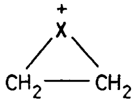
Isomeric Gaseous $C_2H_4Cl^+$ Ions

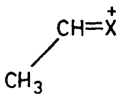
By Joost Monstrey and Christian C. Van de Sande*
[*Laboratory of Organic Chemistry, State University of Gent, Krijgslaan,* 271 (*S*.4), B-9000 *Gent, Belgium*]
and Karsten Levsen, Heinz Heimbach, and Friedrich Borchers
(*Institut für Physikalische Chemie der Universität Bonn, Wegelerstrasse,* 12, D-5300 *Bonn, Germany*)

Summary Gaseous ethylenechloronium ions and their methylchlorocarbenium isomers are stable and can be identified from their collisional activation spectra.

Neighbouring group participation is known to operate in electron impact (EI) induced decompositions[1] and, in the specific instance of bifunctional compounds of the type XCH_2CH_2Y, three-membered ring onium ions (**1**) should result. Evidence for the existence of such oxonium, sulphonium, and ammonium ions (**1**) is available from ion cyclotron resonance[2,3a] (ICR), collisional activation[4] (CA), and appearance energy measurements.[5] The corresponding ethylene halogenonium ions have eluded experimental characterization in the gas-phase so far. Earlier attempt to generate such species by protonation of β-halogeno ethanols in an ICR cell[3] failed. Some evidence, however, was found for the occurrence of methylbromocarbenium ions (**2**, X = Br).[3a] This situation is particularly disturbing as Olah and his co-workers have demonstrated the existence of both cyclic and acyclic halogenonium ions in solution.[6] Moreover, *ab initio* calculations, which neglect solvent effects, also predicted the ions (**1**) and (**2**) (X = Cl) to be stable.[7]



(1)



(2)

We have collected the CA spectra of the $C_2H_4Cl^+$ species (Table) generated from several precursors, selected[8] on the assumption that the presence of $ClCH_2CH_2$- and CH_3CHCl- structural units might lead to the fragments of structures (**1**) and (**2**), respectively, the former as a result of chlorine participation, the latter through normal α-cleavage.

Table. Partial CA spectra[a] of $C_2H_4{}^{35}Cl^+$ ions.

Precursor		Ion structure	*m/z* 47	48	49	50	51
$PhOCH_2CH_2Cl$	(**3**)	(**1**)	35	33	32		
$ClCH_2CH_2CO_2Et$	(**4**)	(**1**)	36	32	32		
$CH_3CHClCO_2Me$	(**5**)	(**2**)	45	47	8		
$CH_3CHClCH_3$	(**6**)	(**2**)	45	46	9		
$CD_3CHClCD_3$	(**7**)	[$^2H_3$]-(**2**)	40	29	21	5	5
$CH_3CDClCH_3$	(**8**)	[$^2H_1$]-(**2**)	38	21	34	7	
$ClCH_2CH_2OH$[b]	(**9**)	(**1**)	27	34	39		

[a] All data are the averages of three independent measurements. Decomposition of stable gaseous ions is induced by collisions with inert neutral molecules (He); the resulting fragments are then separated and collected, thus yielding a 'mass spectrum' of the ionic species (see K. Levsen and H. Schwarz, *Angew. Chem.*, 1976, **88**, 589; *Angew. Chem. Internat. Edn.*, 1976, **15**, 509).

[b] $C_2H_4{}^{35}Cl^+$ ions were generated from (**9**) under chemical ionisation conditions with hydrogen. As this CA measurement was taken on a different instrument (Bonn design) with different operating conditions (3 kV accelerating voltage relative to 8 kV for EI generated fragments) only a qualitative comparison with the other data is possible.

The products from (**3**) or (**4**) and (**5**) or (**6**) clearly are different (see Table and Figure), the former displaying an enhanced loss of a methylene group (*m/z* 49) upon CA. This correlates with the expected cyclic structure (**1**) and parallels earlier observations on other three-membered ring onium ions.[4] Enhanced loss of a methyl radical (*m/z* 48), however, is observed for (**5**) and (**6**), as would be expected for structure (**2**). Note that this reaction occurs with only minor interference from hydrogen randomization as shown by the more abundant fragments at *m/z* 48 (**7**) and 49 (**8**) compared with *m/z* 49 and 48, respectively, in the labelled compounds. $C_2H_4{}^{35}Cl^+$ ions have also been generated under chemical ionisation conditions (see footnotes to Table), *via* protonation of (**9**) and subsequent loss of water. Again the large abundance at *m/z* 49 indicates chlorine participation in contrast to the earlier ICR findings[3] on the corresponding bromine compound. These data constitute the first experimental evidence for the gas-phase stability of chlorinated (**1**) and (**2**).

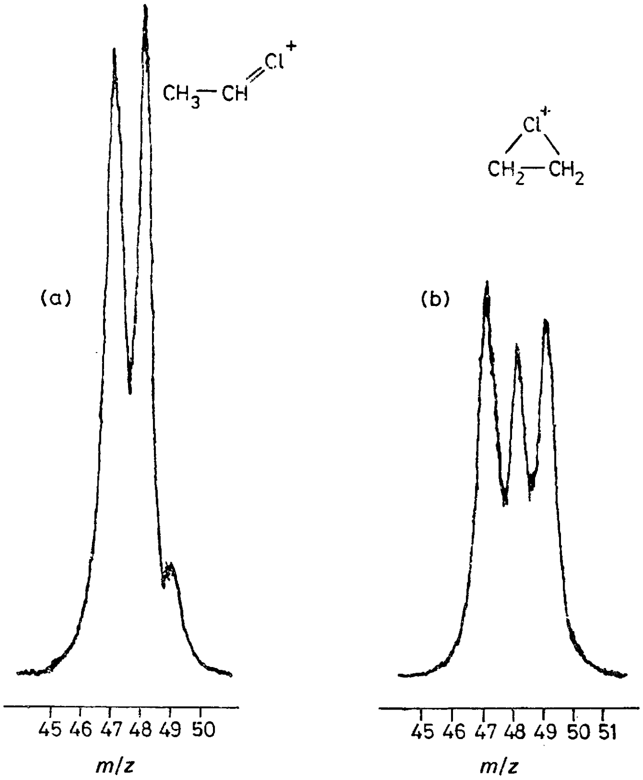


Figure. CA spectral region *m/z* 45—50 for (a) (**5**) and (b) (**4**).

We thank the Belgian 'Nationaal Fonds voor Wetenschappelijk Onderzoek' for financial support and grants as Aspirant (J.M.) and Aangesteld Navorser (C.V.), and the Deutsche Forschungsgemeinschaft, the Fonds der Chemische Industrie, and the Wissenschaftministerium Düsseldorf.

(*Received, 9th June* 1978; *Com.* 604.)

---

[1] For a recent review, see H. Bosshardt and M. Hesse, *Angew Chem.*, 1974, **86**, 256; *Angew, Chem. Internat. Edn.*, 1974, **13**, 252.

[2] J. L. Beauchamp and R. C. Dunbar, *J.Amer. Chem. Soc.*, 1970, **92**, 1477; R. H. Staley, R. R. Corderman, M. S. Foster, and J. L. Beauchamp, *ibid.*, 1974, **96**, 1260.

[3] (a) J. C. Kim, M. C. Findley, W. H. Henderson, and M. C. Caserio, *J. Amer. Chem. Soc.*, 1973, **95**, 2184; (b) R. D. Wieting, R. H. Staley, and J. L. Beauchamp, *ibid.*, 1974, **96**, 7582; R. H. Staley, R. D. Wieting, and J. L. Beauchamp, *ibid.*, 1977, **99**, 5964.

[4] B. Vande Graaf, P. P. Dymerski, and F. W. McLafferty, *J.C.S. Chem. Comm.*, 1975, 978; B. Vande Graafe and F. W. McLafferty, *J. Amer. Chem. Soc.*, 1977, **99**, 6806, 6810; K. Levsen, H. Heimbach, C. C. Van de Sande, and J. Monstrey, *Tetrahedron*, 1977, **33**, 1785; C. C. Van de Sande, S. Z. Ahmad, F. Borchers, and K. Levsen, *Org. Mass Spectrometry*, submitted for publication.

[5] H. Schwarz, R. D. Petersen, and C. C. Van de Sande, *Org. Mass Spectrometry*, 1977, **12**, 391.

[6] G. A. Olah, J. H. Bollinger, and J. Brinich, *J. Amer. Chem. Soc.*, 1968, **90**, 2587; G. A. Olah and J. H. Bollinger, *ibid.*, 1968, **90**, 947; *ibid.*, 1967, **89**, 4744; G. A. Olah, D. A. Beal, and P. W. Westerman, *ibid.* 1973, **95**, 3387; G. A. Olah, P. W. Westerman, E. G. Melby, and Y. K. Mo, *ibid.*, 1974, **96**, 3565.

[7] W. J. Hehre and P. C. Hiberty, *J. Amer. Chem. Soc.*, 1974, **96**, 2665; D. T. Clark and D. M. J. Lilley, *Tetrahedron*, 1973, **29**, 845.

[8] Atlas of Mass Spectral Data, eds. E. Stenhagen, S. Abrahamsson, and F. W. McLafferty, Interscience, New York, 1969, pp. 495, 216, 1276, and 1411.