14) M. P. Hartshorn, K. E. Richard, J. Vaugh, and G. J. Wright, *J. Chem. Soc. B*, 1624 (1972).

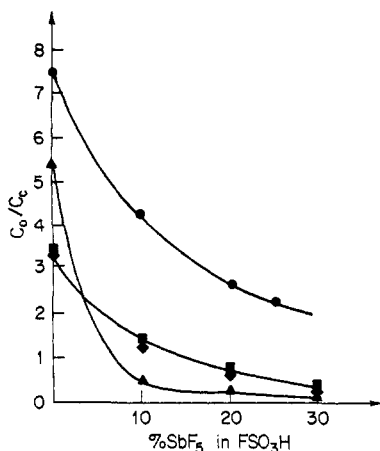(15) G. Bertholon and R. Perrin, *C. R. Acad. Sci., Ser. C*, 275, 645 (1972).

Figure 1. Effect of increasing SbF$_5$ concentration on the ratio of O to C protonation for p-methylanisole (■), p-cresole (♦), p-ethylanisole (▲), and p-methylphenetole (●) at $-30°$.

phenols and anisoles[16] have been studied. Some of them showed similar ambient behavior.[16a]

It is apparent from the data available that the position of protonation of these ambident bases is quite sensitive to the acidity of the solvent and a number of other factors. If the source of these effects can be understood, such ambident bases might provide very useful probes of acidic media. We undertook to characterize more thoroughly the variables which affect the position of protonation of a few of these bases and report some of our observations and conclusions here.

Scheme I
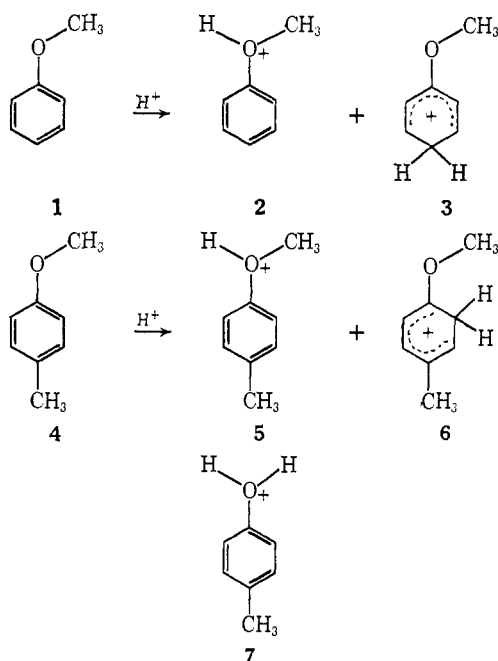
Experimental Section

Chemicals. p-Methylphenetol was prepared by the method of Birosel,[17] p-isopropyl tolyl ether by the method of Vogel,[18] and p-

isopropylanisole by the method of Hiers.[19] All other chemicals were commercially available. The fluorosulfonic acid was obtained from both Baker and Adamson and Fluka. The acid was flushed with dry N$_2$ for 6 hr and then distilled (bp 162°). Antimony pentafluoride was obtained from both Allied Chemical Co. and Research Org./Inorganic Chemical Co. This material was purged with dry nitrogen for 10 hr and then distilled (bp 142°).

Preparation of Carbonium Ions. Superacid solutions were prepared by mixing SbF$_5$ and FSO$_3$H in Teflon bottles in the concentrations indicated. Ions for pmr study were prepared by adding slowly 300–500 mg of the aromatic compounds to 3 ml of the superacid cooled to $-78°$ under dry nitrogen. Pmr spectra were recorded on a Varian Model HA 100 or A-60A pmr spectrometer equipped with a variable-temperature probe. Care was taken to use the same concentration of a compound for all measurements. After pmr study, solutions were quenched by slowly adding the solution of the carbonium ion to a cold ($-78°$) methanol-Na$_2$CO$_3$ suspension or to crushed ice. After work-up, the starting aromatic ethers were recovered (as indicated by pmr, ir, and glc) showing that no side reaction took place, except where otherwise indicated.

The calorimeter and its use have been previously described.[20]

Results and Discussion

In the work reported here, we have examined the effect of acid strength (SbF$_5$ concentration), temperature, solute concentration, and solute structure on the ambident behavior of some phenols and alkyl phenyl ethers. We shall discuss each of these variables in turn.

Effect of Antimony Pentafluoride Concentration. The work of Olah and Mo[5,6,16] on similar compounds using several mixtures of HF, FSO$_3$H, and SbF$_5$ containing SO$_2$ClF showed a dependence of the position of protonation of several ambident bases on acid composition. The effect of increasing the concentration of SbF$_5$ on the ratio of oxygen to carbon protonation for p-methylanisole, p-cresol, p-ethylanisole, and p-methylphenetol is shown in Figure 1. The nmr assignments are given in Table I for the four compounds in question. In all cases the positions of protonation are those shown in Scheme II.

Scheme II

R = Me, R' = Me
R = H, R' = Me
R = Me, R' = Me
R = Et, R' = Me
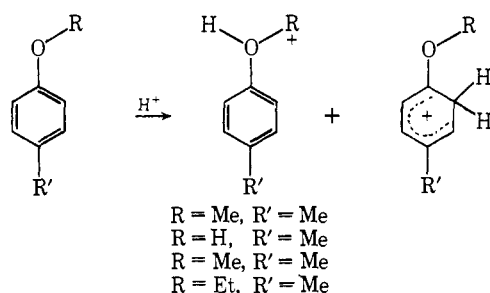
The most striking feature is the identical behavior of p-methylphenol and p-methylanisole, particularly in light of the often repeated observations that the methoxy group stabilizes protonated aromatic rings to a greater extent than hydroxy.[6] It appears that the stabilizing effect of a methyl group is nearly the same as a proton. Arnett[21] has recently suggested hydrogen bonding as a source of stabilization of cations in strong acids and has observed similarities in the stabilizing effect of a methyl group and of a proton (through H-bonding) on

(16) G. A. Olah and Y. K. Mo, *J. Org. Chem.*, **38**, 2212 (1973).
(16a) Note Added in Proof. See also the recent study by G. Bertholon and R. Perrin, *Bull. Soc. Chim. Fr.*, 113 (1974).
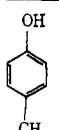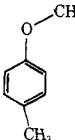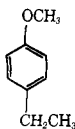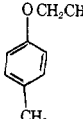(17) P. M. Birosel, *J. Amer. Chem. Soc.*, **53**, 1408 (1931).
(18) J. Vogel, *J. Chem. Soc.*, 616 (1948).

(19) G. S. Hiers and F. D. Hager, "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 1941, p 58.
(20) E. M. Arnett and J. W. Larsen in "Carbonium Ions," Vol. 1, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N. Y., 1968.
(21) E. M. Arnett and J. F. Wolf, *J. Amer. Chem. Soc.*, **95**, 978 (1973).

Table I. [1]H Magnetic Resonance of Some Protonated Alkyl Phenyl Ethers in 20% SbF_5–HSO_5F^a at $-40°$

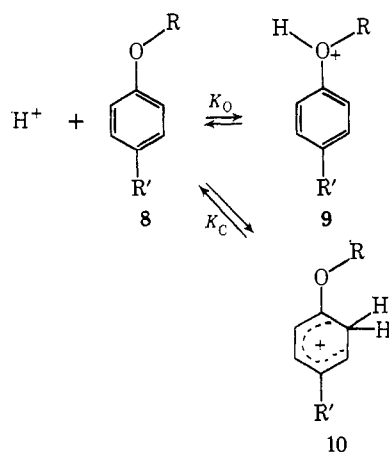| Type of ion	OR — $-CH_2$	OR — $-CH_3$	Ring protons	CH_2	Ar–R' — CH_2	Ar–R' — CH_3	HO^+R
O protonated			7.60 (s)			2.47 (s)	12.30 (br s)
C protonated			8.70 (d), 7.60^d J_{HH} = 9 Hz	4.47 (br s)		2.37 (s)	
O protonated		4.75 (s)	7.48 (s)			2.48 (s)	11.90 (br s)
C protonated		4.50 (s)	8.55^e (q), 7.40^d J_{HH} = 9 Hz	4.38 (br s)		2.38 (s)	
O protonated		4.83 (s)	7.57 (s)		2.82 (q) J_{HH} = 7 Hz	1.35 (t) J_{HH} = 7 Hz	11.70 (br s)
C protonated		4.52 (s)	8.73 (br t), 7.57^d J_{HH} = 9 Hz	4.42 (br s)	2.70 (q) J_{HH} = 7 Hz	1.30 (t) J_{HH} = 7 Hz	
O protonated	5.34 (dq) J_{HH} = 8.2 Hz	1.78 (t) J_{HH} = 8 Hz	7.44 (s)			2.44 (s)	11.49 (br s)
C protonated	4.77 (q) J_{HH} = 8 Hz	1.72 (t) J_{HH} = 8 Hz	8.61 (br d), 7.40^d J_{HH} = 8 Hz	4.36 (br s)		2.37 (s)	

^{a} Proton chemical shifts are referred to Me_4N^+ internal standard in parts per million, the chemical shift of Me_4N^+ was taken as δ -3.20 ppm relative to TMS; s = singlet, d = doublet, t = triplet, q = quartet, br = broad. ^{b} Multiplet partially hindered by signal for ring protons of the oxonium ion. ^{c} Becomes broad doublet or singlet at higher temperatures.

oxygen protonation in fluorosulfonic acid. Our data are consistent with this suggestion.

It is significant that the substituent effects are solvent dependent. This is particularly striking in the case of *p*-ethylanisole. We know of no obvious explanation for this behavior. It should be recognized that the energy differences represented by the data in Figure 1 are quite small, and any dissection of the effects responsible for the observed behavior will be quite difficult.

Gillespie has recently published one acidity function for FSO_3H–SbF_5 mixtures based on nitroaromatic indicators and it is of interest to examine the acidity function behavior of these molecules.[22] Since these compounds were present in the high concentrations necessary for nmr studies the conclusions drawn must be
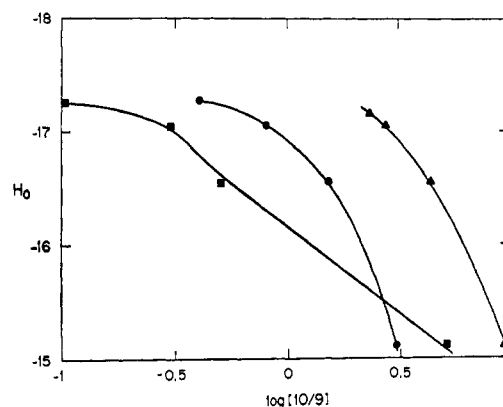
Scheme III

Figure 2. Ratio of carbon to oxygen protonation as a function of H_0 for *p*-methylanisole (●), *p*-methylphenetole (▲), and *p*-ethylanisole (■) at $-30°$.

treated cautiously, since there is sufficient organic ion present to affect the nature of the solvent. The situation is shown in Scheme III.

Assume that K_O follows H_O and K_C follows a different acidity function, H_C. If both carbon and oxygen protonation follow the same acidity function, log

$$H_O - H_C = pK_O - pK_C + \log([10]/[8]) - \log([9]/[8])$$

$$H_O - H_C = \Delta pK + \log([10]/[9])$$

([10]/[9]) should be a constant equal to ΔpK. In Figure 2, log ([10]/[9]) is plotted *vs.* H_O for the results at $-30°$. It is obvious that log ([10]/[9]) is not a constant. Very rough straight lines might be drawn through the points for *p*-methylphenetol and *p*-ethylanisole. A straight line is expected if one acidity function is a linear function of the other, a circumstance often observed in aqueous systems. The conclusion that carbon and

(22) R. J. Gillespie and T. E. Peel, *Advan. Phys. Org. Chem.*, **9**, 1 (1971); *J. Amer. Chem. Soc.*, **95**, 5173 (1973).

Table II. Effect of Temperature on the Position of Protonation of Some Ambident Bases

Compound	Acid composition wt %	Temp,[a] °C	% O protonated	Ratio O:C
OH / CH₃	10% SbF₅–FSO₃H	−60	59.4	1.5
		−49	54.1	1.2
		−33	51.0	1.04
	20% SbF₅–FSO₃H	−59.5	45.2	0.83
		−46	43.6	0.77
		−27.5	41.0	0.70
	30% SbF₅–FSO₃H	−59.5	29.5	0.43
		−45	28.0	0.38
OCH₃ / CH₃	FSO₃H	−85 ↓ −22		~3.5
	10% SbF₅–FSO₃H	−80	54.0	1.2
		−60	52.4	1.1
		−50	54.5	1.2
	20% SbF₅–FSO₃H	−84	43.3	0.77
		−62	36.7	0.60
		−44	33.7	0.58
	30% SbF₅–FSO₃H	−82	54.0	1.2
		−60	41.0	0.69
		−42	29.5	0.42
	33% SbF₅–FSO₃H	−85	54.8	1.2
		−64	48.7	0.95
		−55	24.1	0.32
		−42	20.1	0.25
OCH₃ / CH₂CH₃	FSO₃H	−60 ↓ −20		~5.5
	10% SbF₅–FSO₃H	−65	27.0	0.38
		−55	26.4	0.36
		−46	28.8	0.39
	20% SbF₅–FSO₃H	−66	22.8	0.3
		−51	18.5	0.2
		−37	16.7	0.2
		−15	17.9	0.3
	30% SbF₅–FSO₃H	−60	24.5	0.34
		−47	16.1	0.19
		−37	13.1	0.15
O–CH₂CH₃ / CH₃	HSO₃F	−74 ↓ −65 ↓ −31 ↓ −23	~88	~7.6
	10% SbF₅–FSO₃H	−55	89.8	7.8
		−45	88.3	7.6
		−31	80.2	4.4
		−15	75.1	3.2
	20% SbF₅–FSO₃H	−55	73.6	2.8
		−40.5	68.2	2.2
	22% SbF₅–FSO₃H	−51	81.0	4.3
		−42	72.1	2.6
		−19	70.5	2.4
OCH₃ / CH(CH₃)₂	HSO₃F	−60 ↓ −20	73.0	2.8
	10% SbF₅–FSO₃H	−60 ↓ −70	30.0	0.43
	20% SbF₅–FSO₃H	−59.5	24.0[b]	
		−30.0	8.0[c]	

[a] All temperatures measured using the difference in chemical shift between the OH and methyl protons in methanol. [b] About 12% of the material was a rearranged product, probably

$$CH_3O-\langle\bigcirc\rangle-\overset{CH_3}{\underset{+}{\overset{|}{C}}}-CH_3$$
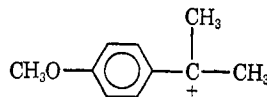
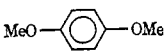[c] About 23% of the material was a rearranged product.

oxygen protonation follow different acidity functions seems inescapable. By measuring the acidity function for O and C protonation for similar compounds in aqueous perchloric acid, Alder, Wai, and Yates earlier came to the same conclusion.[23] Not unexpectedly, it appears that the situation in superacids may be similar

(23) R. W. Alder, personal communication.

to that in aqueous strong acids, with a variety of acidity functions necessary to correlate the behavior of different bases.

Temperature Effects. The effect of temperature on the position of protonation of several ambident bases in mixtures of antimony pentafluoride with fluorosulfonic acid is shown in Table II. The temperature

Table III. Relative Heats of Protonation of Some Ambient Bases in 11.5 mol % SbF₅ in FSO₃H[a]

Compd	Site of protonation	Temp, °C	ΔH_S acid (kcal/mol)	ΔH_S CCl₄	ΔH_T
C₆H₅-OMe	C	−63	−6.53 ± 0.41	+0.37 ± 0.02	−6.90 ± 0.41
C₆H₅-OH	C	−65	−0.49 ± 0.53	+6.27 ± 0.07	−6.76 ± 0.54
MeO—⟨O⟩—OMe	O[b]	−65	−4.86 ± 0.72	+5.84 ± 0.28	−10.7 ± 0.77
CH₃OH	O	−60	−22.6 ± 0.4	+3.99 ± 0.07	−26.6 ± 0.4

[a] These data were obtained in the laboratories of Dr. E. M. Arnett. We are grateful for permission to use them here. [b] Reference 6.

effect is a manifestation of differing heats of protonation (ΔH_p) on carbon and oxygen. The ratio of O:C protonation often decreases as the temperature increases indicating that oxygen protonation is more exothermic than C protonation. A rough estimate of the enthalpy difference between O and C protonation can be obtained from a van't Hoff plot of $1/T$ vs. the log of the ratio of O:C protonation. The results are quantitatively quite uncertain; the nmr technique is too imprecise to yield very reliable enthalpies. However, a comparison of a series of compounds treated in identical fashion seems worthwhile if the imprecise nature of the data is recognized. For p-methylphenol in 10% SbF₅-FSO₃H, a typical case, O protonation is favored by ca. 600 cal/mol over C protonation. The two basic sites have very similar heats of protonation. The difference in heat of protonation of the two sites usually increases as the concentration of antimony pentafluoride is increased. For example, with p-methylanisole, O protonation is favored by ca. 300 cal/mol in 20% SbF₅-FSO₃H and by ca. 400 cal/mol in 33% SbF₅-FSO₃H. In a number of cases shown in Table II, particularly in neat FSO₃H, the ratio of O:C protonation is independent of temperature. It is quite clear that the thermodynamics of O and C protonation of these molecules in SbF₅-FSO₃H solution are quite similar. Thus small changes in conditions can cause large shifts in the ratio of O:C protonation.

The data in Table III are relative heats of protonation obtained in the usual way.[20,24] They are, in fact, heats of transfer from carbon tetrachloride to the indicated acid, but should represent accurately differences in the heats of protonation. A comparison of 1,4-dimethoxybenzene with anisole and phenol indicates that O protonation is somewhat more exothermic than C protonation, verifying the results of temperature dependence of the C:O protonation ratios. The heat of protonation is strongly reduced from that of aliphatic alcohols or ethers. This is due to solvent effects and the change in hybridization in the base from sp³ to sp².[21,25] Thus these data support conclusions drawn from the van't Hoff plots.

Effect of SO₂, H₂O, and the Solute Concentration. Addition of H₂O to a superacid solution containing p-methylanisole causes an increase in O protonation. For example, addition of 5% water to the sample causes a shift from 28% O protonation to 44% O protonation in 11.5 mol % SbF₅-FSO₃H at −50°. The reason for this pronounced effect is not clear. Increasing acidity by increasing the SbF₅ concentration decreases the amount of O protonation. Thus the increase in O

protonation is consistent with a dramatic lowering of the acidity of the solution due to the addition of water.

The effect of SO₂ was examined in more concentrated SbF₅-FSO₃H solutions containing p-methylanisole, for example, in 35% SbF₅-FSO₃H. Addition of SO₂ resulted in the development of nmr signals in addition to those due to oxonium and benzenium ions. The amount of carbon protonated base is slightly higher in comparison with the samples without added SO₂, indicating that addition of SO₂ has some influence on the basicity of the acidic system.

The ratio of oxygen to carbon protonation was also found to be dependent on the concentration of the starting base. An increase in the concentration of the base causes an increase in the oxonium ion concentration at lower temperatures as well as a greater temperature dependence of the O:C ratio. For example, 50% increase in the concentration of p-methylanisole in 20% SbF₅-FSO₃H causes a change in O:C protonation ratio to 1.35 at −60° and to 0.6 at −20°, significantly different from those indicated in Table III. These changes are consistent with a decrease in acidity caused by the organic solute. This clearly indicates the importance of measurements at low solute concentration.

Effects of the Solute Structure. An enormous amount of work in this area has been published by Olah and coworkers.[5,6,16] We shall limit our attention to the effect of changing alkyl substitution as shown in Figure 1. The most important feature of these data is that the substituent effect is dependent on the antimony pentafluoride concentration. There seems to be little rationale for these data. p-Methylanisole and p-cresol show identical behavior over the range of acids considered, though in a number of other similar systems, methoxy is known to have a greater stabilizing effect than hydroxy. This behavior was discussed in an earlier section of this paper.

Replacing an O-methyl group by an O-ethyl group increases the stability of the O protonated form relative to the C protonated form in all acid systems. This is consistent with the increased polarizability of the ethyl group stabilizing the nearby positive charge when oxygen is protonated.[25] The behavior of p-ethylanisole is singular, and we see no obvious reason for the sudden increase in O protonation in neat FSO₃H. Our knowledge of the nature of strong acids and of solvent-solute interactions will have to improve enormously before such small energy changes can be rationalized with confidence.

A number of conclusions can be drawn from the work discussed here. Although C and O protonation of these ambient bases follows different acidity functions, the thermodynamics of their protonation are similar and small changes in a number of variables will cause

(24) E. M. Arnett and J. W. Larsen, J. Amer. Chem. Soc., **91**, 1438 (1969).
(25) J. I. Brauman and L. K. Blair, J. Amer. Chem. Soc., **93**, 4315 (1971).

significant shifts in the ratio of O:C protonation. Reliable quantitative data will only come from measurements at low solute concentration, well below the concentrations necessary for continuous wave nmr work, using carefully purified acids of precisely deter-

mined composition. Ambient bases have not yet been the subject of such a study in superacid media.

Nucleophilic Reactivities of Halide Ions in Molten Triethyl-n-hexylammonium Triethyl-n-hexylboride

Warren T. Ford,* Robert J. Hauri, and Stanley G. Smith

Contribution from the Roger Adams Laboratory, Department of Chemistry, University of Illinois, Urbana, Illinois 61801. Received December 21, 1973

Abstract: Reactions of tetraethylammonium halides with methyl p-toluenesulfonate in molten triethyl-n-hexylammonium triethyl-n-hexylboride ($N_{2226}B_{2226}$) at 35° proceed with relative rate constants Cl⁻ 2.1, Br⁻ 1.2, and I⁻ 1.0. The halide ions in $N_{2226}B_{2226}$ follow the same reactivity order as dissociated halide ions in polar aprotic solvents, but the range of relative rate constants in $N_{2226}B_{2226}$ is much narrower, probably because the smaller the halide ion, the more its activity is reduced by neighboring tetraalkylammonium ions.

Molten tetraalkylammonium tetraalkylborides[1] are a unique class of solvents. They can interact with themselves or with solutes only by electrostatic, ion-dipole, ion-induced dipole, and dispersion forces; their structures permit no Lewis acid–base interactions. One goal of our investigation of this new class of solvents is to determine how they affect rates of several important types of chemical reactions.[2]

The rates of bimolecular nucleophilic substitution reactions of anions with neutral substrates are markedly affected by ion association. Before 1960 the accepted relative nucleophilicities of the halide ions were I⁻ > Br⁻ > Cl⁻, based only on data in protic solvents.[3] Winstein and coworkers[4] found the reactivity order Cl⁻ > Br⁻ > I⁻ for reactions of dissociated halide ions with n-butyl p-bromobenzenesulfonate in acetone, and the same order has been found for SN2 reactions in other dipolar aprotic solvents.[5-8] We report here rates of reaction of tetraethylammonium halides with methyl p-toluenesulfonate in molten triethyl-n-hexylammonium triethyl-n-hexylboride ($N_{2226}B_{2226}$), which provide information on the effect of neighboring tetraalkylammonium ions on halide ion reactivities.

Results

Rates of disappearance of halide ions were followed

titrimetrically. However, the calculated second-order rate constant[9] decreased throughout each kinetic run. The deviation of the data from a second-order rate law was greater for reactions of iodide salts than for reactions of bromide and chloride salts.

To determine the cause of the decreases in observed rate constants, the stabilities of methyl tosylate and methyl iodide in $N_{2226}B_{2226}$ were investigated. The pmr spectrum of a 0.44 M solution of methyl tosylate in $N_{2226}B_{2226}$ remained unchanged after 24 hr at 35°, but at 60° the methyl tosylate methyl signals disappeared with a first-order rate constant of 1.0×10^{-6} sec⁻¹. Similar pmr experiments with initially 0.15–0.28 M methyl iodide in $N_{2226}B_{2226}$ showed that methyl iodide disappeared with a half-life of less than 24 hr at 35°. In the pmr spectra of both the methyl tosylate and the methyl iodide solutions, a new singlet appeared at δ 0.16, which we attribute to methane, the area of the B–CH₂ multiplet decreased, and the area of the broad methyl and methylene signals increased. Because these results are explained by eq 1 and are consistent with

$$R_3\bar{B}\text{—}CH_2CH_3 + CH_3I(CH_3OTs) \longrightarrow$$
$$R_2BCHRCH_3 + CH_4 + I^-(OTs^-) \quad (1)$$
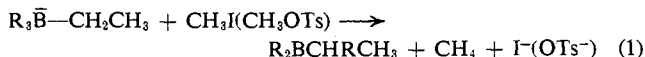
earlier results of Haag and Hesse,[10] who found that tetraalkylboride ions acted as hydride donors toward alkylating agents, no further investigation was made of the products of reactions of methyl iodide with N_{2226}-B_{2226}.

In the reactions between iodide salts and methyl tosylate, the product, methyl iodide, reacts with the solvent to generate iodide ion, which results in a downward drift of the second-order rate constants calculated from titrimetric data. Presumably the lesser drifts in calculated rate constants of the reactions of chloride and bromide salts with methyl tosylate are due to reactions of methyl chloride and methyl bromide with $N_{2226}B_{2226}$.

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