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Mass spectrometry of halogen-containing organic compounds

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ABSTRACT. The mechanisms involved in the formation of the mass spectra of halogen-containing compounds are correlated. All types of processes involving halogens are examined, the material being presented according to the type of fragmentation.

The bibliography includes 192 references.

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I. Introduction

Halogen-containing compounds (with the exception of purely synthetic laboratory chemicals) frequently form part of complex mixtures, so their identification and structural determination are mainly carried out by mass spectrometric methods, which are the most informative and particularly effective when combined with chromatographic separation methods. Hence there is an obvious need to elucidate the general mechanisms involved in the formation of the mass spectra of halogen-containing compounds. As a rule, this information is dispersed amongst a large number of articles in which, with the exception of a number of publications,[1–7] only a small proportion of the problems relating to the interpretation of the mass spectra of halogen-containing organic compounds are reviewed.

In this review, in contrast to the traditional approaches, all types of processes involving halogens rather than classes of halogen-containing compounds are reviewed.

By presenting the material according to the type of fragmentation the authors have been able to adopt a thermochemical approach to the interpretation of the mass spectra. This approach is used throughout the whole article both in examining simple bond cleavage and in analysing the peak intensities of the molecular ions, including ways of stabilising a molecular ion. The source of organic compounds in environmental materials, as has now been established, is mainly provided by human activity and to a much lesser extent by natural chlorine-, bromine-, and iodine-containing compounds of vegetable (including petroleum) and animal origin. Therefore we consider it necessary to consider the analytical aspects of the mass spectrometry of halogen-containing compounds in a separate section.

II. Electron-impact mass spectrometry

1. Positive ions

One of the pathways of the fragmentation of organic monohalogen-containing compounds RCH_2X from electron impact (EI) leads to ions of the type $\overset{+}{C}H_2-\ddot{X}\longleftrightarrow CH_2-\overset{+}{X}$, in the same way as other electron-donating groups (alkyl, OR, SR, NH_2, $CH=CH_2$, Ph, etc.). A comparison of the exothermicities Q of the isodesmic[4,8] reaction

$$CH_3^+ + CH_3X \rightarrow \overset{+}{C}H_2X + CH_4$$

gives the following series of stability of these ions compared to the CH_3^+ cation (kcal mol^{-1}): CH_3^+ (0), $\overset{+}{C}H_2F$ (25), $\overset{+}{C}H_2Cl$ (31), $\overset{+}{C}H_2Br$ (35), $\overset{+}{C}H_2I$ (35), $\overset{+}{C}H_2CH=CH_2$ (59), $\overset{+}{C}H_2OH$ (65), $\overset{+}{C}H_2SH$ (69), $\overset{+}{C}H_2NH_2$ (96).

This means that in terms of their donor properties halogens are inferior to other groups, and the stabilising ability of halogens increases in the series F < Cl < Br < I. Halogens can be eliminated as free radicals X$^\cdot$, and the exothermicity Q (kcal mol^{-1}) of the isodesmic reaction

$$\dot{C}H_3 + HX \rightarrow CH_4 + X^\cdot,$$

that reflects the relative thermodynamic stability of X$^\cdot$ decreases in the series $I^\cdot$ (33.5) > $Br^\cdot$ (17) > $Cl^\cdot$ (1.6) > $F^\cdot$ (−31.5).[4] Therefore abundant loss of X$^\cdot$ is to be expected only for $I^\cdot$ and $Br^\cdot$. Together with dehalogenation, dehydrohalogenation with elimination of HX is also typical of halogen-containing compounds.

Calculated[4] thermochemical properties of the simple bond cleavage processes and loss of HX for a C_2H_5X molecule are given in Table 1, and the peak intensities of the corresponding ions are given in Table 2.[9] The enthalpies of formation of molecules, ions, and radicals are taken from a monograph[4] while the ionisation potentials (IP) are taken from a reference book[10] (E_{cr} = AP − IP, the critical energy or energy of activation for dissociation of $[C_2H_5X]^+$ molecular ions (AP is the appearance potential of a fragment ion).

Contrary to expectation the critical energies for separation of X were similar for all halogens (0.78 − 1.22 eV). This occurs because, whereas during homolytic cleavage of a bond by the direct process

$$C_2H_5\text{—}X \longrightarrow C_2H_5^\cdot + X^\cdot$$

the strength of the bond with X decreases in the series F, Cl, Br, I because the stability of X$^\cdot$ increases in the same series, on electron impact it is the molecular ion that dissociates rather than the initial molecule. In the latter, (because of the increase in IP in the series RI→RBr→RCl→RF) the value of E_{cr} decreases in this series, although the absolute values of IP increase from I to F in complete

agreement with processes involving homolytic bond cleavage. The competing fragmentation processes for formation of $CH_3\overset{+}{C}HX$ and $\overset{+}{C}H_2X$ can only occur in organofluorine compounds (both processes have a similar (AP), whereas when X = Cl, Br, I its AP and E_{cr} are substantially higher than for processes involving separation of X. Therefore, in the mass spectra of aliphatic monohalogen derivatives intense peaks due to $\overset{+}{C}H_2F$ and $R\overset{+}{C}HF$ ions occur but there are only weak peaks due to the other $\overset{+}{C}H_2X$ and $R\overset{+}{C}HX$ ions. Simple bond cleavage processes involving a single halogen atom are restricted to those considered above, to which can only be added the loss of neutral [XC≡CH from halobenzenes; XCH=CHR; H(X)C=O; XC≡N] or charged ($\overset{+}{X}C=\ddot{O}$ in a number of disubstituted furans) ring fragments from carbocyclic and heterocyclic compounds. They may be extended to all classes of compounds.[1,4]

Table 1. Thermochemical properties (in eV) of fragmentation processes of ethyl halides

C_2H_5X ($C_2H_5^+ + \dot{X}$; $\overset{+}{C}H_2X + \dot{C}H_3$; $CH_3\overset{+}{C}HX + \dot{H}$; $C_2H_4^{\overset{+}{\cdot}} + HX$)

Compound (M)	IP (M)	IP	E_{cr}	AP	E_{cr}	AP	E_{cr}	AP	E_{cr}
		$C_2H_5^+$		$\overset{+}{C}H_2X$		$CH_3\overset{+}{C}HX$		$C_2H_4^{\overset{+}{\cdot}}$	
C_2H_5F	12.0	12.89	0.89	12.84	0.84	11.99	0	10.93	0
C_2H_5Cl	11.0	11.78	0.78	12.51	1.51	11.97	0.97	11.25	0.25
C_2H_5Br	10.3	11.17	0.87	12.40	2.10	11.95	1.65	11.32	1.02
C_2H_5I	9.34	10.56	1.22	12.31	2.97	12.24	2.90	11.42	1.22

Table 2. Peak intensities of characteristic ions in the mass spectra of C_2H_5X at 70 eV (as a percentage of total ion current).[9]

Compound	$M^{\overset{+}{\cdot}}$	$C_2H_5^+$	$CH_3\overset{+}{C}HX$	$\overset{+}{C}H_2X$	$C_2H_4^{\overset{+}{\cdot}}$
C_2H_5F	5.8	1.1	50.8	13.6	3.4
C_2H_5Cl	28.8	15.7	1.7	7.6	21.4
C_2H_5Br	49.6	15.6	0.75	2.5	8.9
C_2H_5I	54.0	19.2	0.32	1.0	1.4

In compounds containing other substituents in addition to halogens, the primary fragmentation processes (they constitute a determining factor in establishing the structure of the initial compound if it is not known) are controlled by these substituents (this relates in particular to fluorine- and chlorine-containing compounds). However, here also—at advanced stages of the fragmentation—the participation of halogens definitely manifests itself, primarily in the elimination of HX and by the presence of peaks of metastable ions corresponding to these processes.

Let us examine the behaviour on electron impact of polyhalogen-containing compounds in simple bond cleavage processes. In systems that have the perhalogen-containing groups CCl_3-, CBr_3-CBr_2-, $-CCl_2-$ (for perfluoroalkyl groups, see below), abundant loss of Cl or Br occurs because of the increase in IP of the molecule and the decrease in bond strength (polyiodine-containing compounds have hardly been studied at all).[4,11] Of perfluoroalkyl ions it is only CF_3^+ ions that are intense, as a rule. While the stability of alkyl cations increases in the series: $CH_3^+ < C_2H_5^+ < CH_3CH_2CH_2^+ < (CH_3)_2CH^+ < (CH_3)_3C^+$, for perfluoroalkyl cations the stability decreases in a similar series: $CF_3^+ > CF_3CF_2^+ > CF_3CF_2CF_2^+ > (CF_3)_2CF^+ > (CF_3)_3C^+$, which is due to the presence of powerful electron-withdrawing CF_3 groups on the cation site. This also follows from a comparison of the IP of the corresponding free radicals R_F (eV): $\dot{C}F_3$ (8.9); $C_2\dot{F}_5$ (9.1); $CF_3CF_2\dot{C}F_2$ (9.2); $(CF_3)_2\dot{C}F$ (9.5) and $(CF_3)_3\dot{C}$ (10.2).[12] Such high values of the IP have the result that in functional compounds such as $RCOCH_2COR_F$ when the $C-R_F$ bond is cleaved, the charge always remains on the residue not containing R_F, and the latter is released as a free radical. In perfluoroalkyl-containing compounds, in particular perfluoroalkanes, perfluoroalkylperfluorocycloalkanes, fluorinated esters, perfluoroalkyl-1,3-diketones, and others, a peak due to the CF_3^+ ion with mass 69 is observed. The other ion homologues as a rule do not give intense peaks. Nevertheless, peaks from 119^+ or 169^+ ions ($C_2F_5^+$ and $C_3F_7^+$ respectively) appear in the mass spectra of certain compounds. We can attribute this formation of R_F^+ at the advanced stages of fragmentation of $M^{\overset{+}{\cdot}}$ to a pair with very stable neutral molecules that compensate the instability of R_F^+:[12]

$$C_2F_5^+ \longleftarrow\!/\!- \underset{M^{\overset{+}{\cdot}}}{CF_3CF_2CF_2COOCH_3^{\overset{+}{\cdot}}} \longrightarrow \underset{[M-OCH_3]^+}{CF_3CF_2-CF_2-C\equiv\overset{+}{O}} \longrightarrow$$

$$\longrightarrow CF_3\overset{+}{C}F_2 + CF_2=C=O,$$

2.5% base. (70 eV)

$$C_3F_7-CF_2-CF_2-CF_2-CO-CH_2-\overset{+}{C}-\ddot{O} \longrightarrow$$

$$\uparrow\ [M-CF_2]^+$$

$$M^{\overset{+}{\cdot}} -\!/\!\longrightarrow C_3F_7^+$$

$$\longrightarrow C_3F_7^+ + C_2F_4 + CF_2=C=O + CH_2=C=O.$$

%Σ: 2.4 (70 eV): 3.5 (20 eV): 3.2 (12 eV).

The stability of the neutral residues in the absence of more favourable fragmentation pathways explains the appearance of intense peaks from ions with acceptor groups—$(CF_3)_2\overset{+}{C}Cl$ (100%) from $(CF_3)_2CClSO_2Cl$ and $(CF_3)_2\overset{+}{C}H$ (100%) from $(CF_3)_2CHSO_2OH/H_2O$.[13]

Simple bond cleavage processes have the most direct bearing on such an important characteristic of a compound and its mass spectrum as the intensity of the molecular ion peak. It is the value of the critical energy E_{cr} for the most favourable simple bond cleavage that governs the intensity of the $M^{\overset{+}{\cdot}}$ peak (see Table 2). The value of E_{cr} is determined by two quantities—the AP and IP. The absence of peaks due to $M^{\overset{+}{\cdot}}$ ions in the mass spectra of many polyfluorine-, polychlorine-, and polybromine-containing compounds is due primarily to high values of the IP, since halogen-containing groups that include powerful withdrawing halogen atoms (especially F and Cl) increase the IP and, as a result, reduce E_{cr}. If E_{cr} is equal to zero, i.e., the thermochemical threshold for formation of the fragment ion obtained by simple bond cleavage is the same or less than the IP of the molecule, any $M^{\overset{+}{\cdot}}$ immediately decomposes and is therefore not recorded. Examples of compounds, mainly fluorine-containing ones, which do not produce an $M^{\overset{+}{\cdot}}$ peak are

given in Table 3. It follows from Table 3 that identification of the molecule ion is possible from the primary fragment ion (by mass), usually $[M - F]^+$, but this method is not always reliable. It is advisable to change the method of ionisation, and to use chemical ionisation in particular (see below).

Table 3. Halogen-containing compounds not displaying a molecular ion peak.[4,9,11,13–28]

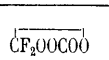
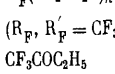
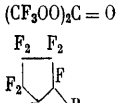
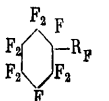
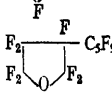
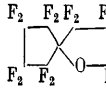
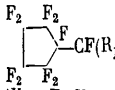
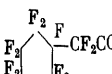
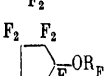
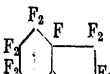
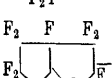
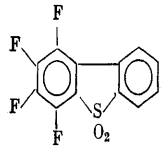
Compound	Ion with greatest *m/z*	Compound	Ion with greatest *m/z*
CF_4	$M-F^+$		$M-CO_2^+$
1, 3, 5, 7-$(CF_3)_4$-adamantane	$M-F^+$	$C(NF_2)_4$	$M-NF_2^+$
$R_F(CF_2CF_2O)_nR'_F$	$M-F^+$	$(CH_3)_2C(NF_2)_2$	$M-NF_2^+$
(R_F, $R'_F = CF_3$, C_2F_5)		$F_2CH_2CH_2CH_2F_2$	$M-NF_2^+$
$CF_3COC_2H_5$	$M-C_2H_5^+$	$F_2NC(F)N{=}N$	$M-F^+$
$F_2CHCOOC_2H_5$	$M-C_2H_5^+$	$F_2CN(F)NF$	$M-NF^+$
CF_3COOCH_3	$M-F^+$	$H-NCF_2CF_2O$	$C_2F_4^+$
	$M-F^+$	$F-NCF_2CF_2O$	$M-NO^+$
$RCOOCF(CF_3)_2$ ($R = F$, CF_3, C_2F_5)	$M-F^+$	$R_FR(N_F)COF$	$M-F^+$
$CH_3OCO(CF_2)_nCOCH_3$ ($n = 6-9$)	$M-F^+$	$CF_2CF_2N{=}N$	$M-N^+$
$FC(O)OC(O)F$	$CF_2{=}O^+$	$F_2NCF_2NCF(NF_2)NF$	$M-N_2F_4^+$
$(CF_3OO)_2C{=}O$	$CF_3OOC{\equiv}O^+$	$F_2NCF_2FC-OCH(CF_3)_2$	$M-F^+$
	$M-F^+$	NH	
		$F_2NC(F)CF(NF_2)NN{=}CFNF_2$	$M-F^+$
		$F_2CCF_2NFCF_2NF$	$M-CF^+$
	$M-F^+$	SF_6	$M-F^+$
		CF_3SF_3	$M-F^+$
		$(CF_3)_2CHSO_2R$ ($R = CH_3$, CF_3, $CH(CF_3)_2$)	$(M+H^-)^+$*
	$M-F^+$		$M-OCF_3^+$
	$M-F^+$	$CF_3COOCH_2CH(CH_3)_2$	$M-H^+$
		$CF_3COOC(CH_3)_3$	$M-CH_3^+$
	$M-F^+$	$CF_3COOSi(CH_3)_3$	$M-CH_3^+$
		$C_2F_5COOC(CH_3)_3$	$M-CH_3^+$
		$C_2F_5COOSi(CH_3)_3$	$M-CH_3^+$
	$M-F^+$	$CHF_2COOSi(CH_3)_3$	$M-CH_3^+$
		cyclo-$C_6F_{11}COOCH_3$	$M-HF-H^+$
		$SF_5N{=}CFC_2F_5$	$M-F-H^+$
	$M-F^+$	$(CF_3)_2C{=}NN{=}S(CF_3)_2$	$M-F^+$
		$FSO_2O(CF_2)_3OSO_2F$	$M-SO_3F^+$
		$CF_3(CF_2)_6OSO_2F$	$M-F^+$
		$Cl(CF_2)_3OSO_2F$	$M-Cl^+$
	$M-OCF_3^+$	$(CF_3)_2NCF_2Cl$	$M-F^+$
		$CF_3N(CHCl_2)_2$	$M-Cl^+$

Table 3 (contd.).

Compound	Ion with greatest *m/z*	Compound	Ion with greatest *m/z*
$(CF_3)_2NCHCl_2$	$M-Cl^+$	$CF_3CON{=}S(F)CF_3$	$M-F_2^+$
CCl_3CCl_3	$M-Cl^+$	$C_2F_5N{=}S(F_3)N(CH_3)_2$	$M-F_2^+$
$CCl_3C{\equiv}N$	$M-Cl^+$	$C_2F_5N{=}S(Cl)CF_3$	$M-Cl^+$
$C_2H_5CF_2CF_2OCF_2CF_2SO_2F$	$M-F-HF^+$	$(CF_3)_2CFN{=}S(Cl)CF_3$	$M-F^+$
$R_FSF_2R_F$	$M-F^+$	$Cl(CH_2)_5Cl$	$M-Cl^+$
$CF_3SO_2CF_3$	$M-CF_3^+$	$CFCl_3$	$M-Cl^+$
$R_FSO_2OSO_2R_F$ ($R_F = CF_3$, C_2F_5)	$R_FSO_3^+$	C_2F_5Cl	$M-F^+$
		$ClC(F){=}N{-}$	$M-N^+$
	$M-O^+$	$CCl_3COOC_2H_5$	$M-H^+$
		$ClCH_2COOSi(CH_3)_3$	$M-CH_3^+$
		RSO_2Cl (R-alkyl, CH_3SO_2)	$M-Cl^+$
		$SF_2C(F)ClSF_2CFX$ (X=F, Cl)	$M-F^+$
		3-Br-Ad-$COOCH_3$	$M-Br^+$
$(CF_3)_2CClSO_2Cl$	$M-O^+$	$(CH_3)_3CBr$	$M-Me^+$
$CF_3SN{=}C(Cl)SSCF_3$	CF_3SS^+	CF_3NCF_2NBr	$M-Br^+$
$R_FS(O)N(CH_3)SCCl_3$	$M-Cl^+$	$CF_2{=}NCF_2CF_2Br$	$M-CF_2N^+$
$CF_3S(F){=}NCF(CF_3)_2$	$M-F_2^+$	$F_5SN{=}CBr$	$M-F^+$
$(CF_3)_2CFS(F){=}NCOCF_3$	$M-CF_3^+$	$TeF_5N{=}CBr_2$	$M-Br^+$
$CF_3S(F){=}NCOCF_3$	$M-F_2^+$	$Ph_2CBrCOCH_2Br$	$M-Br^+$
SF_5CHRSO_2F ($R = H$, $COOCH_2CF_3$)	$M-F^+$	$(CF_3)_2CFO(CF_2)_4Br$	$M-F^+$

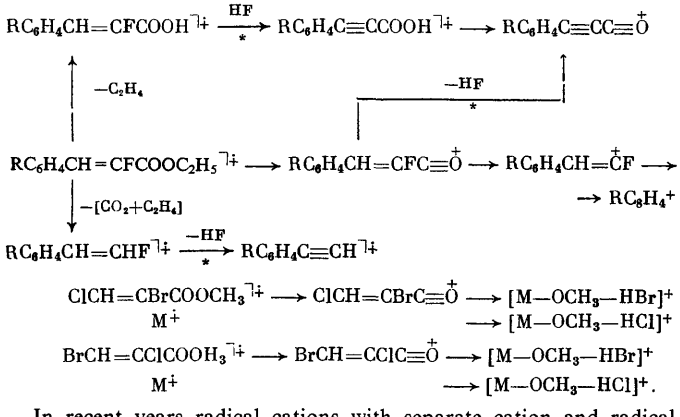
*In the EI mass spectrum.

Another way of obtaining an M^+ peak is chemical modification. The introduction of a group that has a substantially lower IP than an unmodified molecule gives rise to a new fragmentation pathway with E_{cr} not equal to zero, which makes it possible to generate an M^+ peak. This method can only comparatively rarely be applied to halogen derivatives, but nevertheless such examples do exist. In the electrochemical fluorination of acid chlorides, acid fluorides are obtained with a fluorinated chain (more frequently an acid mixture is obtained). Since neither they, nor the methyl esters or trimethylsilyl esters to which it is usual to convert the reaction mixture of acid fluorides give M^+ peaks, it is advisable to react this mixture with phenols or naphthols:[4,11] aryl esters of fluorinated acids give M^+ peaks. For example, the M^+ peak in $C_2F_5COOCH_3$ can only just be detected (0.07% base at 12 eV), the M^+ peak in $C_2F_5COOSi(CH_3)_3$ does not appear, whereas the M^+ peak in $C_2F_5COOC_6H_5$ amounts to 25 and 100% at 70 and 20 eV respectively.[11]

An iodine atom can serve as a group that reduces the IP of a molecule and stabilises M^+, while in compounds with acceptor groups even a bromine atom can be used. Thus, the M^+ peak is absent from the mass spectrum of $RCF_2OCF_2CF_2SO_2F$ ($R = C_2H_5$) and appears (0.4%) when $R = (CH_2)_4I$.[23] In $CH_2{=}CHCF_2R$ compounds, where $R = -CF_2CH{=}CH_2$, $-CF_2CH_2CH_2C_2F_5$, and $-CF_2CHICH_2C_2F_5$, the intensity of the M^+ peak is 0, 2.9, and 33% respectively.[29]

Hydrogen rearrangements for halogen-containing groups are quite similar and they actually comprise a single type of process — loss of

HX. The data in Table 1 (see above) clearly show that loss of HF is extremely favourable; E_{cr} for this process in C_2H_5F is equal to zero, but the actual thermochemical threshold for formation of $[M-HF]^+$ is even lower (by 1.1 eV) than the IP of the molecule. This process is always accompanied by the appearance of a peak of the corresponding metastable ion, which makes it possible (when the M^+ peak is absent) to reach the mass number of the molecular ion. In fluorine- and chlorine-containing (to a lesser extent bromine-containing) compounds loss of HX definitely occurs also at the advanced stages of fragmentation, even if the halogen atom is situated in a "strong" position (on the aromatic ring or on a multiple bond). For example:[30,31]



In recent years radical cations with separate cation and radical sites, so-called "distonic" ions[4] such as $CH_3\overset{+}{X}\dot{C}H_2$, $CH_3\overset{+}{X}\dot{C}HX$ (X = Cl, Br),[32] $CH_3\dot{C}H\overset{+}{X}H$ (X = Cl, Br),[33] $\dot{C}H_2\overset{+}{X}H$ (X = F, Cl),[34] have been detected and carefully studied (including a determination of the mechanisms of their formation and thermochemical properties). The appearance of I^+ (together with CH_3^+) in the mass spectrum of CH_3I may also, in our opinion, be due to the involvement of the $\dot{C}H_2\overset{+}{I}H$ ion in the process, without having to resort to assumptions about separate states of M^+, as Weber et al. have done.[35] A fluorine shift with formation of the unusual ion $HF\overset{+}{C}HFCl$ was observed by Seibl.[36]

By neutralisation and reionisation (repeated ionisation) of such ions it was possible to prove the existence of the uncharged species

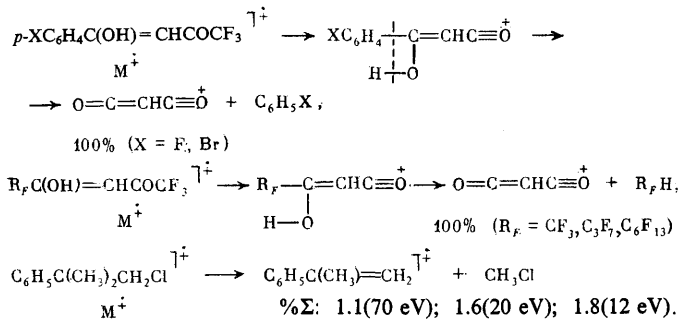
$$CH_3\dot{C}H-Cl-H,\ \dot{C}H_2CH_2ClH,\ \dot{C}H_2-CH_2-Br-H$$

and

$$CH_3CH-Br-H$$

in the mass spectrometer.[37] An attempt to identify neutral CH_2XH (X = F, Cl) was not successful.[34]

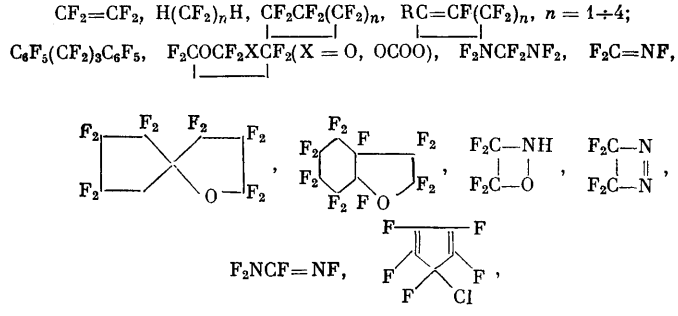
Apart from loss of HX, elimination of RH, where R are halogen-containing groups, occurs in certain cases:[12,3]



On the whole the role of hydrogen rearrangements in the fragmentation of halogen-containing compounds, with the exception of HX loss, is minor.

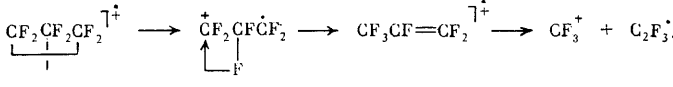
2. Skeletal rearrangements

Skeletal rearrangements occur widely in a number of halogen-containing compounds when subjected to electron impact. We shall only examine those rearrangements in which halogens and halogen-containing groups are directly involved. A knowledge of them is necessary for an accurate determination of the structure of a compound if it is unknown. Thus, in the mass spectra of many compounds an intense peak from the CF_3^+ ion occurs when this fragment is not present in the initial molecule.[1,4,9,13–15,18,39,40]

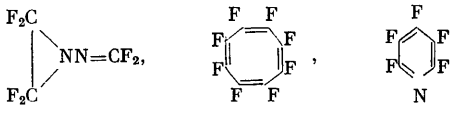


$(F_2N)_3CNCO$, $SF_5NHCOCF_2CF_2COOH$, $CF_2=NCF_2CF_2Br$.

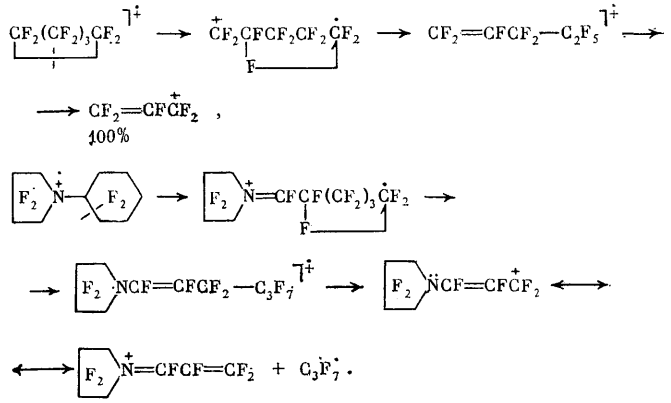
The CF_3^+ ion is formed in cyclic compounds after ring opening (while in aliphatic compounds it is formed in a fragment ion) by migration of an F atom (or atoms) to a cation or radical site. For example:



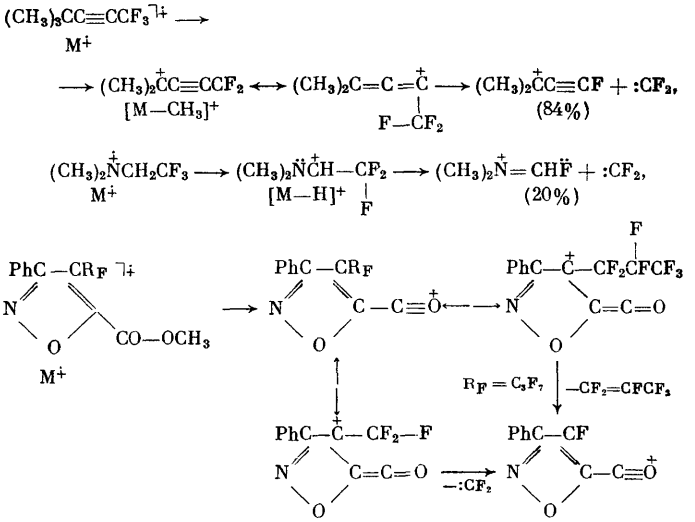
The $M-CF^{\overset{+}{\cdot}}$ ion is obtained in a similar manner in the following compounds:[9,14]



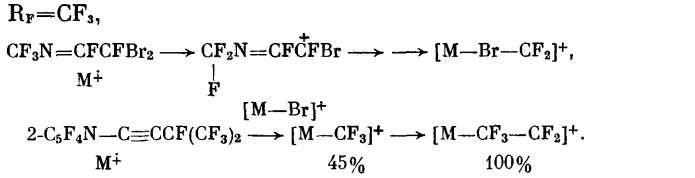
The perfluoroallyl cation is formed by the same route in cyclic compounds:[9,41]



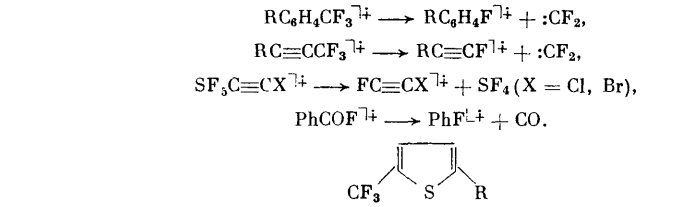
A fluorine atom can migrate to a C atom on which there are no other fluorine atoms:[12,14,18,42,43]



$R_F = CF_3$,



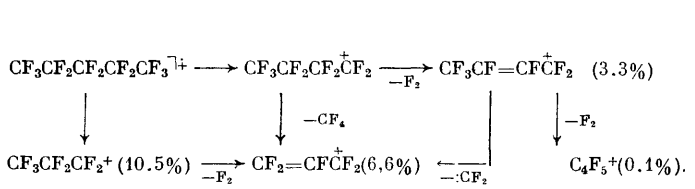
A fluorine atom can migrate to a π-system in a radical cation, particularly in the molecular ion:[9,44,45]



$[M-CF_2]^+$: 50% (R = H); 43% (CF_3); 32% (C≡CH).

However, this process does not occur with all R groups. For example, in $RC_6H_4CF_3$ (R = $COOCH_3$), OCH_3 rather than CF_2 is eliminated.[46] In $RC{\equiv}CCF_3$ migration of F occurs when R = $C(CH_3)_3$, but not when R = $Si(CH_3)_3$ or $Ge(CH_3)_3$.[42] It is true that elimination of CF_2 takes place in the fragment ions $M-OCH_3^+$ and $M-CH_3^+$ respectively.[42,46]

In perfluorcarbons, since R_F^+ ions are unstable (apart from CF_3^+), stable allylic types of ions are formed. For the latter to be obtained, a skeletal rearrangement occurs in the system with formation of F_2, CF_4, etc.:[9]



The elimination of other F-containing neutral molecules should be noted:[12,14,18,20,46]

The driving force of all these processes is not only the formation of stable F-containing neutral molecules or difluorocarbene (with low enthalpies of formation) but also the conversion through rearrangment of powerful acceptor substituents (CF_3, R_F, CF_3CO, $-CF_2-$) (destabilising a positively charged system) to donor groups, when the F atom (or atoms) either on a cation site or on a π-system is conjugated with that site. This is shown particularly clearly in aromatic systems with several substituents, when as a result of a very complex rearrangement of the fragment ion (involving ring expansion), F-substituted analogues of the tropylium ion $C_7H_7^+$ are formed at the last stage[12,46] (Table 4). The abundant loss of F from the CF_3 group in a heterocyclic aromatic system most likely also occurs with ring expansion as in its CH_3 analogue.[47] Thus, it is difficult to explain the high intensity of the peak from the $M-CF_3^+$ ion or possibly $M-F-CF_2^+$ ion (87%) in the fragmentation of 2,5-di(trifluoromethyl)thiophene.[45] We can give an example of a complex skeletal rearrangement with a rare case of the migration of CF_3 to a radical site:[39,48]

We can give examples of complex skeletal rearrangements involving F atoms or fluorinated groups with a mechanism that is unclear. A knowledge of these together with the rearrangements examined above is useful for an interpretation of the mass spectrum of both a known and an unknown structure in order to rule out possible suspicions of impurities being present. This doubt always arises if it is not possible to explain the appearance of a given unusual ion:[1,9,11,14,49]

The formation of peaks from $M-COX^+$ ions as well as $M-2COX^+$ (dioxins) and $M-COX-X_2^+$ (furans), where X = Cl, Br, in the mass spectra of polychloropolybromodibenzo-dioxins and

Table 4. Peak intensities of ions with the postulated structure of substituted tropylium ions at 70, 20, and 12 eV (as % Σ_{29}).

Compound	Neutral species	Ion	70 eV	20 eV	12 eV
p-$CF_3C_6H_4COOCH_3$	OCH_3+CO	$C_7H_4F_3^+$	19	8,2	0.31
	COOH	$C_8H_6F_3^+$	0.23	0.51	1.2
m-$CF_3C_6H_4COOCH_3$	OCH_3+CO	$C_7H_4F_3^+$	20	13	12
	F	$CH_3OOC-C_7H_4F_2^+$	1.6	1,0	–
p-$C_2F_5C_6H_4COOCH_3$	OCH_3+CO	$C_8H_4F_5^+$	4.6	5,2	–
	OCH_3+CO+CF_2	$C_7H_4F_3^+$	17	4.9	0,55
	CF_3	$CH_3OOC-C_7H_4F_2^+$	2.9	2,6	1,1
p-$C_3F_7C_6H_4COOCH_3$	OCH_3+CO	$C_9H_4F_7^+$	3.8	2.2	4.9
	C_2F_5	$CH_3OOC-C_7H_4F_2^+$	11	24	15
	OCH_3+CO+C_2F_4	$C_7H_4F_3^+$	11	1,5	0.49
	OCH_3+CO+CF_2	$C_8H_4F_5^+$	2.4	0.78	–
p-$(CF_3)_3CC_6H_4COOH$	CF_3+C_2F_4	$HOOC-C_7H_4F_2^+$	2,0	0,53	–
	COOH+CF_4	CF_2=$CF-C_7H_4F_2^+$	6,3	5,3	0.46
	CF_3+CF_2	$HOOC-C_8H_4F_4^+$	2,0	0,53	–
m-$CF_3CH_2C_6H_4Br$	Br	$C_8H_6F_3^+$	2,4	2,0	2,1
	Br+CF_2	$C_7H_6F^+$	5,3	2,4	–
m-$CF_3CH_2C_6H_4COOH$	CO+OH	$C_8H_6F_3^+$	2,1	0,39	–
	CO+OH+CF_2	$C_7H_6F^+$	7,0	–	–
p-$(CF_3)_3CCH_2C_6H_4COOCH_3$	OCH_3+C_4F_8+CO	$C_7H_6F^+$	16	13	0.10

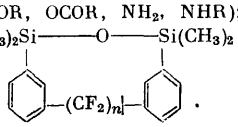
-furans[50] must be accompanied by complex skeletal rearrangements. The unusual ions $M-C_2H_5^{+}$ occur during fragmentation of $I(CH_2)_4CF_2CF_2OCF_2CF_2SO_2F$[23] and $TeBr_2^{+}$ is formed from F_5TeN = CBr_2.[21] We can attribute the high intensities of the $M-CF_3^{+}$ and $M-I^{+}$ peaks (100% at 12 eV) in the mass spectra of $(CH_3)_3CC{\equiv}CCF_3$ and $(CH_3)_3CC{\equiv}CI$ [42] respectively to isomerisation of their molecular ions to the isomeric cyclopropenyl radical cations,[51] since simple bond cleavage to form ethynyl cations is evidently unfavourable. The loss of CH_3Cl in the fragmentation of the molecular ions of *o*-$CH_3OC_6Cl_4OC_6Cl_5$ [52] and the elimination of Cl_2 in the fragmentation of $(C_6Cl_5)_2$ [53] and $C_{10}Cl_8$ [54] have been recorded.

The migration of F in organoelemental and organometallic compounds is particularly marked. The driving force of these processes is the formation of an element–fluorine or metal–fluorine bond, since radical cations, fragment cations, radicals, and neutral molecules that are isomeric with the initial molecular ions and which contain F on the element or metal have extremely low enthalpies of formation. Thus, while replacement of CH_3 by F in neopentane, i.e., $(CH_3)_4C{\rightarrow}(CH_3)_3CF$, reduces the enthalpy of formation of the molecule by only 8 kcal mol^{-1}, a similar replacement in the Si analogue, i.e., $(CH_3)_4Si{\rightarrow}(CH_3)_3SiF$, leads to a reduction of 56 (!) kcal mol^{-1}. A similar replacement of CH_3 by other halogens, i.e., $(CH_3)_4Si{\rightarrow}(CH_3)_3SiX$ reduces the enthalpy of formation by 42 (Cl), 40 (Br) and 35 (I) kcal mol^{-1} respectively.[4,12] Several conclusions can be drawn from these observations: 1) the driving force of rearrangement is formation of a much more stable shell of the ion (radical, neutral molecule) rather than a better charge stabilisation on the element atom compared to a C atom; 2) migration of a halogen to an element (metal) will occur in both a radical cation (primarily in the molecular ion) and a cation; 3) the migrating ability of the F atom is higher than that of the other halogens.

It is interesting to note that the size of the transition state for migration of halogens in both a cation and the radical part of a radical cation has no fundamental significance. Thus, on the one hand, a halogen atom "finds" an element atom at any distance between them. For example, the $(CH_3)_2SiX^{+}$ ion (X = F, Cl, Br, I) in $X-(CH_2)_nOSi(CH_3)_3$ is formed when n = 2–11, although with different intensities for different X at different values of n.[55] The $(CH_3)_2SiX^{+}$ ion (*m*/*z* 77) is formed in the fragmentation of compounds of virtually any structure:[1,11,14,42,44,56]

$(CH_3)_3SiCF_2CF_2CHF_2$; $(CH_3)_3SiC{\equiv}CCF_3$; $R_FCOOSi(CH_3)_3$, (R_F=CF_3, C_2F_5); $F(CH_2)_nSi(CH_3)_3$; $(CH_3)_3SiC{\equiv}CSF_5$;

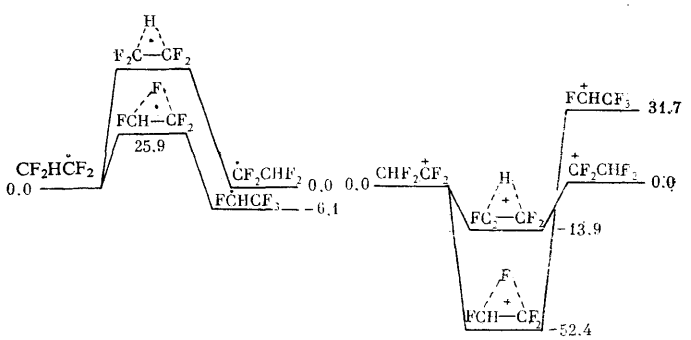
m-$(CH_3)_2Si(H)C_6H_4(CF_2)_nC_6H_4Si(H)(CH_3)_2$; $C_6F_5Si(CH_3)_2X$, (X = CH_3, OR, OCOR, NH_2, NHR); $(CH_3)_3SiN{=}C{=}NCOCF_3$;



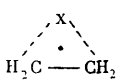
Peaks from $FSi^{+}(CH_3)OCH_3$ ions occur in the mass spectrum of $C_6F_5Si(OCH_3)(CH_3)_2$ [57] while peaks from $[M-SiF_3]^{+}$ and SiF_3^{+} ions are present in the mass spectrum of $(C_6F_5)_3SiH$.[58]

On the other hand, migration of F via a three-membered transition state (1,2-shift) is more favourable than the analogous H

shift, as follows from quantum-chemical calculations[59] for carbon analogues (enthalpy of formation in kcal mol^{-1}):



The evidently favourable nature of a three-membered transition state for an F shift in a cation should be noted, although in our view the values quoted are too optimistic (especially −52.4 kcal mol^{-1}). According to other data[60] the cyclic isomer



is more stable for X = Cl, Br, I and slightly less stable for X = F than its open isomer $XCH_2\dot{C}H_2$.

In the mass spectra of compounds containing both Si and F atoms, peaks from other types of rearranged ions also occur:[1,11,14,42,61]

$CH_3C{=}CH$, $(CF_3C{\equiv}C)_4Si$, $C_6F_5Si(OCH_3)(CH_3)_2$, $(CH_3)_3EC{\equiv}CCF_3$,
$F_2Si{-}SiF_2$ $E = Si, Ge$
$\overset{+}{S}iF_3$ $[M{-}SiF_3]^+$ $F\overset{+}{S}i(O)$ $(CH_3)_2\overset{+}{E}F$; $CH_3\overset{+}{E}F_2$
$(CH_3)_3SiN{=}C{=}NCOCF_3$, $(CF_3)_2NSi(CH_3)_3$, $ArSiF_2Ar'$,
$F\overset{+}{S}i{=}O$ $F_2\overset{+}{S}i$ $[M{-}SiF_2]^+$
$RCH(NHCOCF_3)COOSi(CH_3)_3$, $F_2CHCOOSi(CH_3)_3$
$[M{-}CO_2{-}(CH_3)_3SiF]^+$ $[M{-}CH_3{-}CO]^+$, $(CH_3)_2\overset{+}{S}iF$

Numerous examples of the migration of F (including repeated migration) to atoms of elements and metals containing fluorine groups or ligands are given in two monographs.[1,62] As there has been no slackening of interest in research into these compounds, new studies on their mass spectra continue to appear, as for example those of the chelates of fluorinated diketones ZrR_4 (R = R′$COCH_2$COR″, where R′ = Ar, CH_3; R″ = CHF_2, CF_3, C_2F_5, C_3F_7),[63] in which are observed peaks from ions obtained by an F shift to the metal. The migration of other halogen atoms to elements and metals also occurs on electron impact[1,62] (see also above for the Si atom). In addition to the processes common to F-containing compounds, the migration of CH_2Br can occur for Br-containing compounds (because of the lower electronegativity of Br).[12] We should mention those studies in which migration of chlorine to a Si atom was recorded: trimethylsilyl esters of chlorine-containing acids;[1,10] trimethyl- and t-butyldimethyl-silyl ethers of chlorine-containing alcohols;[61] and the loss of $SiCl_2$ in $ArSiCl_2Ar'$ compounds.[61]

III. Negative-ion mass spectrometry

The fragmentation mechanisms of organic compounds in dissociative electron capture (DEC) with the formation of negative ions has been studied in detail in three monographs,[4,66,67] in which considerable attention is given to halogen-containing compounds. An atlas of mass spectra has been published, but unfortunately it is in a deposited version.[68] We shall therefore only examine the general fragmentation mechanisms of anions and radical anions. The large values of the electron affinity (EA) of halogen atoms—3.448 (F), 3.614 (Cl), 3.37 (Br), and 3.059 (I)—give rise to the appearance of intense peaks from X^{-1} ions, and the formation of other stable anions is suppressed:[11]

$$CH_3O^- \leftarrow XCH_2COOCH_3^{\ddagger} \rightarrow X^-$$

X=Cl	0.38% Σ (6.6 eV)†	M–none	Cl^- 99.2% Σ (0.3 eV)
X=Br	3.50% Σ (5.5 eV)	XCH_2COO^-	Br^- 92.4% Σ (0 eV)
X=I	0.0004% (4.0 eV)	Cl 0.18% Σ (1.6 eV)	I^- 84.7% Σ (0.2 eV)
		Br 0.04% Σ (1.5 eV)	
		I 0%	

Of the other halogen-containing ions that give intense peaks, we should mention $(CF_3)_3C^-$, $(CF_3)_2\bar{C}R$, $C_6F_5^-$, CF_3O^-, CF_3S^- [46,67,69] (EA = 4.1, 3.3, and 2.9 eV for $(CF_3)_3\dot{C}$, $(CF_3)_2\dot{C}H$, and $(CF_3)_2\dot{C}F$ respectively):[4,67]

$(CF_3)_2\bar{C}CH_2C_6H_4COOCH_3 \leftarrow$ *m*-$(CF_3)_3CCH_2C_6H_4COCCH_3 \rightarrow (CF_3)_3C^-$
5.7% Σ (3.2 эВ) M^- 90% Σ (0.5 eV)
3.1% Σ (3.1 eV)

$F^-(0.3\%) \leftarrow CF_3SCF_3^{\ddagger} \rightarrow CF_3S^-$ (100%).

However, the high electronegativity values of the radicals and hence the high thermodynamic stability of their corresponding anions do not always determine the fragmentation pathway. Thus, even though the EA for F is similar to the EA of other halogens, the intensities of the peaks due to F^- ions are small in comparison with those of other halogens. For example, the contribution of the F^- ion to the spectrum of XCH_2COOCH_3 is 15% Σ compared to 99.92, and 85% Σ for Cl^-, Br^-, and I— respectively. Similarly, despite the presence of many F atoms and the many ways of forming F^- in C_2F_5CN and n-C_3F_7CN, the intensity of its peaks at several resonance states is less than 0.5%, whereas the main ion is $^-C{\equiv}N$,[70] although the EA values for F˙ and ˙C≡N are similar (3.45 and 3.82 eV respectively).[4] Another phenomenon that is currently still hard to explain is that the intensities of the peaks due to $XC_6H_4COO^-$ ions are unusually small or these ions are not formed at all,[46] despite the high EA (3.4 eV) [4] for C_6H_5COO˙ and the evidently even higher EA for XC_6H_4COO˙ with electron-withdrawing groups X:

n-$XC_6H_4COOCH_3^{\ddagger}$ —/→ $XC_6H_4COO^-$ (X = CCl_3, FCH_2, $(CF_3)_3CCH_2$, C_2F_5, $(CF_3)_2CF$)
M^- → $XC_6H_4COO^-$
0.22% (CF_3); 0.007% $(CF_3)_3C$.

It is true that in the aliphatic series the intensities of the peaks due to haloalkanecarboxylate ions are high[6] (EA = 4.5 eV for CF_3COO˙):[4]

$CF_3COOR^{\ddagger} \rightarrow CF_3COO^-$,
M^- 100%
R = CH_3, $C(CH_3)_3$, iso-C_4H_9, $CH_2CH{=}CH_2$,
$C_2F_5COOR^{\ddagger} \rightarrow C_2F_5COO^-$, *n*-$C_3F_7COOCO_3^{\ddagger} \rightarrow C_3F_7COO^-$.
M^- 100% $(C(CH_3)_3)$; 30% (CH_3) M^- 28%

† Here and subsequently the position of the resonance maximum (i.e., the maximum on the ionisation efficiency curve) is given in brackets in eV; the intensity is recorded at this maximum.

We should note that halogen atoms directly situated on an anion site stabilise the latter by the inductive effect and destabilise it by a conjugation mechanism with the result that the intensities of the $C_2F_5^-$, CF_3^-, F_2CH^-, FCH_2^- are low—the EA of their corresponding radicals are 1.92, 1.74, 0.7, and 0.11 eV.[4] Because the polarisability of other halogens is greater than for F, the EA in $\dot{C}H_2X$, $\dot{C}HX_2$, and $\dot{C}X_3$ (X = Cl, Br, I) increases and the peak intensities of their corresponding ions are greater.[1,10] Amongst simple bond cleavage processes we should mention the loss of the ring fragment $CF_2=O$ in the fragmentation of perfluoro-2-propyltetrahydropyran and perfluoro-2-butyltetrahydrofuran.[71]

In contrast to the previously expressed view[66] that rearrangement processes are not very typical of DEC mass spectra, in recent years in studies on negative ions formed from esters of haloalkanecarboxylic and haloalkylbenzoic acids[4,11,12,46] it has been shown that various rearrangement processes frequently predominate in the fragmentation of anions. In these studies there are numerous examples of rearrangements that are both similar to those of positive ions and characteristic only of anions and radical anions. For example, in the mass spectra of $RCOOCH_3$ compounds, instead a peak due to the $RCOO^-$ ion (which is of low or medium intensity) an intense peak due to the $M-HF^{\dagger\cdot-}$ ion appears: 100% [R = FCH_2, C_2F_5, n-C_4F_9, p-$FCH_2C_6H_4$, p-$(CF_3)_2CFC_6H_4$]. The analogous ion $M-RF^{\dagger\cdot-}$ occurs in the fragmentation of CF_3COOR': 3.3% (R' = CH_3), 3.2% [R' = $CH_2CH(CH_3)_2$], 12% [R' = $C(CH_3)_3$], 16% (R' = $CH_2C\equiv CH$), 44% (R' = C_6H_5), 100% [R' = $Si(CH_3)_3$]. In these studies it was established for the first time that there are many hidden rearrangements. For example, in $R_FC(R_F')FCOOCH_3$ compounds there is a peak from the $M-OCH_3^{\dagger-}$ ion, which is attributed to the structure of the stable rearranged ion $R_F\bar{C}(R_F')-CFO$ rather than its unstable isomer $R_FC(R_F')(F)-\bar{C}=\ddot{O}$.[4,11,12]

We should mention the formation of the rearranged ions CF_3^- and $F_2^{\dagger\cdot-}$ in the fragmentation of perfluorocyclobutane,[72] CF_3O^- from perfluoro-2-propyltetrahydropyran and perfluoro-2-butyltetrahydrofuran,[71] and $Cl_2^{\dagger\cdot-}$ from cyclic perchlorocarbons.[73]

Thus, in studying new halogen-containing compounds, the appearance of peaks from rearranged ions involving halogens in their DEC mass spectra is to be expected.

A further important conclusion follows from the studies considered here.[4,11,46] While for the majority of organic compounds containing functional groups or multiple C—C bonds (including aromatic systems) but not containing halogens the presence of a fairly intense peak from the $M-H^{\dagger-}$ ion is typical, which makes it possible to determine the molecular ion of the compound and its empirical formula (from the isotope peaks), there is quite a different pattern for halogen-containing compounds. It is a common occurrence for the $M^{\dagger\cdot-}$ peak to be absent in $RCOOCH_3$ compounds (where R = haloalkyl). However, an unusual feature is the absence of the $M-H^{\dagger-}$ peak (particularly strange if a mobile H is present) when R = FCH_2, ICH_2, $CHCl_2$, CCl_3, C_2F_5, cyclo-C_6F_{11}, CF_3CH_2, CF_3CHF, $(CF_3)_3CCH_2$, $(CF_3)_2CF$, n-C_3F_7, n-C_4F_9, $(CF_3)_3C$, while at the same time it occurs in compounds that are not very different from the above—when R = $ClCH_2$, $BrCH_2$, $(CF_3)_2CH$. In aromatic compounds with acceptor groups, molecular ion peaks usually occur,[4,66] but halogen-containing substituents introduce a modification here also. Thus, the intensity of the $M^{\dagger\cdot-}$ peak in p-$CF_3CF_2CF_2C_6H_4COOCH_3$ is 100% while that in its isomer p-$(CF_3)_2CFC_6H_4COOCH_3$ is 0.03% (i.e., the latter simply cannot be detected, being indistinguishable from a background peak).[46] This example indicates the highly specific nature of DEC mass spectra, which is certainly difficult to predict. There are no $M^{\dagger\cdot-}$ and $M-H^{\dagger-}$ peaks in the mass spectra of $RC_6H_4COOCH_3$ (R = p- and m-$(CF_3)_3CCH_2$), the $M^{\dagger\cdot-}$ peak is weak (0.7%) in the mass spectrum of p-$(CF_3)_3CC_6H_4COOCH_3$ and the $M-H^{\dagger-}$ peak is absent.[46] These facts should be borne in mind when the DEC mass spectra of unknown compounds are analysed.

IV. Chemical ionisation and other ionisation mass spectrometry

In continuing the previous section, let us start our examination of chemical ionisation (CI) spectra with negative ions. Under CI conditions aromatic compounds give intense peaks from $M^{\dagger\cdot-}$ molecular ions when there is a low degree of fragmentation, while peaks due to $M-H^{\dagger-}$ ions occur for compounds that do not have a system of conjugated bonds. Methane is often used as a working gas for CI, but in certain cases mixtures with halogen-containing compounds such as CH_3OH + $CHCl_3$,[74] CH_4 + CH_2Cl_2,[75] NF_3, CF_2Cl_2, CF_3Br [76] are used. Under these ionisation conditions studies have been made of the mass spectra and optimum detection conditions for a series of pentafluorophenyl compounds C_6F_5R (R = CH_3, F, OH, OCH_3, NH_2, SH, $OCOCH_3$, CHO, NO_2, CN),[77] pentafluorobenzoyl derivatives of amino acids,[78] chloro- and fluoroethylenes,[79,80] pentafluoropropionates of hydroxylamine derivatives,[81] trifluoroacetyl derivatives of polyhydric alcohols,[82] chloroglucuronides,[83] halogen-containing derivatives of dipeptides and their metabolites,[84] and α,β-difluorocinnamic acid derivatives.[85] Chemical ionisation with negative ions achieves high selectivity (for isomers) and very high sensitivity for polyhalogen-containing compounds. This is used, for example, for quantitative determinations (after GLC separation) of polychloropolybromodibenzo-dioxins and -furans from their $M^{\dagger\cdot-}$ and Br^- ions.[48]

Positive-ion chemical ionisation mass spectra are used to establish the molecular formula of a compound being analysed that does not give an $M^{\dagger+}$ peak in its EI mass spectrum. The $M + H^{\dagger+}$ ion, which is formed in compounds containing groups to which the proton of a π-system can be added (aromatic compounds, alkenes, alkynes), carbonyl-containing groups (ketones, aldehydes, acids and their derivatives), groups with coordinate bonds

$(NO_2, -C\equiv\overset{+}{N}\rightarrow\bar{O}, -S(O)-, -SO_2-, SO_2OR, N_3, -P(O)_2OR)$.

is used for this purpose. Thus, while the $M^{\dagger\cdot+}$ peak is absent during EI, an $M + H^{\dagger+}$ peak occurs in CI of the compounds $CF_3(CF_2)_2CF(CF_3)COOC_2H_5$,[86] $SF_5N(Cl)C_2F_5$ and $SF_5N=CFC_2F_5$,[27] $FO_2S(CF_2)_2O(CF_2)_2R$,[87] $F_5EN=CBr_2$ (E = S, Te),[21] and $CF_3O(CF_2)_2O(CF_2)_2SO_2F$.[88] The mass spectra of RSF_5 (R are fluorinated groups with an $-SO_2$ residue) obtained under CI conditions have been studied by Terjeson et al.[19] In the CI of the compound $C_2H_5(CF_2)_2O(CF_2)_2SO_2F$ the $[M + H]^+$ ion does not appear but the $M-F^{\dagger+}$ ion is recorded instead.[23] In the fragmentation of $(CF_3)_3COH$ and $C_4F_9\overset{\frown}{CF(CF_2)_3O}$, $M + F^{\dagger+}$ ions are recorded together with the formation of $M + H^{\dagger+}$.[28]

The fact that a determination of structural elements under CI conditions (if the compound is unknown) is either not feasible or only insignificant information about the structure is contained in the CI spectra is a disadvantage. The reason for this is that the general fragmentation mechanisms of the so-called pseudomolecular ions, such as $M + H^{\dagger+}$ and even more so for $M + X^{\dagger+}$ (or $M + X^{\dagger-}$), have not yet been established and only empirical rules for the formation of positive ions of the individual yet numerous classes of

organic chemicals generated during CI have been put forward.[89] Moreover, in the protonation of compounds with several "sites" for the possible addition of a proton (or other ion), it is as though a mixture of products is obtained (with an unknown relative content of each of them), each of which fragments by its own pathways. Therefore a structural analysis of halogen-containing compounds can be conducted as before (despite the development of new ionisation methods and techniques) by means of the traditional electron impact. In this respect we should mention other methods and techniques. Thus, detection of negative ions is possible during thermal spray ionisation in liquid chromatograph–mass spectrometers used for the analysis of nonvolatile or thermally unstable compounds such as certain pesticides.[90–92] The formation of anions is controlled by the addition of halogen-containing compounds to the eluent. For example, introduction of only 0.1–1% chloroacetonitrile substantially increases the sensitivity of detection of phenols through the formation of $M + Cl^{-}$ ions.

For an analysis of compounds that are nonvolatile under normal EI conditions, such as organic hydrohalide salts[92] or certain pesticides,[94] desorption from the surface in a strong electric field can be used, including that combined with separation of mixtures on a liquid chromatograph.[95] A widely used method for the analysis of unstable compounds with low volatility is fast atom bombardment, which has been used, in particular, to study fluoroalkylsulphonates,[96] metabolites of 2-chloro-*N*-isopropylacetanilide,[97] iodoxamic acid and its dimethyl ester,[98] halides of certain Group IV elements,[99] and complexes with tetrabutylammonium fluoride.[100] The mass spectra of dihalomethanes[101] have been obtained under conditions of collision-activated positive ions, and the mass spectra of chlorodibenzodioxins[102] have been obtained with negative ions. In the latter study[102] both low-energy and high-energy processes during collision with oxygen have been investigated.

The mass spectra of halomethanes,[103] 1,1-difluoroethane,[104] 1,1-dichlorodifluoroethylene,[105] fluoroethylenes,[106] and 5-fluorouracil derivatives[107] have been obtained under photoionisation conditions and interpreted. Photoionisation mass spectrometry is mainly used to obtain thermochemical characteristics of the molecules (including halogen derivatives), ionisation potentials (IP), and, what is particularly valuable, the appearance potentials (AP) of the fragment ions. The enthalpies of formation of halogen-containing ions, radicals (carbenes), and neutral molecules are calculated from the AP. In recent years various reactions involving the transfer of particles, principally H^{+} as well as CH_3^{+}, Cl, and others, have been studied in the gas phase by high-pressure mass spectrometry[108] and ion cyclotron resonance.[109] Together with photoionisation mass spectrometry, these are valuable methods for a determination of the enthalpies of formation of ions, radicals, carbenes, and neutral molecules. Without a knowledge of the latter it is impossible to represent thermochemically the ionisation, isomerisation, and fragmentation processes of halogen-containing compounds on electron impact, under chemical ionisation conditions, etc. Without them a rational interpretation of the mass spectrum and representation of the decomposition pathways and mechanisms are made difficult. By having a knowledge of the thermochemical values, it is possible to predict the direction of isomerisation and fragmentation of molecular and fragment ions. We shall give a brief summary of the sources of information on the thermochemical properties of halogen-containing compounds and their fragments. Enthalpy of formation values of halogen-containing molecules appear in two reference books,[110,111] a review,[112] and two monographs.[4,113] IP values of molecules containing halogens are included in three reference books,[10,114,115] two reviews,[116,117] and individual publications.[12,118,119] Calculated values of the IP, EA, and enthalpies of formation of all the isomeric compounds ranging from tetra- to octa-chlorodibenzo-dioxins and -furans are given by Koester and Hites.[120] Experimental values of the energies of formation (IP_2) of the doubly charged ions of 9 halomethanes and 6 haloethanes that can be obtained not only in a mass spectrometer but also above the earth's ozone layer were derived in two studies.[121,122] In the monograph by Takhistov[4] information is given on the enthalpies of formation of halogen-containing ions and the electron affinity values for 24 halogen-containing radicals. In several studies data are given on the enthalpies of formation of halogen-containing ions—haloacyl ions,[123] 20 novel fluorine-containing ions,[124] trifluoroallyl ions,[125] trifluorobenzenium ions.[126] The proton affinity (PA) values for many halogen-containing molecules and the heats of formation of $M + H^{+}$ ions calculated from the PA values are given by Lias et al.[127] Correlations between the PA of molecules and their adiabatic IP have been derived,[119] which makes it possible to obtain values for the enthalpies of formation of $M + H^{+}$ ions from the IP of halogen-containing molecules. The acidity values of halogen-containing molecules, from which in combination with the heats of formation of the corresponding radicals (see below) it is possible to calculate the heats of formation of anions, are given in several studies.[128–134] The electron affinity values of halogen-containing molecules which are needed to calculate the enthalpies of formation of radical anions are given in two studies.[131,135] We should mention the study of Lias et al.,[136] in which the reaction

$$HCXY + B: \rightarrow :CXY + BH,$$

where B is a base, X and Y = F and Cl, has been investigated; and the study of Mishima et al.,[137] in which Cl^{-} transfer was used to determine the enthalpy of formation of $XC_6H_4\dot{C}H_2$. In two further studies by Mishima et al.[138,139] the proton affinity values of 10 halogen-containing (F, Cl, CF_3) styrenes and α-methylstyrenes respectively have been obtained. In a study by McMahon et al.[140] the values of affinity towards CH_3^{+} have been obtained for a number of halogen-containing molecules.

The enthalpy of formation values of halogen-containing free radicals (formed as pairs with cations and anions in the mass spectrometer) are given in five studies.[4,141–144] In three publications[4,141,142] the energy values for homolytic bond cleavage are given, from which additional information about the enthalpies of formation of free radicals may be obtained. Takhistov[4] provides information about the enthalpies of formation of all the halogen-containing carbenes (:CXY and :CHX) as well as small molecules and radicals that are expressly of interest for mass spectrometry.

V. Analytical aspects of the mass spectrometry of halogen-containing compounds

The prevalence of halogen-containing compounds is steadily increasing. Halogen-containing compounds (freons, pesticides, polyhalobiphenyls, polyhalodibenzodioxins, polyhalodibenzofurans) head the list of those compounds whose contaminating effect has already assumed a global (worldwide) character. Of the 230 volatile organic compounds detected in the atmosphere above a large forest, 18 were halogen-containing compounds.[145] They are found in virtually any living organism in any corner of the earth. Hence there is an urgent need to identify or establish the structure of novel compounds containing halogens. It is therefore useful to summarise

the literature of recent years in which mass spectra are examined (we shall not deal with questions concerning the determination of aromatic chlorine-containing compounds by mass spectrometric methods which were considered in detail in two reviews).[148,149]

For benzene compounds, mass spectra have been obtained for benzenes polysubstituted by Br, CF_3, $CF=CCl_2$,[150] halogen-substituted stilbenes,[151] aromatic sulphones with $-CHF$ and $-CF_2-$ chain residues,[152] benzenes with CF_3CH_2X, O, or NR groups,[153] 10 phenyl-containing β−F-amines,[154] tris(*p*-chlorophenyl)methanol found in biological products,[155] novel natural hexasubstituted dichlorobenzenes,[156] S- and Cl-containing products from the bioconversion of hexachlorobenzene,[157] metabolites of chloropropham (3-chloroaniline and 3,3′-dichloroazobenzene),[158] 86 methyl polychlorobiphenyl sulphones,[159] *p*-methylthioperchlorostyrene (a product of the mussel metabolism of perchlorostyrene),[160] novel chlorine-containing aromatic compounds (anilines, benzonitriles, benzophenones, fluoroenones, xanthen-9-ones) detected during the combustion of domestic waste products,[161] methyl polychlorophenyl sulphones (products of the metabolism of polychloro- and polychloronitro-benzenes by garden plants),[162] polychlorocumenes,[163,164] α-methylstyrenes,[163] the ethylesters of isomeric chlorophenylpropionates and chlorophenylbutyrates,[165] and fluorobromobenzocyclanones.[166]

For heterocyclic compounds mention should be made of mass spectrometric studies on 2-R-substituted furans, thiophenes, pyrroles, and also benzenes [R = $-(CF_2)_nCl$, n = 4,6,8],[167] and furans and thiophenes containing CF_3 and $CF=CCl_2$ groups,[45] 2,5-difluoro-2,5-bis(trifluoromethyl)-2,5-dihydro-furan and -thiophene,[45] 3-chloro-4-dichloromethyl-6-hydroxy-2(5*H*)-furan and 2-chloro-3-dichloro-methyl-4-keto-butene-2-oic acid obtained in the chlorination of natural and waste water,[168] 18 mixed chloro- and bromo-dibenzodioxins and 18 mixed chloro- and bromo-dibenzofurans,[50] 3-methoxy-2,6-dichlorodibenzodioxin (a methylated product of the metabolism of 2,5-dichlorodibenzodioxin by goldfish),[169] bromosubstituted nitropyridines and their oxides,[170] imidazoles with RC_6F_4 groups,[171] quinoxalines with $(CH_3)_2CF$ and $C_2H_5(CH_3)C(F)$ groups,[172] F- and CF_3-containing *spiro*-3-indolines,[173] perfluoroalkyl-sorbitan, -isosorbide, and -isomannide (EI and CI mass spectra),[174] products of the electrochemical fluorination of *N*-cycloalkylpyrrolidines and *N*-cycloalkylpiperidines,[175] perfluorobicyclic amines and amino acids,[176] and 1,2-diazacyclopentadienes with isomeric fluorobutyl groups.[177] In a review[178] on the synthesis of heterocyclic compounds with F and CF_3 groups on the ring, references to their MS studies may also be found.

The mass spectra of aliphatic compounds have been studied in the case of β-ketoesters with perfluoroalkyl groups and F atoms at the 3-position,[179,180] 3-substituted ethyl trifluoromethylacetoacetates,[181] their derivatives and also ketones $CF_3COCH(R)(R')$,[181,182] amines with a CF_3CH_2 group and their Cl and Br derivatives,[183] ω-chloroperfluoroacyl(amino)ethylenes,[184] polynitrogen-containing compounds with an F_2NCF_2 group,[20] telomers of chlorofluoropropionitrile fluorides with hexafluoropropylene oxide,[185] the perfluoroacrylate of 1-adamantol,[186] pentamethyl-5-X-cyclopentadienes (X = Cl, Br, I),[187] and halogen-substituted thioesters.[188]

Two reference books[9,14] remain important as sources of information on the mass spectra of halogen-containing compounds.

In conclusion we shall examine certain aspects of the application of the mass spectrometry of halogen-containing compounds. The majority of high-resolution instruments are equipped with computers that are used to calculate the empirical formulae of the ions. In our view, some of the data obtained in this manner must be treated with caution, since errors are possible. Thus, in analysing the results of Hudlicky and Glass[189] we noticed that the computer set to record F-containing ions in the analysis of the compound cyclo-$C_6F_{11}CF_2COOCH_3$ yielded the formula $C_8F_{13}^+$ for the $M-47]^+$ ion with loss of an impossible CH_3OO fragment instead of $M-F-CO]^+$ (the latter is typical of F- and CO-containing compounds) or $C_8H_3F_{12}O^+$ (the authors did not detect this error). In the mass spectra of diketones with a CF_3 group, such as $XC_6H_4COCH_2COCF_3$, $CH_3COCH_2COCF_3$, and $R_FCOCH_2COCF_3$, an intense peak from an ion with m/z 69 appears, to which both a computer and operator (after manual determination of the exact value of the mass ion) with a good resolution of 10−12 000 would undoubtedly assign the formula CF_3^+. In fact, however, this is an ion with empirical formula $C_3HO_2^+$, and a better resolution (about 15−18 000) is required to distinguish it from CF_3^+, while the CF_3 fragment is eliminated in the primary process:[12]

$$\underset{M^+}{XC_6H_4C(OH)=CHCOCF_3]^+} \longrightarrow \underset{[M-CF_3]^+}{XC_6H_4C(OH)=CHC\equiv\overset{+}{O}} \longrightarrow O=C=CHC\equiv\overset{+}{O}$$

$$69^+ : [M-CF_3-XC_6H_5] .$$

Hence there is an obvious need for more careful treatment of the data supplied by a computer.

Some aspects of the analysis of halogen-containing compounds have been considered above. It may be noted in addition that halogens have proved to be elements that can be successfully determined using the empirical formula of compounds and it is possible to establish exactly which halogen occurs in the molecule. The presence of Cl and Br atoms in any quantity and combination is readily established from their characteristic isotope patterns.[4] Since there are several or many F atoms in the majority of F-containing compounds (fluorinated chain, R_F, SF_5, and C_6F_5 groups, several CF_3, NF_2, OCF_3, SCF_3 groups, etc.), the presence of fluorine, which is monoisotopic, can be assessed from the weak intensity of the isotopic (from ^{13}C) peak of the ion next to any peak at large masses. Taking into account its high atomic weight (127), iodine also gives a similar reduced peak. In the literature there are examples of the difficulties and occasionally the impossibility of distinguishing the isomers of fluorinated compounds obtained in a single process (in electrochemical fluorination, for example). Thus, the isomers cyclo-$C_6F_{11}CF_2COOCH_3$ and cyclo-$C_5F_9CF_2CF_2COOCH_3$ or cyclo-$C_5F_9-C_4F_9$ and cyclo-$C_6F_{11}-C_3F_7$ cannot be distinguished in the EI mass spectrum.[189] At the same time it is possible to distinguish positional isomers and the geometric isomers $ClCH=C(Br)COOCH_3$ and $BrCH=C(Cl)COOCH_3$.[24] The isomers *p*-$CF_3CF_2CF_2C_6H_4COOCH_3$ and *p*-$(CF_3)_2CFC_6H_4COOCH_3$ were readily distinguished in DEC mass spectra (in contrast to the EI mass spectra).[46]

Halogens can be used to analyse other compounds. Thus, a fluorine or chlorine "label" in the form of an XC_6H_4 or $X_2C_6H_3$ (3,5-$Cl_2-C_6H_3-$) group is used for a number of aryl (usually phenyl) groups at different positions, since the direction of fragmentation when C_6H_5 is replaced by these groups does not alter and these halogens do not introduce any new pathways for the decomposition of molecular and primary (secondary) ions (their effect only becomes evident at the advanced stages of fragmentation). The $Si(CH_3)_2CH_2Cl$ group is used in mass spectrometry to "protect" hydroxyl-containing groups; it is more successful than the traditional group—$Si(CH_3)_3$. Although the M^+ peak does not appear in the modified compound, as in the initial

HO-containing compound, the $M-CH_2Cl^+$ ion has the highest mass (and is considerably more intense than the $M-CH_3^+$ ion in $(CH_3)_3Si$ derivatives).[4] This group can also be of help in distinguishing stereoisomers.

The groups CF_3CO, C_2F_5CO, and C_3F_7CO serve as valuable protecting groups in complex molecules of biological origin. By replacing hydroxyl groups with them, it is possible to increase substantially the molecular weight of the compound being analysed and to shift the peaks of the characteristic mass ions to higher mass, having thus eliminated the effect of impurities, the solvent, metabolites, if the analysis is conducted from a biological fluid (blood, urine, plasma). Although M^+ naturally does not appear in such systems, the characteristic series $M-R_FCOOH^+$, such as $M-CF_3COOH^+$ (or $M-114^+$), $M-2CF_3COOH^+$ (or $M-228^+$), etc., can be detected.

A review of the methods for introducing the CF_3CO group, including those using the convenient novel reagent 2-trifluoroacetoxypyridine, is presented by Koemi et al.[190] The mass spectra of C_3F_7CO-substituted amines have been reported by Mikaya et al.[191]

Mass spectrometry is a versatile method for detecting an element in a sample even when any other element is present in the latter, owing to the unique nature of the isotopic composition of each of them. The problem is merely that of obtaining volatile forms of the elements. A versatile, synthetically accessible class of organometallic compounds that is suitable for analysis using mass spectrometric methods is made up by complexes of metals with fluorinated ketones, in particular $CF_3COCH_2COCH_3$ and $CF_3COCH_2COC(CH_3)_3$.[4] Volatile chelates of about 60 elements of the Periodic Table are known, even including those of the "awkward" Group I elements (as double salts with rare earth elements). A series of different halogen-containing diketones and their sulphur-containing analogues are reviewed by Takhistov.[4] Methods of modifying compounds to forms that are convenient for mass spectrometric analysis are described in a monograph by Zaikin and Mikaya,[192] as well as in the above review.[4]

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