

A MINDO/3 STUDY OF HALONIUM ION-CARBOCATION EQUILIBRIA.

A THEORETICAL EVALUATION OF THE IMPORTANCE OF CARBOCATION SOLVATION.

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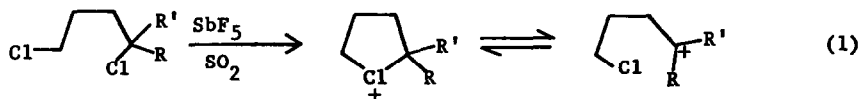
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The relative importance of cyclic halonium ions and their isomeric haloalkyl carbocations has been a topic of interest in recent years.¹⁻⁴ It has been demonstrated that under stable ion conditions, substitution at the carbocationic carbon by alkyl groups increases the stability of the open carbocation relative to that of its cyclic halonium ion isomer.^{1,2} Thus, whereas unsubstituted ethylene- (1) and tetramethylenehalonium (2) ions tend to exist as static,



closed ions, disubstituted derivatives may exist as a halonium ion-carbocation equilibrium mixture,¹ e. g.



Of course, chemical reactions of such equilibrating ionic species may proceed via either intermediate; hence, any factor which can affect the equilibrium may alter the product composition. It has been argued recently⁵ that solvent polarity is such a factor. In fact, it has been shown that changing the solvent from SO₂ to SO₂ClF alters the equilibrium depicted in eq. (1).³ The

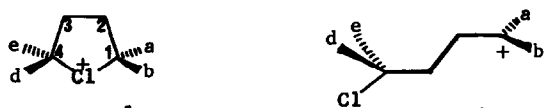
less nucleophilic SO_2ClF does not solvate the open carbocation as well as does SO_2 , and the equilibrium in eq. (1) is shifted further to the left when the solvent is SO_2ClF .⁶

One would predict that the equilibrium in eq. (1) would be shifted to the left most dramatically in the absence of solvent, *i.e.* in the gas phase. In the gas phase the halogen should serve as a donor in internally solvating the carbocation to form the cyclic halonium ion. This communication reports preliminary MINDO/3 SCF MO calculations⁷ on halonium ions and carbocations which confirm this prediction and provide an estimate of the importance of carbocation solvation effects.

Table I gives the heats of formation of several cyclic chloronium ions and their isomeric chloroalkyl carbocations. Although the MINDO/3 method has produced a number of exciting and quite valuable results for a variety of chemical applications,^{7,8} Dewar and co-workers have noted that the calculated heats of formation tend to be too positive for compact, globular molecules.⁷ We have considered three classes of molecules (*i.e.* the alcohol series $\text{CH}_3\text{CRR}'\text{OH}$, the alkyl halide series $\text{CH}_3\text{CRR}'\text{Cl}$, and the geminally substituted cyclopentanes, $\text{C}_5\text{H}_{10}\text{RR}'$) which structurally model the ions under study. We find that the average errors in ΔH_f as predicted by MINDO/3 are: -6.5 ± 0.3 , -1.9 ± 1.0 , $+12.6 \pm 2.6$ for $\text{R} = \text{R}' = \text{H}$; $\text{R} = \text{CH}_3$, $\text{R}' = \text{H}$; $\text{R} = \text{R}' = \text{CH}_3$, respectively. The "corrected" values in Table I were estimated by subtracting the average errors above from the MINDO/3 ΔH_f 's. It should be noted that MINDO/3 calculations for the corresponding branched boranes follow the same pattern, although insufficient experimental ΔH_f values are available for calculation of the errors. Thus, for the present study the same branching corrections have been applied to the open carbocations and the closed halonium ions in Table I.

It can be seen in Table I that MINDO/3 predicts that all of the cyclic chloronium ions considered in this preliminary study are more stable than their open chloroalkyl carbocation isomers. This is true for both the uncorrected and corrected MINDO/3 heats of formation. These results suggest that chlorine is quite effective in internally solvating the carbocations in the absence of solvent. Furthermore, MINDO/3 predicts that a tertiary carbocation is more than 10 Kcal mol⁻¹ less stable than its isomeric chloronium ion. The corresponding difference measured in SO_2 or SO_2ClF solvent is only *ca.* 0-2 Kcal mol⁻¹;^{1,3} therefore, these solvents must supply a substantial amount of stabilization to the open carbocation through solvation.⁹

Table I. MINDO/3 Heats of Formation for Some Cyclic Chloronium Ions and Their Isomeric Chloroalkyl Carbocations.



Substituents	ΔH_f (Kcal mol ⁻¹ , 25°) ^a		ΔH_f (Kcal mol ⁻¹ , 25°) ^b		$\Delta\Delta H_f$ (Kcal mol ⁻¹)
	Uncorrected	Corrected ^c	Uncorrected	Corrected ^c	
a=b=d=e=H	153.8	160.3	182.1	188.6	28.3
a=CH ₃ , b=d=e=H	141.8	143.7	165.5	167.4	23.7
a=CH ₂ CH ₃ , b=d=e=H	135.8	137.7	157.4	159.3	21.6
a=d=CH ₃ , b=e=H	130.5	134.3	160.0	163.8	29.5
a=b=CH ₃ , d=e=H	140.6	128.0	154.3	141.7	13.7
a=b=d=CH ₃ , e=H	129.7	119.0	148.5	137.8	18.8

^aA complete geometry optimization was performed except that dihedral angle 1234 was fixed at 0°. ^bA complete geometry optimization was performed except that dihedral angle 1234 was fixed at 180°. ^cSee text.

It is worthwhile to note that the "corrected" MINDO/3 heats of formation are in excellent qualitative agreement with experimental observations throughout the series studied in this work. For example, the order of stability for the 1-ethyl-, 1,4-dimethyl-, and 1,1-dimethyltetramethylene chloronium ion isomers is exactly that expected based on the experimental observations of Peterson¹, Olah² and others¹⁰.

Other ring-sizes and complete energy-surface calculations for chloronium ion ring-opening and rearrangement processes are underway currently in these laboratories. The results of these studies will be presented in our full account of this work.

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