BIBLIOGRAPHY

[1] *H. Meyer*, Ber. deutsch. chem. Ges. *62*, 143 (1909).
[2] *G. Kortüm & P. Krieg*, Chem. Ber. *102*, 3033 (1969), and papers cited therin.
[3] a) *Y. Hirshberg*, J. Amer. chem. Soc. *78*, 2304 (1956); b) *R. Korenstein, K. A. Muszkat & E. Fischer*, Israel J. Chemistry *8*, 273 (1970), and earlier papers cited therein.
[4] *G. Kortüm & G. Bayer*, Ber. Bunsenges. *67*, 24 (1963).
[5] *K. A. Muszkat & E. Fischer*, J. chem. Soc. B *1967*, 662.
[6] *A. Bromberg & K. A. Muszkat*, J. Amer. chem. Soc. *91*, 2860 (1969).
[7] *H. Brockmann & R. Muehlmann*, Chem. Ber. *81*, 467 (1948); *82*, 348 (1949).
[8] *L. J. Dombrowski, C. L. Groncki, R. L. Strong & H. H. Richtol*, J. physic. Chemistry *73*, 3481 (1969); *L. A. Harrah & R. Becker*, *ibid.* *69*, 2487 (1965), and recent work (in press).
[9] *D. S. Tarbell & P. Holland*, J. Amer. chem. Soc. *76*, 2451 (1954).

---

252. Mass Spectrometric Studies of Mono- and Di-Haloacetylenes

by **Else Kloster-Jensen**[1]**, C. Pascual** and **J. Vogt**

Physikalisch-Chemisches Institut der Universität Basel

(12. X. 70)

Summary. The mass spectra of the four monohaloacetylenes X-C≡C-H with X = F, Cl, Br, I and the six dihaloacetylenes X-C≡C-Y with X, Y = Cl, Br, I have been recorded. The dissociation energies of the carbon-carbon triple bonds of these compounds have been determined from the appearance potentials of the CH^+ and CX^+ ions. The appearance potentials of the singly- and doubly-charged molecular ions are also reported.

Monohaloacetylenes, X–C≡C–H (X = F, Cl, Br, I), and dihaloacetylenes, X–C≡C–Y (X, Y = Cl, Br, I), have recently been the subject of a variety of physico-chemical studies [1] [2]. The availability of these compounds in our laboratory gave us the opportunity to carry out some mass spectrometric studies of their thermodynamic properties. Our main interest was to determine the dissociation energies of the carbon-carbon triple bonds.

The bond dissociation energy (D) is defined as the difference in energy between the parent molecule (in its equilibrium configuration) and the two fragments (also in their equilibrium configurations) after bond breaking [3]. Therefore, the bond dissociation energy can be written as the difference between the heats of formation of the fragments and the heat of formation of the parent molecule:

$$D(\mathrm{A{-}B}) = \Delta H_f(\mathrm{A}) + \Delta H_f(\mathrm{B}) - \Delta H_f(\mathrm{AB}).$$

The determination of bond dissociation energies by electron impact is based upon the following considerations [4]. For the process

$$\mathrm{AB} \rightarrow \mathrm{A}^+ + \mathrm{B} + e$$

the appearance potential of A^+ is

$$AP(\mathrm{A}^+) = D(\mathrm{A{-}B}) + IP(\mathrm{A}) + E\,, \tag{1}$$

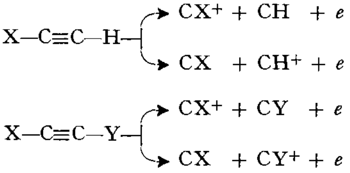
where E is the excess energy (both internal and translational) of the products. Many

---

[1] Permanent address: Department of Chemistry, University of Oslo, Blindern, Oslo 3, Norway.

mass spectrometric fragmentations do not involve excess energy. In most cases, the amount of excess energy involved is a few kilocalories per mol, which is comparable to the error in the determination of the appearance potentials. Thus, if the ionization potential of A, $IP(\mathrm{A})$, is known and $AP(\mathrm{A}^+)$ is determined experimentally, the bond dissociation energy, $D(\mathrm{A{-}B})$, may be calculated.

The error in the determination of appearance potentials depends upon the method used to interpret the ionization efficiency curves. The semi-logarithmic plot method [5] has been widely used to determine appearance potentials of fragment ions. However, it should not be used in cases where the linear portions of the semi-logarithmic plots of the fragment ion and the reference molecule, usually a noble gas, are not parallel. In the determination of the appearance potentials of the fragment ions produced by the cleavage of the carbon-carbon bonds in haloacetylenes as in processes (2) to (5), the appropriate plots were not parallel. Thus, the semi-logarithmic plot method could not be applied. Instead we used the energy-distribution-difference method recently proposed by *Winters et al.* [6].



$$\mathrm{X{-}C{\equiv}C{-}H} \rightarrow \mathrm{CX^+ + CH + \mathit{e}} \qquad (2)$$

$$\mathrm{X{-}C{\equiv}C{-}H} \rightarrow \mathrm{CX + CH^+ + \mathit{e}} \qquad (3)$$

$$\mathrm{X{-}C{\equiv}C{-}Y} \rightarrow \mathrm{CX^+ + CY + \mathit{e}} \qquad (4)$$

$$\mathrm{X{-}C{\equiv}C{-}Y} \rightarrow \mathrm{CX + CY^+ + \mathit{e}} \qquad (5)$$

We tested this method by determining the appearance potential of the $\mathrm{CH^+}$ ion from acetylene. For the process

$$\mathrm{H{-}C{\equiv}C{-}H} \rightarrow \mathrm{CH^+ + CH + \mathit{e}}$$

the appearance potential of $\mathrm{CH^+}$, according to Equation (1), is

$$AP(\mathrm{CH^+}) = IP(\mathrm{CH}) + D(\mathrm{HC{\equiv}CH}) + E\,,$$

so that

$$IP(\mathrm{CH}) \leqslant AP(\mathrm{CH^+}) - D(\mathrm{HC{\equiv}CH})\,.$$

The dissociation energy of the carbon-carbon triple bond in acetylene has been reported as $D(\mathrm{HC{\equiv}CH}) = 230$ kcal mol^{-1} [7]. The experimentally determined appearance potential of $\mathrm{CH^+}$ from acetylene was $AP(\mathrm{CH^+}) = 21.5$ eV (see Table 1). Therefore, $IP(\mathrm{CH}) \leqslant 11.5$ eV. The spectroscopic value reported by *Douglas & Herzberg* is $IP(\mathrm{CH}) = 11.13 \pm 0.22$ eV [8]. However, *Douglas & Morton* [9] have later pointed out that the correct spectroscopic value is probably $IP(\mathrm{CH}) = 11.33$ eV.

It is difficult to estimate the error in our experimentally determined $AP(\mathrm{CH^+}) = 21.5$ eV from acetylene. We think that the error in the appearance potentials of fragment ions as determined by *Winters'* method should be less than $\pm\ 0.2$ eV, since the method gives very good results for ionization potentials [6]. Under this assumption, we conclude that the amount of excess energy involved in the formation of the $\mathrm{CH^+}$ ion from acetylene does not exceed the difference value between our $IP(\mathrm{CH})$ and the spectroscopic value. This difference is comparable to the expected error in our appearance potential determination, that is, a few kilocalories per mol. Such an upper limit of excess energy will be assumed for processes (2) to (5).

Monohaloacetylenes. Figure 1 shows the mass spectra of the four monohaloacetylenes I–IV.

$X{-}C{\equiv}C{-}H$ I : X = F III : X = Br
II : X = Cl IV : X = I

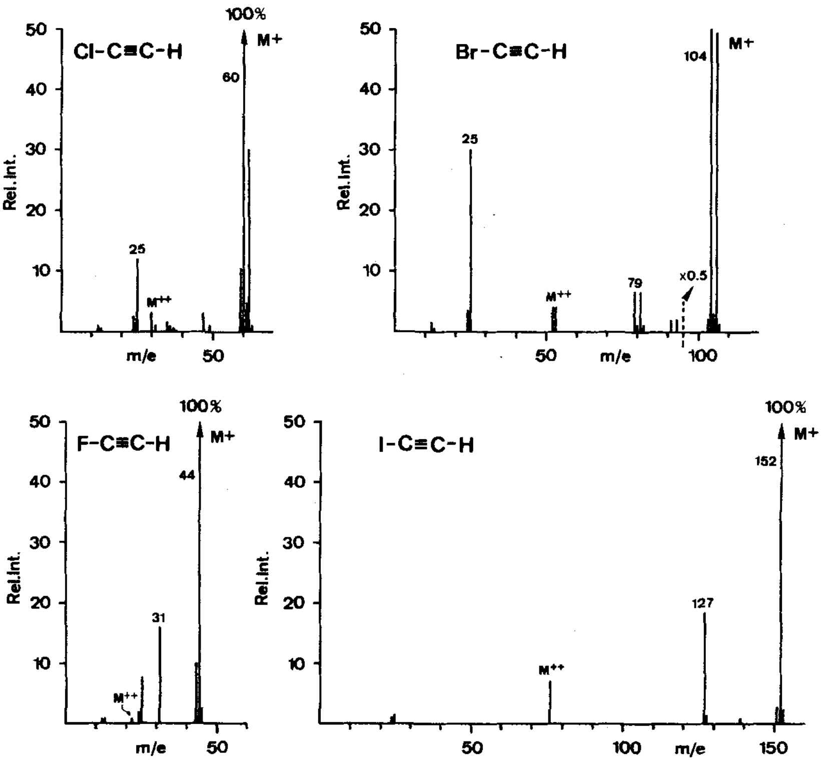


Fig. 1. *Mass spectra of monohaloacetylenes I–IV*

Table 1 summarizes the appearance potentials (AP) of the fragment ions CX^+ (X = F, Cl, Br, I) and CH^+ as well as those of the singly- and doubly-charged molecular ions for the four monohaloacetylenes I–IV.

Table 1. *Appearance potentials of the fragment ions CX^+ and CH^+ and the singly- and doubly-charged molecular ions in the monohaloacetylenes I–IV* (all values in eV)

	X	$AP(M^+)$ [b]	$AP(CH^+)$	$AP(CX^+)$	$AP(M^{++})$
	H [a]	11.5	21.5	–	–
I	F	11.5	19.2	17.0	31.5
II	Cl	10.7	18.7	17.2	29.0
III	Br	10.3	20.3	18.1	28.4
IV	I	9.9	[c]	18.1	26.9

[a] Acetylene has been included as a reference compound.

[b] The appearance potentials of the singly-charged molecular ions correspond to the vertical ionization potentials.

[c] The very low abundance of this ion prevented the determination of its appearance potential.

The dissociation energies of the carbon-carbon triple bonds of monohaloacetylenes I–IV were obtained using Equation (6) and the appearance potentials, $AP(CH^+)$, listed in Table 1.

$$AP(CH^+) = IP(CH) + D(XC{\equiv}CH)\,. \tag{6}$$

For the ionization potential of CH, the value $IP(CH) = 11.5$ eV, obtained from acetylene, was used.

Table 2 summarizes the dissociation energies of the carbon-carbon triple bonds of monohaloacetylenes I–IV, obtained in this way.

Table 2. *Dissociation energies of the carbon-carbon triple bonds in monohaloacetylenes* (values in kcal mol^{-1})

	Compound	D (XC≡CH)
	H–C≡C–H [a]	230
I	F–C≡C–H	178
II	Cl–C≡C–H	166
III	Br–C≡C–H	202
IV	I–C≡C–H	[b]

[a] Acetylene has been included as a reference compound.

[b] The very low abundance of the CH^+ ion in the mass spectrum of this compound prevented the determination of this value.

The ionization potentials of the radicals CX (X = H, F, Cl, Br) given in Table 3 were obtained using in Equation (7) the appearance potentials $AP(CX^+)$ and the dissociation energies $D(XC{\equiv}CH)$ listed in Tables 1 and 2 respectively.

$$AP(CX^+) = IP(CX) + D(XC{\equiv}CH)\,. \tag{7}$$

Table 3. *Ionization potentials of the radicals CX (X = H, F, Cl, Br)* (values in eV)

IP(CH)	IP(CF)	IP(CCl)	IP(CBr)
11.5	9.3	10.0	9.4

Dihaloacetylenes. Figures 2 and 3 show the mass spectra of the six dihaloacetylenes V–X.

X–C≡C–Y
V: X = Y = Cl
VI: X = Y = Br
VII: X = Y = I
VIII: X = Cl, Y = Br
IX: X = Cl, Y = I
X: X = Br, Y = I

Table 4 contains their appearance potential data.

Table 4. *Appearance potentials of the fragment ions CX^+ and CY^+ and the singly- and doubly-charged molecular ions of dihaloacetylenes V–X* (all values in eV)

	X	Y	$AP(M^+)$ [a]	$AP(CX^+)$	$AP(CY^+)$	$AP(M^{++})$
V	Cl	Cl	10.3	15.4		27.6
VI	Br	Br	9.7	16.1		25.8
VII	I	I	9.2	16.8		23.7
VIII	Cl	Br	10.0	16.4	16.0	26.8
IX	Cl	I	9.7	17.5	16.4	25.5
X	Br	I	9.4	16.9	16.9	24.7

[a] The appearance potentials of the singly-charged molecular ions correspond to the vertical ionization potentials.

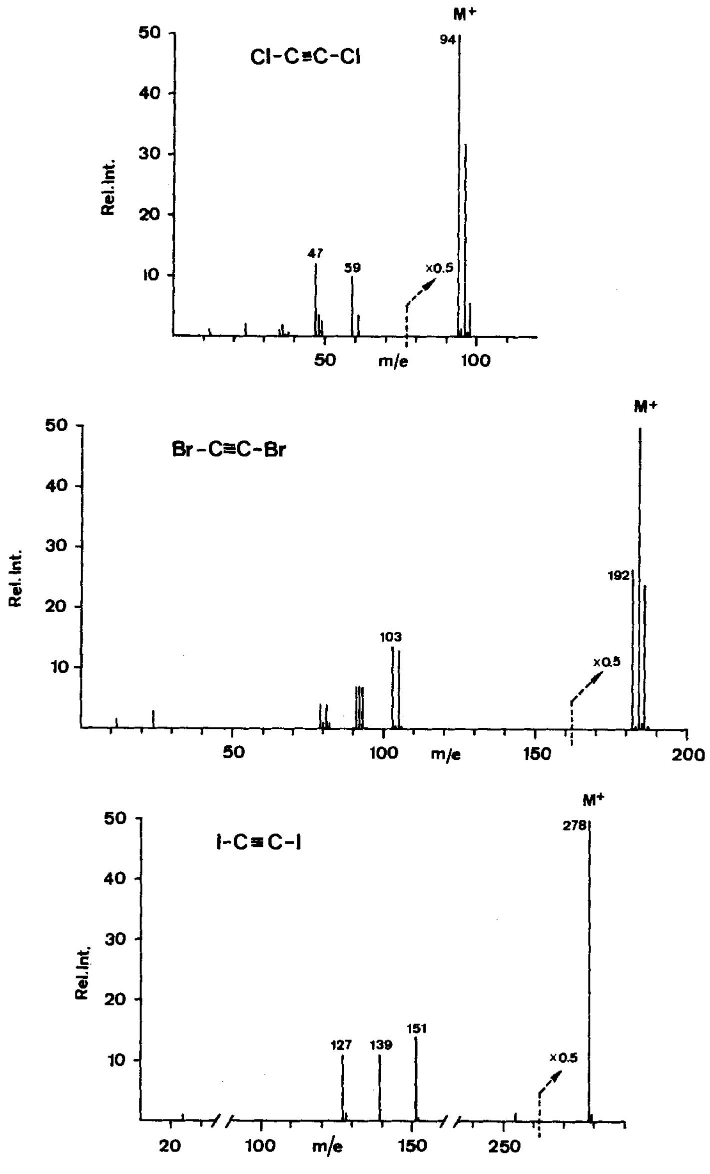


Fig. 2. *Mass spectra of dihaloacetylenes V–VII*

The dissociation energies of the carbon-carbon triple bonds of dihaloacetylenes V–X were determined using in Equation (8) the ionization potentials $IP(CX)$ listed in Table 3.

$$AP(CX^+) = IP(CX) + D(XC{\equiv}CY)\,. \tag{8}$$

Table 5 summarizes the dissociation energies of the carbon-carbon triple bonds of compounds V–X, obtained in this way.

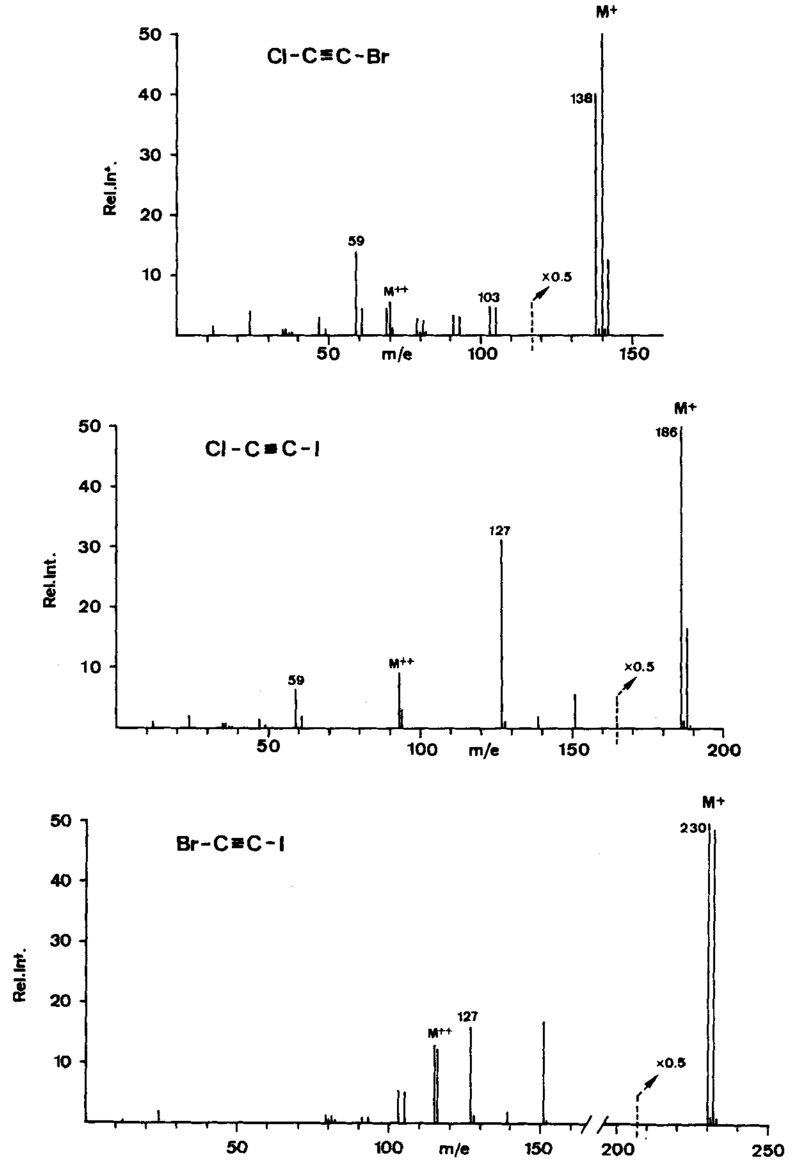


Fig. 3. *Mass spectra of dihaloacetylenes VIII–X*

Discussion. – The dissociation energies of the carbon-carbon triple bonds of haloacetylenes I–X listed in Tables 2 and 5, which were obtained from appearance potential data, are much lower than the dissociation energy of acetylene. Furthermore, they are apparently very dependent upon the nature of the halogen substituents. Based on the results obtained from the determination of the appearance potential of the CH^+ ion in acetylene, we have assumed that a negligible amount of excess energy

Table 5. *Dissociation energies of the carbon-carbon triple bonds of dihaloacetylenes V–X* (values in kcal mol^{-1})

	Compound	D (XC≡CY)
V	Cl–C≡C–Cl	125
VI	Br–C≡C–Br	155
VII	I–C≡C–I	[a]
VIII	Cl–C≡C–Br	150
IX	Cl–C≡C–I	173
X	Br–C≡C–I	174

[a] This value could not be determined since IP(CI) is not known (see Table 2).

was involved in processes (2) to (5). Still, the dissociation energies listed in Tables 2 and 5 should be considered as upper limits, since any excess energy would lower these values.

A value of the heat of formation of CF, $\Delta H_f(\mathrm{CF}) = 61.5 \pm 2.5$ kcal mol^{-1}, which was determined both from the emission spectrum of CF [10] and from electron impact studies [11], has been recently reported. This value allows one to estimate the heat of formation of monofluoroacetylene, using either of the following equations[2]:

$$\Delta H_f(\mathrm{FC{\equiv}CH}) = \Delta H_f(\mathrm{CF}) + \Delta H_f(\mathrm{CH^+}) - AP(\mathrm{CH^+}),$$

$$\Delta H_f(\mathrm{FC{\equiv}CH}) = \Delta H_f(\mathrm{CF}) + \Delta H_f(\mathrm{CH}) - D(\mathrm{FC{\equiv}CH}).$$

The value which is obtained, $\Delta H_f(\mathrm{FC{\equiv}CH}) = 25.5$ kcal mol^{-1}, is in very good agreement with the value 24.5 kcal mol^{-1} predicted [13] by a semi-empirical MINDO/2 calculation [14]. The ionization potential obtained for CF, $IP(\mathrm{CF}) = 9.3$ eV (see Table 3), is also in very good agreement with the value 9.23 ± 0.08 eV reported recently by *Walter et al.* [11], which was obtained from photoionization studies of tetrafluoroethylene and carbon tetrafluoride.

Several values ranging between 316 kcal mol^{-1} and 394 kcal mol^{-1} have been reported for the heat of formation of the CCl$^+$ ion [15] [16]. These values were obtained by electron impact studies of different parent molecules. One has to assume that different amounts of excess energy may be involved in these values. Under this assumption, the lowest value, 316 kcal mol^{-1}, should be the best approximation for $\Delta H_f(\mathrm{CCl^+})$. This value was determined from the appearance potential of the CCl$^+$ ion in Cl–C≡N [16]. The heat of formation of monochloroacetylene can be estimated using the equation

$$\Delta H_f(\mathrm{ClC{\equiv}CH}) = \Delta H_f(\mathrm{CCl^+}) + \Delta H_f(\mathrm{CH}) - AP(\mathrm{CCl^+}).$$

The value obtained in this manner is 61 kcal mol^{-1}, as compared to 52 kcal mol^{-1} predicted [13] by a semi-empirical MINDO/2 calculation [14].

The value of the carbon-carbon dissociation energy of dichloroacetylene, $D(\mathrm{ClC{\equiv}CCl}) = 125$ kcal mol^{-1}, is extremely low but seems thermodynamically

---

[2] The reported value for ΔH_f(CH) is 142 kcal mol^{-1} [12].

reasonable. In fact, if we calculate the heat of formation of dichloroacetylene using the equations

$$\Delta H_f(\mathrm{ClC{\equiv}CCl}) = \Delta H_f(\mathrm{CCl^+}) + \Delta H_f(\mathrm{CCl}) - AP(\mathrm{CCl^+})\ ,$$

$$\Delta H_f(\mathrm{CCl}) = H_f(\mathrm{CCl^+}) - IP(\mathrm{CCl})\ ,$$

the value obtained is 47 kcal $\mathrm{mol^{-1}}$, which is in good agreement with the value 52 kcal $\mathrm{mol^{-1}}$ predicted [13] by a semi-empirical MINDO/2 calculation [14].

Ionization potentials of the CX radicals. The ionization potentials $IP(\mathrm{CX})$ (X = F, Cl, Br, I) can be qualitatively rationalized using a simple model. Upon ionization of the CH radical, the ejected electron vacates an unperturbed *p*-orbital which, because of orthogonality, cannot mix with the 1*s*-orbital of the CH hydrogen. Therefore, the ionization potential of the CH radical, $IP(\mathrm{CH}) = 11.5$ eV, should be nearly equal to the valence state ionization potential of a carbon 2*p*-orbital, $\mathrm{VSIP}(C_{2p}) = 11.4$ eV [17]. If the hydrogen is replaced by a halogen, interaction leads to degenerate pairs of bonding and antibonding π-orbitals (see Fig. 4).

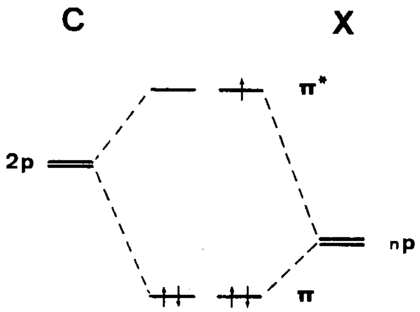


Fig. 4. *Interaction diagram for the splitting of the* p*-orbitals of carbon and halogen in the CX radicals*

In these CX radicals all π-orbitals are occupied. The ejected electron comes from a singly occupied π^*-orbital. Therefore, one would expect the ionization potentials of the CX radicals (X = F, Cl, Br, I) to be lower than the ionization potential of the CH radical. The relative energies of these π^*-orbitals for the different CX radicals should depend on two factors: firstly, on the amount of overlap between the *p*-orbitals of the carbon and halogen atoms and, secondly, on the relative energy difference of their valence state ionization potentials. Based on semi-empirical MO-calculations [18], one would expect these two effects to partially compensate, as their influence on the ionization potential operates in opposite directions. Accurate values of these π^*-energy levels cannot be determined by a semi-empirical calculation since they are very sensitive to small changes in the atomic parameters used in these calculations. Since the differences in $IP(\mathrm{CX})$ (see Table 3), which we obtain from appearance potential data of monohaloacetylenes I–III, are quite small, we cannot propose an explanation for the relative values of $IP(\mathrm{CX})$ at this time.

Doubly-charged molecular ions. As can be seen in Table 6, the relative abundances of the doubly-charged molecular ions (M^{++}) in the 70 eV mass spectra show a good qualitative correlation with their appearance potentials; the higher the appearance potential, the lower the abundance of the doubly-charged molecular ion.

Unfortunately, only a limited number of appearance potential values for doubly-charged molecular ions of organic compounds have been reported, so that it is not possible to establish whether such a correlation is normal within a series of compounds.

The appearance potentials of the doubly-charged molecular ions of haloacetylenes I–X show another interesting correlation with the appearance potentials of the singly-charged molecular ions (vertical ionization potentials). Figure 5 shows a plot of the appearance potentials of the doubly-charged molecular ions *vs.* the appearance potentials of the singly-charged molecular ions of haloacetylenes I–X. At the present stage, it is difficult to interpret the exact meaning of such a linear correlation.

Table 6. *Relative abundances ($\%\Sigma_{12}$) and appearance potentials of the doubly-charged molecular ions of haloacetylenes I–X*

	Compound	Relative abundance $\%\Sigma_{12}$	$AP(M^{++})$ eV
I	F–C≡C–H	0.7	31.5
II	Cl–C≡C–H	2.3	29.0
III	Br–C≡C–H	2.9	28.4
IV	I–C≡C–H	5.2	26.9
V	Cl–C≡C–Cl	4.2	27.6
VI	Br–C≡C–Br	5.2	25.8
VII	I–C≡C–I	7.0	23.7
VIII	Cl–C≡C–Br	4.1	26.8
IX	Cl–C≡C–I	6.0	25.5
X	Br–C≡C–I	8.8	24.7

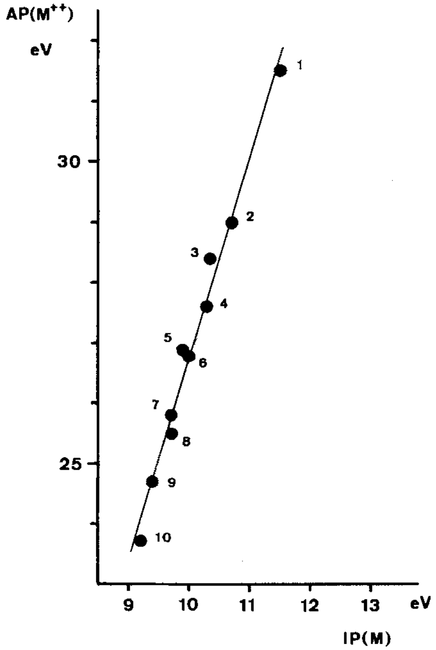


Fig. 5. *Correlation of the appearance potentials of the doubly-charged molecular ions with the vertical ionization potentials of the parent molecules*

1: Monofluoroacetylene, 2: Monochloroacetylene, 3: Monobromoacetylene, 4: Dichloroacetylene, 5: Monoiodoacetylene; 6: Chlorobromoacetylene, 7: Dibromoacetylene, 8: Chloroiodoacetylene, 9: Bromoiodoacetylene, 10: Diiodoacetylene.

Further work on similar compounds is in progress in our laboratories. These studies should provide a better understanding of the appearance potentials of doubly-charged molecular ions of organic compounds.

Experimental. – The syntheses of the mono- and di-haloacetylenes used in these studies have been recently reported [2] [19]. Acetylene was commercially obtained (*The Matheson Company, Inc.*, East Rutherford, New Jersey, U.S.A.), purity $>99.6\%$. The mass spectra were run on a *Hitachi Perkin-Elmer* RMU-7 double-focussing mass spectrometer (all-glass inlet system at 50°, source temperature 180°, ionizing energy 70 eV, ionizing current 40 μA). The appearance potentials were determined by the energy-distribution-difference method [6]. The reported appearance potentials are the average of three separate determinations. The standard deviation of these determinations was ± 0.1 eV.

This work is part of project Nr. SR 2.120.69 of the *Schweizerische Nationalfonds zur Förderung der wissenschaftlichen Forschung*. We wish to thank Dr. *Joseph Seibl*, Dr. *Peter Kriemler* and Mr. *Werner Schmidt* for helpful discussions. One of us (*E.K.-J.*) is indebted to the University of Oslo for a leave of absence. The financial suport by *J.R.Geigy S.A.* and *CIBA AG* (Basel) is gratefully acknowledged.

BIBLIOGRAPHY

[1] *P.Klaeboe, E.Kloster-Jensen, D.H.Christensen & I.Johnsen*, Spectrochim. Acta, *26A*, 1567 (1970); *E.Heilbronner, V.Hornung & Else Kloster-Jensen*, Helv. *53*, 331 (1970); *L.Lunazzi, D.Macciantelli & F.Taddei*, Molec. Physics *19*, 137 (1970); *A.Bjørseth, Else Kloster-Jensen, K.-M.Marstokk & H.Møllendal*, J. mol. Structure *6*, 181 (1970).

[2] *H.J.Haink, E.Heilbronner, V.Hornung & Else Kloster-Jensen*, Helv. *53*, 1073 (1970).

[3] *B.E.Knox & H.B.Palmer*, Chem. Reviews *61*, 247 (1961).

[4] *M.Krauss & V.H.Dibeler* in 'Mass Spectrometry of Organic Ions', p. 117, Ed. *F.W.McLafferty*, Academic Press, New York and London 1963.

[5] *F.P.Lossing, A.W.Tickner & W.A.Bryce*, J. chem. Physics *19*, 1254 (1951).

[6] *R.E.Winters, J.H.Collins & W.L.Courchene*, J. chem. Physics *45*, 1931 (1966); *J.H.Collins, R.E.Winters & G.G.Engerholm*, *ibid. 49*, 2469 (1968).

[7] *S.W.Benson*, J. chem. Education *42*, 502 (1965).

[8] *A.E.Douglas & G.Herzberg*, Canad. J. Research *20A*, 71 (1942).

[9] *A.E.Douglas & J.R.Morton*, Astrophys. J. *131*, 1 (1960).

[10] *T.L.Porter, D.E.Mann & N.Acquista*, J. Mol. Spectroscopy *16*, 228 (1965).

[11] *T.A.Walter, Ch.Lifshitz, W.A.Chupka & J.Berkowitz*, J. chem. Physics *51*, 3531 (1969).

[12] *F.D.Rossini, D.D.Wagman, W.H.Evans, W.H.Levine & I.Jaffe*, Natl. Bur. Standards, Circ. No. 500 (1952).

[13] *M.J.S.Dewar*, private communication.

[14] *M.J.S.Dewar & E.Haselbach*, J. Amer. chem. Soc. *92*, 590 (1970).

[15] *D.L.Hobrock & R.W.Kiser*, J. physic. Chemistry *68*, 575 (1964); *R.I.Reed & W.Snedden*, Trans. Farad. Soc. *54*, 301 (1958); *L.P.Blanchard & P.LeGoff*, Canad. J. Chemistry *35*, 89 (1957).

[16] *J.T.Herron & V.H.Dibeler*, J. Amer. chem. Soc. *82*, 1555 (1960).

[17] *H.O.Pritchard & H.A.Skinner*, Chem. Reviews *55*, 745 (1955).

[18] *R.Hoffmann*, J. chem. Physics *39*, 1397 (1963).

[19] *Else Kloster-Jensen*, J. Amer. chem. Soc. *91*, 5673 (1969); Tetrahedron Letters *1969*, 5323; Tetrahedron, submitted for publication.