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SOLVENT EFFECTS ON HALONIUM ION $\rightleftharpoons$ CARBONIUM ION EQUILIBRIA

Samuel P. McManus*

Department of Chemistry, The University of Alabama in Huntsville, Huntsville, Alabama 35807

Paul E. Peterson*

Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208

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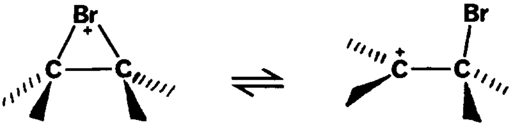
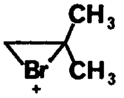
Although the polar bromination of alkenes has long been postulated[1] to involve ethylenebromonium ion intermediates, some product studies have led to suggestions[2-4] of the intermediate's solvent dependence. These reports originated from studies of stilbene derivatives[2] and now include a variety of types.[3,4] The conclusion is that there is more bromonium ion character, as opposed to carbonium ion character, as the solvent polarity decreases.[5] One of us recently proposed[4] that the observed solvent dependence of polar bromination reactions may be the result of differential solvation requirements of the bromonium ion and the carbonium ion in their equilibria, eq. (1). It was inferred that owing to differences in electronic configurations,[6] the ethylenebromonium ion derivative can better accommodate the positive charge in the absence of strong solvation.


(1)

Beauchamp and his coworkers[7] have now determined that relative to simple carbonium ions, cyclic halonium ions exhibit a greater relative stability in the gas phase than in fluorosulfuric acid.[8] Following a logic in common with that of McManus and Ware,[4] Beauchamp et al [7] attributed the increased relative bromonium ion stability to internal solvation of the carbonium ion by the neighboring bromine atom. We now report quantitative data on halonium $\rightleftharpoons$ carbonium ion equilibria in solution which lends support to the proposals of Beauchamp[7] and McManus.[4]

Olah[9] and Peterson[10] and their coworkers have previously suggested that the temperature dependence of the ^1H and ^{13}C nmr spectra of certain halonium ions, e.g. **1-4**, results from a halonium $\rightleftharpoons$ carbonium ion equilibria, e.q. eq.(1), which is fast on the nmr time scale. Employing FT ^{13}C techniques, Henrichs and Peterson[10] quantified this equilibria for several halonium ions in SO_2. We now report temperature dependence of the C-1 chemical shift of ions **3** and **4** in SO_2ClF.[11] Using estimated chemical shifts (eq. 2) of the halonium ions (**3**h and **4**h) and the carbonium ions (**3**c and **4**c) obtained as previously discussed,[10] the characteristics of the **3**h$\rightleftharpoons$**3**c and **4**h$\rightleftharpoons$**4**c equilibria were calculated (Table 1).[12]



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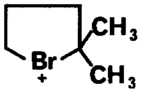

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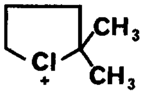

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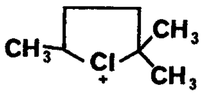

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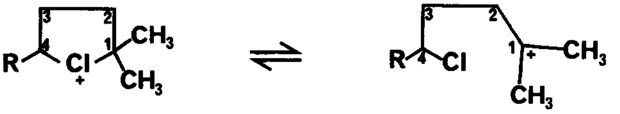

(2)

3h : R=H, δ_{C-1} = 149.2 ppm **3**c : R=H, δ_{C-1} = 333 ppm

4h : R=CH_3, δ_{C-1} = 147.5 ppm **4**c : R=CH_3, δ_{C-1} = 333 ppm

A comparison of the equilibria of **3** and **4** in the SO_2 and SO_2ClF at -60° (Table II) reveals a measurable solvent effect on the equilibria.[13] The preference for the halonium ion relative to the carbonium ion in SO_2ClF is further evidenced by our failure to generate cation **2** in SO_2ClF. Rearrangement of the ethyl derivative **5** to **2** in SO_2 occurs in 20 min at -20° [9] or 1.25 hr at -27°.[10] In SO_2ClF, however, no detectable rearrangement of **5** to **2** occurred upon warming **5** to -40° for 4.5 hr or upon storage at -70° for 15 days. Warming of **5** at -20° or above was accompanied by decomposition and again no **2** was detected by ^{13}C nmr.

While we were unable to find any useful quantitative comparison of SO_2 and SO_2ClF in the literature, Olah and Olah[14] have stated that SO_2ClF is the preferred solvent for the formation of stable carbonium ions since SO_2 reacts with some carbonium ions to yield sulfinic acids or sulfonyl fluorides. Thus, the oxygen atoms in SO_2 are apparently more nucleophilic than those in SO_2ClF allowing the former to better solvate carbonium ions.

In summary, our results indicate that cyclic halonium ions become relatively more stable than carbonium ions as the solvent becomes less capable of nucleophilic solvation. Hence the numerous literature reports of increased stereoselectivity in electrophilic alkene halogenations in non-polar solvents and at low temperature serve as qualitative examples of solvent and temperature effects on halonium ⇌ carbonium ion equilibria.

5 2

(3)

Table I. Experimental and Calculated Parameters for Halonium-Carbonium Ion Equilibria in SO_2ClF.

Cations	Temperature (°C)	$K_{eq.}$	ΔG (Kcal/mole)	X_h[a]	C-1 (ppm)[b]
	-100 ± 2	0.118 ± 0.036	0.735 ± 0.1	0.895 ± 0.025	168.6 ± 0.1
	-94	0.130	0.726	0.885	170.4
	-85	0.141	0.732	0.877	171.9
	-82	0.145	0.735	0.874	172.4
3h ⇌ 3c	-61	0.206	0.666	0.829	180.6
	-47	0.222	0.677	0.818	182.6
	-33	0.327	0.533	0.754	194.5
	-102 ± 2	0.013 ± 0.008	1.483 ± 0.2	0.987 ± 0.012	149.8 ± 0.1
	-92	0.016	1.479	0.984	150.5
4h ⇌ 4c	-82	0.020	1.486	0.980	151.1
	-73	0.025	1.460	0.975	152.1
	-36	0.059	1.336	0.944	157.8

[a] Mole fraction of cyclic halonium ion (halonium ion ⇌ carbonium ion equilibrium); values calculated as discussed in ref. 10. [b] Relative to TMS (ext. cap).

Table II. Comparison of Halonium-Carbonium Ion Equilibria in Sulfur Dioxide and Sulfuryl Chloride Fluoride at -60° (see ref. 13).

Cations	Solvent	Δδ[a]	X_h	$K_{eq.}$	ΔG (kcal/mole)
3h ⇌ 3c	SO_2[b]	147.0[c]	0.75	0.31	0.46 ± 0.01
	SO_2ClF	144.0[c]	0.82	0.21	0.67 ± 0.02
4h ⇌ 4c	SO_2[b]	133.4[d]	0.95	0.056	1.23 ± 0.04
	SO_2ClF	132.6[d]	0.97	0.032	1.42 ± 0.05

[a] The ^{13}C chemical shift of C-3 of 3 in SO_2ClF is 36.38 ± 0.07 (rel to TMS, ext) and temp independent; in SO_2 (ref 10), it is at 40.0 ± 0.5 ppm. In 4, the C-4 group is essentially temp independent with the values at -60° in SO_2 (ref 10) and SO_2ClF being 22.1 ± 0.1 and 21.11 ± 0.04, respectively. [b] Data from ref 10. [c] C-1 compared to C-3. [d] C-1 compared to the C-4 methyl.

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5. To our knowledge there has been no correlation with a specific parameter such as μ, ε, or Y, but see M. F. Ruasse and J. E. Dubois, J. Amer. Chem. Soc., 97, 1977 (1975).

6. Solvation of the carbonium ion and bromonium ion would be quite different. The carbonium ion contains only six electrons in its outer shell and would accept a solvent electron pair in its empty p orbital. The bromonium ion, however, has fully occupied 3d, 4s, and 4p orbitals, hence it would likely accept a pair of solvent electrons in a 4d orbital.

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11. The ions were prepared as ~ 0.7M solutions by adding the dihalide precursor (ref 10) to a SO_2ClF solution 2.5M in SbF_5. Vigorous stirring during the additions (at -70 to -78°) prevented overheating and discoloration.

12. The model compounds, the tetramethylenechloronium ion and its 1-methyl derivative, showed little solvent dependence of their chemical shifts. Assumed chemical shift values were calculated using the method described in ref. 10.

13. The errors shown for K, ΔG, and X in Table I result predominantly from an uncertainty in ν_c and ν_h (ref. 10). This error vanishes for comparison purposes. So that the statistical difference will be obvious, the constant error is not included in the ΔG values in Table II.

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