# Negative-Ion Mass Spectra of Polyatomic Molecules

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A mass-spectrometric investigation has been made of negative-ion formation in twelve different halogenated molecules under conditions where ion-pair formation is the major ionization process. The relative abundances are reported for the ions formed and some general patterns for negative-ion formation have been deduced.

When molecules are bombarded with electrons in the ion source of a mass spectrometer both positive and negative ions may be formed, the latter often several orders of magnitude less abundantly. If the energy of the ionizing electrons is greater than about 30 eV the relative abundances of the positive ions produced are generally independent of electron energy and positive-ion mass spectral data for many molecules are available.<sup>1-3</sup> However, few data have been reported <sup>4</sup> regarding the identity and distribution of the negative-ion species produced when molecules of chemical interest undergo electron bombardment.

For negative ions there are three mechanisms by which ion formation may occur, viz., at low electron energies ( $\sim < 2 \text{ eV}$ ) by electron capture,

### $XY + e \rightarrow XY^{-};$

at intermediate energies ( $\sim 2-10 \text{ eV}$ ) by a dissociative resonance process,

$$XY + e \rightarrow X + Y^{-};$$

and at higher electron energies by ion-pair formation,

$$XY + e \rightarrow X^+ + Y^- + e$$
.

Hence the ions observed and their abundance are markedly energy-dependent, and at high ion-source pressures all three formation processes may occur concurrently because of secondary reactions. However, at energies above about 30 eV and with ion source pressures of  $10^{-5}$  mm Hg, the predominant mode of negative-ion formation is by ion-pair formation.

In view of the lack of information on negative ion mass spectra we have examined a variety of halogenated molecules and identified the ion species formed and their relative abundances with a view to evaluating the general features which determine the patterns of negative-ion formation. No attempt has been made to measure the appearance potentials of the ions observed.

### EXPERIMENTAL

Mass spectra were measured using a Bendix time-of-flight mass spectrometer, model 3015. Spectra were recorded using a Kent 1 mV potentiometric recorder. The same ion-source pressure  $(10^{-5} \text{ mm Hg})$  was used for all compounds in order to reduce the differences in the relative abundances of the ionic species due to possible ion-molecule reactions, and also to minimize the contributions of processes involving capture of the slower secondary electrons produced in the ion-pair formation step. All spectra were measured with ionizing electrons of energy 70 eV unless otherwise specified.

### RESULTS

We have tabulated our results for the intensities of the negative-ion species observed relative to the intensity of the most extensively formed ion (usually  $CI^{-}$  or  $F^{-}$ ).

| (a) symmetrical tetrachloroethane, $(30 \text{ eV})$                               |         |            |                                       |                        |                    |            |  |                         |  |  |                         |   |
|--|---------|------------|---------------------------------------|------------------------|--------------------|------------|--|-------------------------|--|--|-------------------------|---|
| $CHCl_2 - CHCl_2$  | H-      | <b>C</b> - | CH-                                   | $C_2^-$                | $C_2H^-$           | Cl-        | CCl-   | C <sub>2</sub> Cl       | $- Cl_2^-$                             | $HCl_{2}^{-}$                                    | $CCl_2^-$               | $C_2Cl_3^-$                             |
| currents   | 0.7     | 0.3        | 0.5                                   | 3.2                    | <b>4</b> ·0        | 1000       | 1.2  | 2.5                     | <b>3</b> 8· <b>5</b>                   | 3.8  | 0.3                     | 13.5                                    |
| (b) UNSYMMETRICAL TETRACHLOROETHANE  |         |            |                                       |                        |                    |            |  |                         |  |  |                         |   |
| $CCl_3$ — $CH_2Cl$<br>relative ion cu  | irrents | Cl<br>1·6  | C                                     | 'H<br>I ∙6             | $CH_2^-$<br>1.0    | C<br>17    | 2<br>•0  | C₂H <sup></sup><br>10·1 | C1-<br>1000                            | CC<br>5.   | 1-<br>7                 | $\underset{6.7}{\overset{Cl_2}{_{-7}}}$ |
| (c) tetrachloroethylene (30 eV)  |         |            |                                       |                        |                    |            |  |                         |  |  |                         |   |
| $CCl_2 = CCl_2$<br>relative ion cu   | irrents | C<br>1·    | 5                                     | C <sub>2</sub><br>33·( | ) 1                | Cl-<br>000 | CC<br>1·1  | 51-<br>I                | C <sub>2</sub> Cl <sup>-</sup><br>21·3 | $Cl_2^-$<br>7.5                                  | (                       | $C_2 Cl_4^-$<br>3.5                     |
| (d) HEXAFLUOROETHANE   |         |            |                                       |                        |                    |            |  |                         |  |  |                         |   |
| $C_2F_6$ relative ion cu   | irrents |            | F-<br>1000                            | I                      | CF-<br>16          | F          | -2<br>5  | C <sub>2</sub>          | F-<br>2                                | $CF_2^-$   |                         | $CF_{\overline{3}}$<br>12               |
| (e) fluoroform   |         |            |                                       |                        |                    |            |  |                         |  |  |                         |   |
| CF₃H<br>relative ion cu  | rrents  | H-<br>1·5  | Ċ                                     | ;<br>2∙4               | CH-<br>0·8         | F<br>10    |  | CF-<br>6·2              | F <sub>2</sub> <sup>-</sup><br>10·0    | CF<br>0  | 8                       | CF <sub>3</sub><br>85·4                 |
| (f) carbon tetrachloride   |         |            |                                       |                        |                    |            |  |                         |  |  |                         |   |
| CCl <sub>4</sub><br>relative ion cu  | irrents |            | C−<br>2·5                             |                        | Cl-<br>1000        | C<br>2     | CC1-<br>20-0   | C<br>13                 | $l_2^-$<br>0                           | $\begin{array}{c} CCl_2^-\\ 4\cdot 0\end{array}$ | (                       | $CCl_{\overline{3}}$<br>2.0             |
| (g) chloroform   |         |            |                                       |                        |                    |            |  |                         |  |  |                         |   |
| CHCl <sub>3</sub><br>relation ion c  | urrents |            | C-<br>1·5                             |                        | CH-<br>7·1         | 1          | C1-<br>000   | C(<br>3                 | Cl-<br>·3                              | $Cl_2^-$<br>4·3                                  | (                       | $CCl_2^-$<br>1.0                        |
| (h) METHYLENE DICHLORIDE   |         |            |                                       |                        |                    |            |  |                         |  |  |                         |   |
| CH <sub>2</sub> Cl <sub>2</sub><br>relative ion cu                                 | irrents |            | C-<br>1                               |                        | CH-<br>6           | C          | $2^{H_2^-}$  | C<br>10                 | 21-<br>100                             | CCI-<br>2  |                         | $Cl_2^-$<br>21                          |
| (i) METHYL CHLORIDE (30 eV)  |         |            |                                       |                        |                    |            |  |                         |  |  |                         |   |
| CH <sub>3</sub> Cl relative ion cu   | irrents | H−<br>2·6  |                                       | C−<br>1·3              | CH-<br>4∙6         | C]<br>5    | $H_2^-$<br>·3  | Cl-<br>1000             | CCl <sup>-</sup><br>0·7                | - CH<br>4  | Cl-<br>0                | CH₂Cl <sup>-</sup><br>2·0               |
| (j) methyl iodide  |         |            |                                       |                        |                    |            |  |                         |  |  |                         |   |
| $\begin{array}{c} CH_{3}I & H^{-} \\ relative ion currents & 4\cdot 2 \end{array}$ |         |            | C−<br>7·3                             | (<br>2                 | CH-<br>26·4        |            | $\begin{array}{c} \mathbf{CH}_{2}^{-} \\ 12 \cdot 6 \end{array}$ |                         |  | 1-<br>1000                                       |                         |   |
| (k) HEXAFLUOROACETONE  |         |            |                                       |                        |                    |            |  |                         |  |  |                         |   |
| CF <sub>3</sub> COCF <sub>3</sub><br>relative ion cu                               | rrents  | 0-<br>530  | ) 1                                   | F-<br>000              | CF-<br>6∙6         | H<br>6     | 7 <u>2</u><br>•6   | C₂F−<br>6·6             | $CF_{2}$<br>3.3                        |  | F3<br>8                 | C <sub>3</sub> F <sub>6</sub> O-<br>31  |
| (1) SULPHUR HEXAFLUORIDE   |         |            |                                       |                        |                    |            |  |                         |  |  |                         |   |
| $SF_6$ relative ion cu   | irrents | F-<br>16   | · · · · · · · · · · · · · · · · · · · | 5-<br>0                | $F_{2}^{-}$<br>1·0 | SF−<br>5·6 | SF<br>0•4  | $\frac{5}{2}$ SI<br>4 ( | F <sub>3</sub> S                       | F <sub>4</sub> :                                 | SF <del>5</del><br>13∙6 | SF <del>6</del><br>1000                 |

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#### **NEGATIVE-ION MASS SPECTRA**

#### DISCUSSION

### CHCl<sub>2</sub>—CHCl<sub>2</sub>, CH<sub>2</sub>Cl—CCl<sub>3</sub> AND CCl<sub>2</sub>=CCl<sub>2</sub>

Extensive negative-ion formation occurs for all three compounds. A notable feature is the formation of a molecular ion by tetrachloroethylene, formed presumably because the ion is stabilized with respect to decomposition by virtue of its symmetry and the strong carbon-carbon bonding. The tendency of the three molecules not to fragment symmetrically by carbon-carbon bond fission but for the two carbon atoms to be present in the fragment ions is noted. In ethane, ethylene and acetylene, the ions  $C_2^-$  and  $C_2H^-$  are formed and the intensity of these fragments increases as the bonding between the carbon atoms becomes stronger. This is similar to the behaviour observed for  $CHCl_2$ — $CHCl_2$  and  $CCl_2$ = $CCl_2$ . The  $HCl_2^-$  ion is observed with the symmetrical tetrachloroethane; this is unexpected since it is not formed with the structurally similar chloroform or methylene chloride. The  $CCl_2^-$  ion is absent, or only formed to a minor extent which suggests that  $CCl_2$  has a low electron affinity. With the unsymmetrical compound no fragment ion containing two carbon atoms in conjunction with a halogen atom is observed although such ions are abundant with the other two compounds, and the symmetrical compounds show an appreciably greater tendency to form larger fragment ions. No ion is formed containing carbon, hydrogen and halogen atoms; this is unexpected since the election affinities of CH<sub>3</sub> and CCl<sub>3</sub> are similar.

# CCl<sub>4</sub>, CCl<sub>3</sub>H and CCl<sub>2</sub>H<sub>2</sub>

Negative-ion formation in carbon tetrachloride has been studied by several workers.<sup>5-7</sup> Reese *et al.*<sup>5</sup> have reported that the  $Cl_2^-$  and  $CCl_3^-$  ions are formed 45 and 450 times less respectively than the  $Cl^-$  ion, in good accord with our results where the respective ratios are 75 and 500. We have observed  $CCl^-$  to be formed extensively; there appears to be no previous reference to the formation of this ion in carbon tetrachloride and the ion appears to be formed more readily than is the comparable  $CF^-$  ion from fluorocarbons.

Of interest is the formation of the  $CCl_2^-$  ion since our results for hexafluoroethane and fluoroform would suggest that, by analogy with  $CF_2^-$ , this ion should be produced to only a minor extent. It appears that the greater stability of  $Cl^-$  compared with  $F^-$  also extends to ions containing these species although the work of Page *et al.*<sup>8</sup> has suggested that substitution in an acceptor has little effect on the electron affinity. For chlorinated hydrocarbons, the fragment ions are formed more abundantly and also ions with odd-electron structures are formed more readily than with the fluorinated compounds.

Ions previously reported <sup>9</sup> for chloroform were Cl<sup>-</sup> and HCl<sub>2</sub><sup>-</sup>. We found no evidence for HCl<sub>2</sub><sup>-</sup> ion formation and conclude the ion was incorrectly identified and was confused with Cl<sub>2</sub><sup>-</sup>. We have confirmed the identity of the ion observed by adding fluoroform to the system and using the CF<sub>3</sub><sup>-</sup> ion formed as a mass-marker at (m/e) = 69. Under these conditions, the ion corresponds to Cl<sub>2</sub><sup>-</sup> and not HCl<sub>2</sub><sup>-</sup>.

The ratio of CH<sup>-</sup>/C<sup>-</sup> in methylene dichloride is approximately the same as observed for chloroform and the identity of the  $Cl_2^-$  ion (as distinct from  $HCl_2^-$ ) was confirmed by the addition of fluoroform as the mass marker. No fragment ion which contained carbon, hydrogen and halogen has been observed and the ion  $CCl_2^-$  is absent, whereas it is formed in the spectrum of chloroform and carbon tetrachloride.

A trend exhibited by this series of compounds is that the largest observed chlorinecontaining ion contains one chlorine atom less than the maximum possible number,

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i.e., CCl<sub>4</sub> yields CCl<sub>3</sub>, CCl<sub>3</sub>H, CCl<sub>2</sub> and CCl<sub>2</sub>H<sub>2</sub> gives CCl<sup>-</sup>. It appears that as the proportion of halogen in the molecule decreases so the molecule shows a decreasing tendency to form a large halogenated ion. Ions of the type CHCl<sup>-</sup> are not formed and ions such as CH<sup>-</sup> are produced to a lesser extent than their chlorinated counterparts although the electron affinities of CCl<sub>3</sub> and CH<sub>3</sub> appear to be similar.<sup>8</sup>

# CH<sub>3</sub>Cl and CH<sub>3</sub>I

No mixed ions containing carbon, hydrogen and halogen, nor ions containing carbon and halogen, are observed for the iodide in sharp distinction with the observations for methyl chloride. From the low intensity of the ion currents measured, methyl iodide shows less tendency to form negative ions than does methyl chloride, although this may be expected since the electron affinity of iodine is some 12 kcal mole<sup>-1</sup> less than that for chlorine.

The iodide fairly readily forms ions such as  $CH^-$ ,  $CH_2^-$  and  $CH_3^-$ , whereas with methyl chloride such ions are produced much less abundantly relative to the major ion, and the  $CH_3^-$  ion appears not to be formed when methyl chloride is examined. This behaviour is in marked contrast with our results for methylene chloride, chloroform and fluoroform where no ion containing carbon, hydrogen and halogen together were observed. The H<sup>-</sup> ion is also produced though our values for the relative intensity of this ion must be treated with some reserve in view of the possible mass discrimination towards such a light ion.

### CF<sub>3</sub>H AND C<sub>2</sub>F<sub>6</sub>

The formation of the  $F^-$  and the  $CF_3^-$  ions have been reported previously for hexafluoroethane.<sup>5</sup> The absence of the  $C_2F_5^-$  ion from the spectrum is unexpected since, in view of its stable electronic structure, it might have been formed extensively. In the positive-ion mass spectrum,  $C_2F_5^+$  is an abundant ion, being formed to about 41 % of the major ion  $CF_3^+$ . In the negative-ion spectrum there is no evidence for the formation of ions of the type  $C_2F_3^-$  or for any fragment ion containing two carbon atoms except for a small  $C_2F^-$  ion. This is in marked distinction with results reported for ethane <sup>10, 11</sup> where the  $C_2^-$  and  $C_2H^-$  are the principal carbon-containing ions.

Only the formation of the  $F^-$  ion has been reported previously for fluoroform.<sup>5</sup> The most extensively formed ions are  $F^-$  and  $CF_3^-$  and the negative mass spectrum shows many similar features to that of hexafluoroethane, notably the appreciable formation of the  $CF^-$  and  $F_2^-$  ions and only a low intensity ion due to  $CF_2^-$ . In addition,  $H^-$  and  $CH^-$  are formed but not as abundantly as the analogous fluorine fragments.

The  $CF_3^-$  ion is formed much more extensively (relative to  $F^-$ ) in fluoroform than in hexafluoroethane; this probably reflects the greater tendency for the ion-pair reaction

$$CF_3H + e \rightarrow CF_3^- + H^+ + e$$
,

to occur than the ion-pair reaction

$$CF_3CF_3 + e \rightarrow CF_3^- + CF_3^+ + e.$$

In the positive-ion mass spectrum of fluoroform the major ions are  $CF_3^+$  and  $CF_2H^+$ , the latter being about 90 % of the former. In the negative ion spectrum no fragment ions containing both hydrogen and fluorine are observed although an ion such as  $CF_2H^-$  has a stable electronic structure and, by analogy with  $CF_3^-$ , might have been expected to have been formed extensively. Possibly it is formed but decomposes 2116

by hydrogen fluoride elimination, i.e.,

# $CF_2H^- \rightarrow CF^- + HF$

since CF<sup>-</sup> is formed appreciably.

Comparison of the negative ion spectra of chloroform and fluoroform shows that the CH<sup>-</sup> ion is much more abundant with the former. The most notable difference, however, is in the trihalogenomethyl ion for there is large  $CF_3^-$  ion formation whereas the  $CCl_3^-$  ion is not observed with the chloride.

### HEXAFLUOROACETONE CF<sub>3</sub>COCF<sub>3</sub>

The negative-ion mass spectrum of hexafluoroacetone consists of the ions O<sup>-</sup>,  $F^-$ ,  $CF^-$ ,  $F_2^-$ ,  $C_2F^-$ ,  $CF_2^-$ ,  $CF_3^-$  and  $CF_3COCF_3^-$ . The parent ion is formed abundantly; also another molecular ion was observed with a molecule containing a double bond, viz., tetrachloroethylene.

Apart from the parent ion the largest two-carbon fragment ion is  $C_2F^-$ , and in this respect it is similar to the spectrum of hexafluoroethane where  $C_2F^-$  is the largest two-carbon fragment observed. Also, the ratios  $CF_3^-/CF_2^-$  and  $CF_3^-/C_2F^$ are close to those observed with hexafluoroethane. The actual intensity of the O<sup>-</sup> ion is doubtful because of the background contribution to this ion. In the positiveion spectrum,  $CF_3^+$  is the most extensively formed species, other ions being formed include  $CF_3CO^+$  and a molecular ion of low intensity. We found no evidence for the formation of an ion such as  $CF_3CO^-$ .

### SULPHUR HEXAFLUORIDE, $SF_6$

Negative-ion formation in sulphur hexafluoride has been studied by several workers,<sup>7, 12, 13</sup> particularly at low electron energies where formation of the  $SF_{\overline{6}}$  ion by an electron capture process has been used to indicate the energy spread of the ionizing electrons and also as a calibrant for the electron-energy scale. From our data, although  $SF_{\overline{6}}$  and  $F^-$  are the most abundantly formed ions seven other ionic species, including  $SF^-$  and  $SF_{\overline{2}}$ , are observed. These latter two ions appear not to have been reported previously.

On the basis of their electronic structure it is to be expected that the ions  $SF_{\overline{3}}$  and  $SF_{\overline{5}}$  will be formed abundantly; however, it is surprising that the ion  $SF_{\overline{3}}$  is of such a low intensity. Also, the parent ion is formed much more extensively than the  $F^{-}$  ion, the only case in which the halogen ion is not the most abundant.

#### CONCLUSIONS

Although only a limited range of molecules has been examined, some general patterns of negative ion formation may be deduced. Our results suggest that, for the halogen-containing molecules examined, negative-ion formation is more extensive in chlorine-containing compounds than in those containing fluorine or iodine and that fragmentation tends to favour the formation of ions containing an odd number of halogen atoms and not to produce "mixed" ions such as CHX<sup>-</sup>. Another feature is the ability of all the halogenated molecules to form the ion  $X_2^-$  and comparison of the results for chloroform and fluoroform indicate that the ion is formed more readily when X is fluorine than when X is chlorine. Comparison of  $Cl_2^-$  formation with methylene dichloride and symmetrical-tetrachloroethane indicates that both molecules (which contain the unit-CHCl<sub>2</sub>) readily form this ion.

Production of negative ions is clearly influenced by the size, symmetry and bonding of the molecule being bombarded with electrons; in general, large, symmetrical molecules containing multiple linkages tending to undergo less fragmentation and consequently to form larger negative ions, sometimes including the molecular ion.

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