# STUDIES IN ELECTRON IMPACT METHODS \* PART 2.—THE LATENT HEAT OF SUBLIMATION OF CARBON

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An investigation, by electron impact methods, into the mode of decomposition of CF<sub>4</sub>, CCl<sub>4</sub> and CBr<sub>4</sub> has enabled a mechanism of fragmentation to be assigned to each of these. Values for the bond-dissociation energies have also been obtained as well as the latent heat of sublimation of carbon. Assuming, in accordance with the available evidence, that the particles are formed without kinetic energy and in their lowest electronic states, an average value of  $\sim 7.5$  eV is obtained. It is therefore concluded that the maximum, spectroscopically allowable, value of 7.386 eV is correct.

The evaluation of the heat of sublimation of carbon, the enthalpy change of the reaction  $C(s) \rightarrow C(g)$ , has been the subject of much controversy.<sup>14</sup> The latent heat obtained by direct vapour pressure measurements <sup>2-5</sup> has, with one exception,<sup>6</sup> suggested a high value of ~ 7.6 eV and more recently Goldfinger has also provided evidence to support this.<sup>7</sup> Indirect estimations,<sup>8, 9</sup> apart from Gaydon's interpretation of the spectroscopic evidence <sup>10</sup> lead to other results; those spectroscopically allowed being 7.386 eV, 6.126 eV, 5.887 eV and 5.420 eV.

A study of the dissociation of methane by electron impact methods  $1^{1a}$  yielded  $\mathscr{L}(C) \sim 5.2$  eV, a conclusion which the authors, McDowell and Warren, claim to have substantiated by a similar investigation of methyl cyanide.<sup>11b</sup> These conclusions have been partly re-interpreted by Brackett <sup>12</sup> who has attempted to reconcile these observations with the high value from direct vapour-pressure measurements. A re-investigation of methane by Langer, Hipple and Stevenson <sup>13</sup> by similar methods to McDowell and Warren support a low result of ~ 5.8 eV, in good agreement with these.

Other measurements, made upon nitrogen compounds and which can be related to the heat of sublimation of carbon by a thermochemical cycle have been examined by Long <sup>14</sup> who preferred a value of 5.64 eV and the whole problem has been reviewed by Long and Norrish <sup>15</sup> who favour  $\mathscr{L}(C) = 5.42$  eV.

The use of a thermochemical cycle together with certain data derived from impact studies on carbon monoxide, which originally led Hagstrum <sup>10b</sup> to conclude  $\mathscr{L}(C) \sim 6.13 \text{ eV}$ , has now been re-examined by Kistiakowsky,<sup>15</sup> and his collaborators. They conclude that D(C-O) = 11.11 eV from which the latent heat of carbon becomes 7.386 eV. More recent investigations by Lagergren <sup>17</sup> also support this result.

## EXPERIMENTAL

#### APPARATUS AND METHOD

The measurements were made with a Metropolitan-Vickers M.S. 2 mass-spectrometer with the modifications previously described.<sup>18</sup> For the measurements on the free-radicals, the terminal sinter in the ionization head was removed and replaced near the bulb containing the material under investigation. After passing through the sinter the vapour passed through a valve, to reduce the pressure, and then into a pyrolysis chamber. This contained an electrically heated tungsten wire, the temperature of which could be controlled

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by a manually operated resistance. The gases, after passing over the hot wire, were led along a short rectilinear path into the ionization head.

The experimental procedure was as follows. The mass-spectrometer was adjusted to measure particles of chosen mass and the accelerating voltage of the electron beam set at about 12 eV or other suitable value somewhat greater than the presumed ionization potential. The gas was then admitted to the combustion chamber at a controlled pressure, the tungsten wire heated, and the temperature adjusted until the measured number of particles of the selected mass was a maximum. The chamber was maintained at this temperature and the graph of ion abundance against ionizing voltage constructed in the usual way from which was deduced the ionization potential of the ion.<sup>11, 19</sup>



Measurements of the half-beam width  $^{11a}$  were also made with the results shown in fig. 1. The values for the carbon ions obtained, by electron impact, from the carbon tetrahalides lie close to and slightly below the straight-line of the molecular ions. These C<sup>+</sup> ions represent favourable cases for the detection of kinetic energy and from their position on the graph it is concluded that little or no excess energy is associated with formation of these ions. The reported values are referred to the spectroscopic value of argon (15.816 eV). The materials used were of the greatest possible purity and, except for carbon tetrafluoride, were dried and distilled before use.

The values of appearance and ionization potentials obtained in this investigation are in good agreement with those of them that have been reported by other workers.

#### RESULTS

The results of the investigation are summarized in table 1. The uncertainties attached to the figures are standard deviations.

### DISCUSSION

The ionization potential of the radical  $(R_{a})$  is related to the appearance potential of the ion  $A(R^{+})$ 

$$A(\mathbf{R}^+) \geq I(\mathbf{R}_{\alpha}) + D(\mathbf{R}_{\alpha} - \mathbf{R}_{\beta}),$$

where  $D(\mathbf{R}_{\alpha} - \mathbf{R}_{\beta})$  is the dissociation energy of the bond  $\mathbf{R}_{\alpha} - \mathbf{R}_{\beta}$ . The equality is considered correct provided the particles are formed without kinetic energy as was concluded above and in their lowest electronic states.<sup>20</sup> This latter assumption is also considered to be valid in the present study.

The method of evaluating  $\mathscr{L}(C)$  is based upon the stepwise fragmentation of the molecules CF<sub>4</sub>, CCl<sub>4</sub> and CBr<sub>4</sub>, the bond energies thus obtained being combined with the known heats of formation of the appropriate molecule to yield the latent heat of sublimation of carbon.

The initial dissociation, namely,

$$CX_4 + e \rightarrow CX_3 + X \cdot + 2e, \qquad (1)$$

has already been considered, for CCl<sub>4</sub>, by Farmer <sup>28</sup> and collaborators who have rejected the alternative mechanism

$$CX_4 + \boldsymbol{e} \rightarrow C \dot{X}_3 + \ddot{X} + \boldsymbol{e}$$
 (2)

for the decomposition. The results of these authors, listed above, lead to a value for

$$D(Cl-CCl_3) = 2.95 \pm 0.15 \text{ eV},$$

and the present value

$$D(Cl-CCl_3) \le 3.12 \pm 0.12 \text{ eV}$$

is in good agreement with this. The value 22 of

$$D(Br-CBr_3) = 2.16 \pm 0.05 \text{ eV}$$

has previously been determined by Sehon and Szwarc, and this value is used in the present discussion.

The value  $I(\cdot CF_3) \leq 10.2 \pm 0.1$  eV has been determined in this present investigation and is in good agreement with that already reported. The difference between this value and the appearance potential of the ion obtained from carbon tetrafluoride gives a value for the dissociation energy 4

$$D(F-CF_3) \le A(CF_3) - I(\circ CF_3)$$
  
= 5.25 ± 0.11 eV, (3)

assuming that the fission occurs by mechanism (1), in good agreement with the previously reported value  $^{28}$  of  $5.33 \pm 0.09$  eV. If the decomposition proceeded by mechanism (2) the bond energy would have a still higher value by the electron affinity of fluorine, i.e.  $D(F--CF_3)$  $\leq$  9.20 eV which is improbably high.

No value of I(•CBr<sub>3</sub>) has been determined in these experiments, but by assuming the same mode of decomposition in this case as in the others, and subtracting the known bond dissociation energy of the Br-CBr<sub>3</sub> bond from the measured appearance potential A(CBr<sub>3</sub>), a value of  $I(\cdot \operatorname{CBr}_3) \leq 8.04 \text{ eV}$  is obtained, which is very near the lower limit of electron accelerating potentials available and in consequence may not be determinable by direct experiment. This value seems in reasonable accord with the other ionization potentials. By a consideration of the size of the substituents and the electron distribution around the carbon, the ionization

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(28) ± 0·05

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 $11.83 \pm 0.05$ 

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(21)15·44 ± 0·05

(21)19-3 ± 0-02 16·10± 0·01

(21) ± 0·50  $(21) \pm 0.20$ 

27-2 22.4

 $10.43 \pm 0.02$  $10.11 \pm 0.09$ 

± 0·10  $13{\cdot}10\pm0{\cdot}08$ 

12:9

 $13.81 \pm 0.12$  $13.30 \pm 0.12$  $10.15 \pm 0.06$ 

 $16.35 \pm 0.13$ 

0.0∉

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 $9.95 \pm 0.05$  $12.30 \pm 0.08$ 

 $11.90 \pm 0.07$  $16 \cdot 10 \pm 0 \cdot 02$  $19.35 \pm 0.05$ 23-05 ± 0-07

 $\mathbf{15{\cdot}40}\pm\mathbf{0{\cdot}05}$  $22.33 \pm 0.06$  $27.32 \pm 0.07$ ± 0.04

CX3 CX2 S υ

TABLE

ionization poter tials

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potential should be progressively lowered in the series  $\cdot CF_3$ ,  $\cdot CCl_3$  and  $\cdot CBr_3$ , the difference being most marked between the first and second members of the series. The use of mechanism(2) would have the effect of raising  $I(\cdot CBr_3) \sim 11.4 \text{ eV}$ , i.e. greater than that of even  $\cdot CF_3$  which is unlikely from the high electron affinity of fluorine.

The second ion  $(\overset{+}{C}X_2)$  can arise by any of the processes

$$CX_4 + \boldsymbol{e} \to \overset{+}{C}X_2 + 2X \cdot + 2\boldsymbol{e}, \tag{4}$$

$$\mathbf{CX}_4 + \mathbf{e} \rightarrow \mathbf{C}\mathbf{X}_2 + \mathbf{X}_2 + 2\mathbf{e}, \tag{5}$$

$$\cdot CX_3 + \boldsymbol{e} \to CX_2 + X \cdot + 2\boldsymbol{e}, \tag{6}$$

and is considered to proceed by reaction (5). Thus

$$A(CX_2) \ge I(CX_2) + D(X-CX_3) + D(X-CX_2) - D(X-X),$$
 (7)

where D(X-X) is the bond dissociation for the appropriate halogen molecule (see table 4). Substituting the measured values of the appearance and ionization potentials and the previously determined bond-dissociation energies,

$$D(F-CF_2) \le 5.43 \pm 0.29 \text{ eV},$$
  
 $D(Cl-CCl_2) \le 2.36 \pm 0.22 \text{ eV},$   
 $D(Br-CBr_2) \le 2.00 \pm 0.22 \text{ eV}.$ 

and

The value for  $D(Cl-CCl_2)$  is in good agreement with the value of 2.69  $\pm$  0.31 eV preferred by Blanchard and Le Goff.<sup>23</sup>

This choice of reaction process is supported for CCl<sub>4</sub>, by the consideration that the radical  $\cdot$ CCl<sub>2</sub> is now proposed as a reaction intermediate in the formation of phenolic aldehydes by the Reimer-Tiemann reaction.<sup>24</sup> Consequently, it must be considered to be fairly readily formed and to possess some stability. These conclusions suggest that the dissociation energy of the second bond in CCl<sub>4</sub> should not be much greater than the first, and equally that the third dissociation energy D(CI-CCl) should not be less than the second.

Decomposition of carbon tetrabromide, according to eqn. (4) would lead to a bond-dissociation energy smaller than the above by the amount D(Br-Br)=1.97eV, i.e.  $D(Br-CBr_2) \sim 0$ . Consequently, the removal of the first bromine would be followed by the ready loss of the second and the mass-spectrum would show little evidence for the CBr<sub>3</sub><sup>+</sup> ion.

This is contrary to the experimental observations in which this species is the most abundant in the spectrum at the electron accelerating voltages investigated (table 2). This mechanism has therefore been rejected.

TABLE 2

electron energy eV	species (rel. abundance)			
	CBr <sub>3</sub> +	CBr <sub>2</sub> +	CBr+	C+
20	9.47	4.61	1.00	—
35	2.70	0.68	1.00	0.04
50	1.40	0.80	1.00	0.02

Similar conclusions are reached for the decomposition of carbon tetrachloride by this mechanism which leads to  $D(Cl-CCl_2) \sim 0 \text{ eV}$ , although  $CCl_3^+$  is the most abundant ion in the mass-spectrum.<sup>25</sup> The discussion of reaction (6) which is considered a less likely alternative is given later.

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The four mechanisms for the possible dissociations to give CX are

$$CX_4 + e \rightarrow CX + 3X \cdot + 2e, \qquad (9)$$

$$CX_4 + e \rightarrow \dot{C}X + X_2 + X \cdot + 2e, \qquad (10)$$

$$\bullet CX_3 + e \to CX + 2X \bullet + 2e, \tag{11}$$

$$\cdot \mathbf{C}\mathbf{X}_3 + \boldsymbol{e} \to \mathbf{C}\mathbf{X} + \mathbf{X}_2 + 2\boldsymbol{e}, \tag{12}$$

of which (10) has been preferred. This leads, on the substitution of the measured values and derived bond energies to  $D(F-CF) \le 4.48 \pm 0.59$  eV,  $D(Cl-CCl) \le 3.45 \pm 0.49$  eV, and  $D(Br-CBr) \le 3.73 \pm 0.60$  eV.

Reaction (9) has been discarded for the following reasons. First, the simplest and most consistent reaction sequence is that which preserves a unity in the nature of the successive bond-dissociation processes. Thus it is considered improbable that the ion  $C_X^+$  will be formed by the elimination of three halogen atoms if  $C_{X_2}^+$ was formed by the elimination of a halogen molecule. Secondly, in the particular case of the formation of  $C_{X_1}^-$ , reaction (9) leads to  $D(CI-CCI) \sim 0 \text{ eV}$ , which is an absurd conclusion.

The remaining bond energy D(X-C) was obtained by an examination of the appearance potential of  $\overset{+}{C}$  derived from each halide. Assigning the probable mechanisms,

$$CX_4 + \boldsymbol{e} \rightarrow \overset{+}{C} + X_2 + 2X \cdot + 2\boldsymbol{e}, \qquad (13)$$

to the complete dissociation,

and

$$D(F-C) \le 4.72 \pm 1.02 \text{ eV},$$
  
 $D(Cl-CCl) \le 5.33 \pm 0.90 \text{ eV},$   
 $D(Br-C) \le 3.56 + 0.75 \text{ eV}$ 

are obtained. It will be shown subsequently that the other possible mechanism

$$CX_4 + \boldsymbol{e} \rightarrow \overset{+}{C} + 2X_2 + 2\boldsymbol{e} \tag{14}$$

does not produce consistent nor probable values for the latent heat of carbon.

As the following summary of the bond dissociation energies show, there is a regular variation in these in the three halides studied within the rather wide limits of experimental error.

TABLE 3

dissociation energy (eV) bond F Br Cl X-CX3  $5.25 \pm 0.11$  $\textbf{3.12} \pm \textbf{0.12}$  $2.16 \pm 0.05$  $2.00 \pm 0.22$  $X - CX_2$ 5·43 ± 0·29  $2.36 \pm 0.22$ X---CX  $4.48 \pm 0.59$  $3.45 \pm 0.49$  $3.73 \pm 0.42$ X-C  $4.72 \pm 1.02$  $5.33 \pm 0.90$  $3.56 \pm 0.75$ 

The use of other mechanisms as general ones does not produce such good agreement within the series and this suggests that the assumptions made are probably correct. In particular the choice of the reaction sequence (6, 11) and

$$\cdot \mathbf{C}\mathbf{X}_3 + \boldsymbol{e} \to \mathbf{C} + 3\mathbf{X} \cdot + 2\boldsymbol{e}, \tag{15}$$

whilst having little effect on the magnitude of the bond-dissociation energies for X = Cl, Br yields for X = F a result  $D(F-CF_2) \sim 9.0$  eV, which is inconsistent with the general trend and magnitude of the other values.

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(16)

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The latent heat of sublimation of carbon is obtained by the following thermochemical cycle.16

$$C(s) + 2X_2 \rightarrow CX_4(g) - \Delta H_f$$

$$C(s) \rightarrow C(g) \qquad \mathscr{L}(C)$$

$$C(g) + 4X \cdot \rightarrow CX_4(g) \qquad \Sigma D(X)$$

$$4X \cdot \rightarrow 2X_2 \qquad 2D(X-X),$$

$$D(X-CX_3) + D(X-CX_2) + D(X-CX) + D(X-C);$$

where  $\Sigma D(X)$  $\mathscr{L}(\mathbf{C}) = \Sigma D(\mathbf{X}) - \Delta H_f(\mathbf{C}\mathbf{X}_4, g) - 2D(\mathbf{X} - \mathbf{X}).$ rearranging,

The values of  $\Sigma D(X)$  cannot be obtained with sufficient accuracy, by adding the appropriate bond energy values listed above, to determine unambiguously the most probable value of the latent heat. However, by a consideration of the bond energies and the mechanisms of fission, it is possible to relate the appearance potential of the carbon ion to the successive bond energies. The mechanism chosen for the final bond dissociation includes the stages of all the preceding fragmentations, and accordingly

$$A(\dot{C}) \ge I(C) + D(X-CX_3) + D(X-CX_2) + D(X-CX) + D(X-C) - D(X-X),$$
  
whence  $A(\dot{C}) - I(C) + D(X-X) \ge \Sigma D(X).$  (16)

whence

+

Since the probable error in a single mass-spectrometer determination is smaller than the summation of such errors associated with the evaluation of the bonddissociation energies, this relation (16) allows of a more exact estimate of  $\Sigma D(X)$ .

TABLE 4

F	Cl	Br		
9.45 26	1.06 1c	0.390 27		
1.65 <sup>1</sup> d	2·476 1e	1·97 1 <i>f</i>		
$19.88\pm0.04$	$14 \cdot 26 \pm 0 \cdot 07$	11·45 $\pm$ 0·06		
$7.13 \pm 0.04$	$8.20 \pm 0.07$	$7.12\pm0.06$		
	F 9.45 $^{26}$ 1.65 $^{1d}$ 19.88 $\pm$ 0.04 7.13 $\pm$ 0.04	FCl $9.45\ 26$ $1.06\ 1c$ $1.65\ 1d$ $2.476\ 1e$ $19.88\ \pm\ 0.04$ $14.26\ \pm\ 0.07$ $7.13\ \pm\ 0.04$ $8.20\ \pm\ 0.07$		

By a consideration of these results, together with a knowledge of the spectroscopically permitted values, it is concluded that  $\mathscr{L}(C) = 7.386 \text{ eV}$ . This is the maximum allowable, and the probable error in the present determinations of the latent heat is so small as to exclude consideration of the next lower value 6.13 eVprovided the particles produced in the electron-impact-induced decompositions of these halides are formed without kinetic energy and in their lowest electronic states. The choice of reaction (14) would lead to values of  $\mathscr{L}(C) \sim 8.8 \text{ eV}$ , 10.7 eV, and 9.1 eV respectively, values much greater than 7.386 eV. This, provided that the above assumptions are correct, together with the discordant values obtained for the latent heat by this mechanism, are considered to exclude it as an alternative process.

The selected reaction scheme is applicable to all the halides studied and has been preferred to a possible series of special mechanisms which may differ for the different halides, and for the various stages within any series. Other possible general mechanisms yield a higher value for the latent heat-greater than the maximum spectroscopic value. Thus, if CF is considered as derived from •CF<sub>3</sub> radicals present, the value of  $\mathscr{L}(C)$  will be increased by  $D(F-CF_3) \sim 5.25 \text{ eV}$ .

Errors in the determination of  $I(CX_2)$  and I(CX), provided they are not so great as to lead to an erroneous choice of mechanism, will not affect the value of  $\mathscr{L}(C)$ . This value depends upon a series of thermochemical quantities, the ionization

potential of carbon and the appearance potential of  $\mathbf{C}$  which is the only accurate mass-spectrometric determination required.

These studies are being continued, both on the halogen containing derivatives of methane and on the possible formation of excited radicals under certain electron impact conditions.

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