Isolation and the IR Spectra of Chloro- and Bromo-ethyl Cations in Cryogenic SbF_5 Matrices

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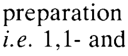
Reaction of $MeCHCl_2$, CH_2ClCH_2Cl and CH_2BrCH_2Br respectively with SbF_5 in a solid matrix at 77–200 K affords the most stable cations **2** and **3** as predicted by previously published high-level *ab initio* calculations.

In continuation of our work[1] on the isolation and spectroscopic characterization of chloromethyl cations we have extended these studies to chloro- and bromo-ethyl carbocations. Halogenated carbocations are of interest as reactive intermediates in the elimination and addition reactions of halogens and also in connection with photoresist applications. Recently published results on high-level *ab initio* calculations[2,3] and gas phase experiments[4] indicate that the most stable form of the chloroethyl cation is **2** while the bridged isomer **1** is only slightly higher in energy (2–5 kcal mol^{-1}) (1 cal = 4.184 J). The opposite is the case with the bromoethyl cation,[3] where the cyclic isomer **3** is more stable than the acyclic form **4** by 3 kcal mol^{-1}.

From gas-phase studies by photoionization mass spectrometry and ion-cyclotron resonance spectroscopy. Beauchamp *et al.*[4] inferred the same reversal of stabilities of the cyclic *vs.* acyclic forms.

In this paper we report that chloro- and bromo-ethyl cations can be prepared and spectroscopically identified in cryogenic SbF_5 matrices, applying the technique used in the preparation and spectroscopic identification of carbocations.[5] For the preparation of chloroethyl cations two precursors were used, *i.e.* 1,1- and 1,2-dichloroethane.

1,1-Dichloroethane was codeposited with SbF_5 on a CsI window cooled to 77 K. The experimental conditions were the same as those described in our previous work.[1] New signals not belonging to the spectrum of the starting material started to appear at 77 K. By warming the matrix to 200 K the signals of the precursor disappeared, and new signals, at 1410, 1130, 975 and 940 cm^{-1}, increased in intensity. Under the same experimental conditions similar results were obtained with 1,2-dichloroethane, *i.e.* the new signals appeared at the same frequencies as in the experiment with 1,1-dichloroethane.



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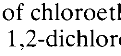

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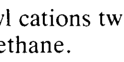

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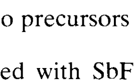

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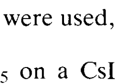

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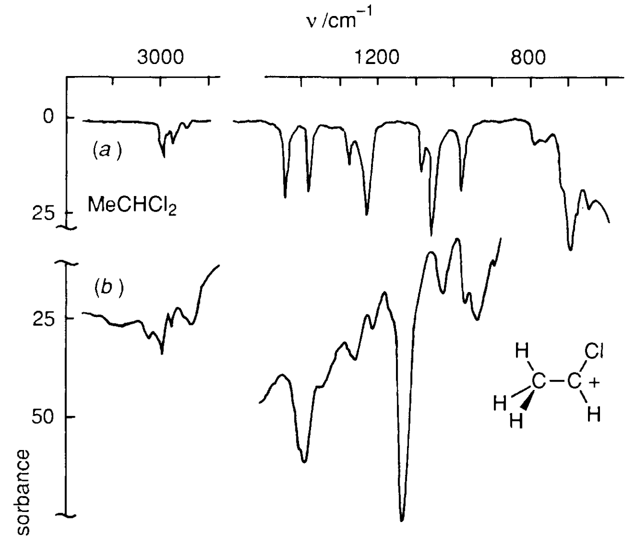

Fig. 1 IR spectra of 1,1- and 1,2-dichloroethane and the SbF_5-matrix spectrum of the $C_2H_4Cl^+$ cation. The dots denote the starting material. (*a*) 1,1-Dichloroethane and (*b*) cation therefrom; (*d*) 1,2-dichloroethane and (*c*) cation therefrom.

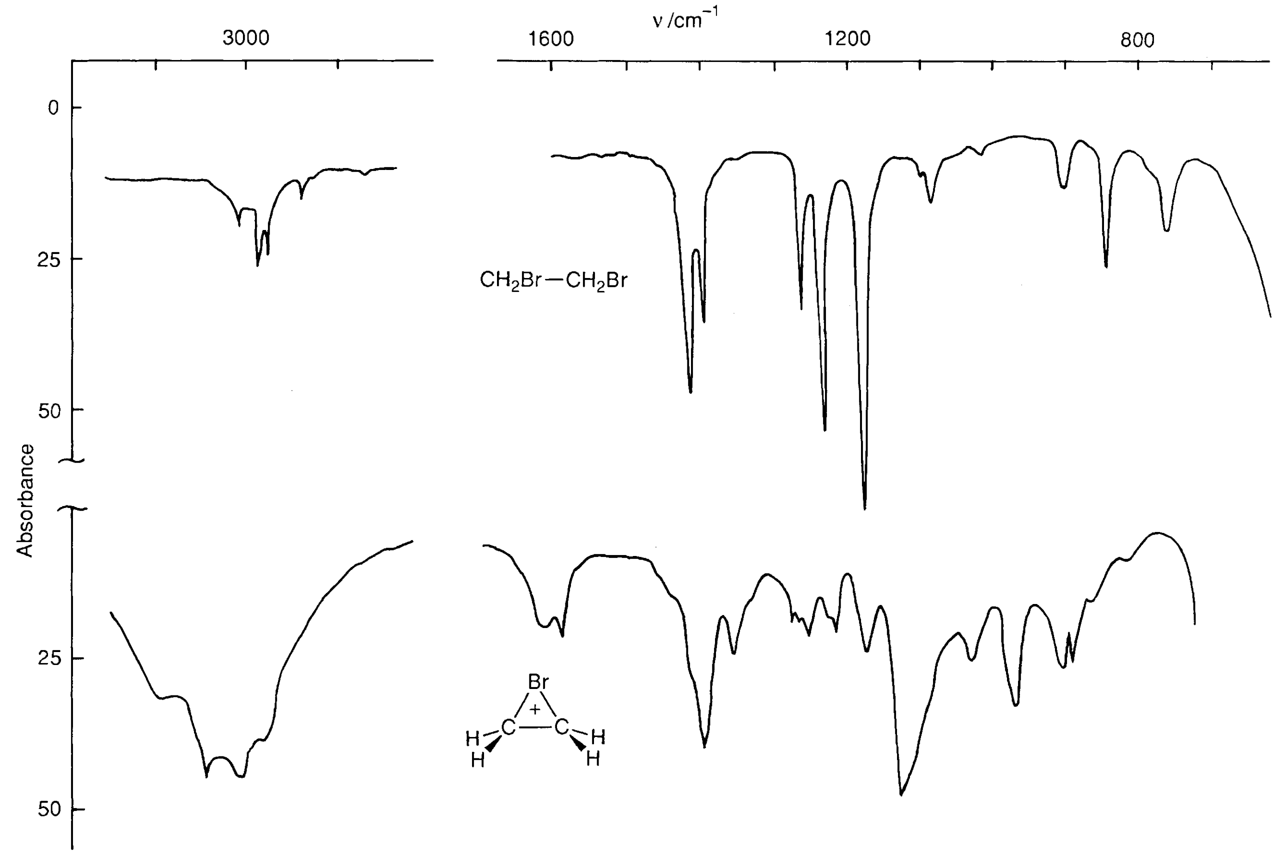

Fig. 2 IR spectra of 1,2-dibromoethane and the SbF$_5$-matrix spectrum of the C$_2$H$_4$Br$^+$ cation

Table 1 Experimental and calculated[3] IR frequencies (in cm^{-1}) for C$_2$H$_4$Br$^+$

	Calculated (scaling factor 0.96)		
Expt.	Isomer **3**	Isomer **4**	Isomer **5**
3140	3359	3267	3265
	3349	3245	3228
3040	3233	3102	3129
	3230	3040	3061
1595^a	1596^a		
	1532	1544	1531
		1506	1511
			1455
1410^a		1424^a	1455^a
		1397	1394
1365			
1260^a	1265^a		
1245^a	1244^a		
1185^a	1173^a	1193^a	
1140^a	1156^a		1145^a
			1120
1040^a		1066^a	1061^a
		1016	
980^a	983^a		
915^a	913^a		
900^a	860^a		

^{a} Frequencies which agree best with the experiment.

Since these reactions are thermodynamically controlled the final product in both cases should be the most stable carbocation **2**. The IR spectra of the ion obtained from both precursors together with the spectra of 1,1- and 1,2-dichloroethane are shown in Fig. 1. The appearance of the most intense peak at 1140 cm^{-1} argues for the formation of carbocation **2**. This vibration, by analogy with a similar one (at 1040 cm^{-1}) observed in the IR spectrum of the chloromethyl cation,[1] could be assigned to the C–Cl stretching vibration having a partial double bond character. Further confirmation for the formation of **2** is provided by the analysis of the C–H stretching region; the IR spectrum shows a band at 3040 cm^{-1} which is characteristic for the C–H stretching vibration on a cationic sp^2 hybridized carbon atom. The published, high-level calculations for the C$_2$H$_4$Cl$^+$ ion[2] do not report the calculated frequencies.

The bromoethyl cation was prepared from 1,2-dibromoethane using the same procedure. The resulting spectrum together with the spectrum of 1,2-dibromoethane is shown in Fig. 2. The experimentally observed IR frequencies and the (scaled) calculated bands[3] for the three proposed structures **3**–**5** are compared in Table 1. It can be seen that the computed frequencies for the cyclic bromonium ion **3** almost completely match the experimental spectrum while only three of the calculated frequencies for acyclic structures **4** and **5** coincide with the experimentally obtained signals. This is a strong indication that the ionization of 1,2-dibromoethane yields the cyclic bromonium ion **3**, as the most stable isomer. The discrepancies between the experimental and calculated frequencies in the C–H stretching region are most probably due to anharmonicity which is not sufficiently corrected by the scaling factor. Attention should be drawn to two additional characterstic bands in the spectrum of this ion. The first is the C–H stretching vibration at 3140 cm^{-1}. Such a high vibrational frequency can be regarded as the result of two effects, (*i*) the rehybridization of the carbon atom and (*ii*) a donation of electrons from the bridging bromine atom to the C–H bonds. Note that the C–H stretching vibration in the chloroethyl cation which appeared at a lower frequency (3040 cm^{-1}), was likely the consequence of only one effect, *i.e.* rehybridization. The second characteristic band is at 1596 cm^{-1} and could be assigned to a carbon–carbon stretching vibration of a partial double bond.

We conclude that by isolation in a solid SbF_5 matrix the most stable chloro- and bromo-ethyl cations can be prepared and characterized. Spectral characteristics of both cations confirm the structures predicted by high level *ab initio* calculations: the chloroethyl cation is the acyclic isomer **2** while the bromoethyl cation has a bridged structure as in **3**.

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