STUDIES IN ELECTRON IMPACT METHODS

PART 6.—THE FORMATION OF THE METHINE AND CARBON IONS

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The mechanism proposed in a previous communication has been extended to a series of related compounds CH_3X where X = H, Br, Cl, CN, I and OH, to CH_2Cl_2 and to $CHCl_3$. Bond-dissociation energies have been derived using $\mathscr{L}$(C) = 7·386 eV and it is suggested that both the formation of the methine ion and the carbon ion are associated with about 3 eV of excess energy. The ionization potentials of the radicals $\cdot CH_2Cl$, $\cdot CHCl_2$, $\cdot CH_2Br$ and $\cdot CHBr_2$ have also been determined.

The evidence in favour of the highest spectroscopically allowed value $\mathscr{L}$(C) = 7·386 eV, some of which has been previously summarized,[1] has been further supported by a determination of the excess energy associated with the electron impact-induced dissociation of methane.[2] A re-investigation of the ultra-violet absorption spectrum of carbon monoxide [3] also supports this value.

EXPERIMENTAL

The apparatus and the technique have been previously described [4] but has been somewhat modified for the production of $\cdot CHCl_2$ radicals. A mixture of $CHCl_3$ and CCl_4 was passed over a heated tungsten wire when the required radical was obtained. The radical was present in low concentration only, but there was sufficient of it for the determination of the ionization potential. In the determination of all the ionization potentials, higher breaks in the ion current against accelerating voltage graphs were observed. Only the lowest values, which are considered to be the potential of the ground-state are discussed here.

RESULTS

The following tables include the values found in the present study. Standard deviations are recorded with the experimental values.

TABLE 1

CH_3X	$D(CH_3—X)$ eV[a]	$D(H—X)$ eV	$A(C\overset{+}{H})$ eV	$A(\overset{+}{C})$ eV	(D_2+D_3+E) eV	
X = H	4·12	4·52	23·0[5]	26·8[5]	12·27[b]	12·46[c]
			22·4 ± 0·1[6]		11·67[d]	
Cl	3·40	4·45	22·5 ± 0·06	26·25 ± 0·1	12·49	12·63
Br	2·33	3·75	21·41 ± 0·05		12·47	
I	2·30	3·06	21·2 ± 0·20		12·29	
CN	4·47	4·94	22·4 ± 0·20	27·0 ± 0·3	11·74	12·73
OH	3·95	5·03	22·31 ± 0·09		12·26	

I(C) ≈ 11·27 eV, [7a]
$I(\cdot CH)$ = 11·13 eV, [8]
$I(CH_2)$ = 11·9 + 0·1 eV, [9]
$I(CH_3)$ = 9·95 ± 0·02 eV.[10]

(*a*) The bond-dissociation energies $D\ (CH_3—X)$ that have been obtained in this study are in good agreement with the values of previous workers [5] and also with the thermochemically derived values.

(*b*) The values listed in this column are obtained from the measured appearance potentials of the methine ion.

(*c*) These figures are obtained from $A(\overset{+}{C})$ measurements.

(*d*) The second result is quoted to enable that for acetonitrile obtained by the same authors to be compared with the other results listed.

TABLE 2

species (X—Y)	appearance potential eV $(\overset{+}{X})$	ionization potential eV (X·)	bond-dissociation energy eV (X—Y)
$CH_2Cl—Cl$	12·89 ± 0·03	9·70 ± 0·09	3·19 ± 0·12
$CHCl_2—H$	13·00 ± 0·10	9·54 ± 0·10	3·46 ± 0·20
$CHCl_2—Cl$	12·43 ± 0·02		2·89 ± 0·12
$CH_2Br—Br$	10·93 ± 0·04	8·34 ± 0·11	2·59 ± 0·15
$CHBr_2—Br$	10·80 ± 0·01	8·13 ± 0·16	2·67 ± 0·17

DISCUSSION

It has been suggested [1] that the step-wise fragmentation of the molecules CF_4, CCl_4 and CBr_4 produces a reasonable and consistent value for the latent heat of sublimation of carbon by assuming a common dissociative process for all members of the series. This argument is now extended to the decomposition of the molecules CH_3X where X = H, Br, Cl, CN, I and OH.

To relate $\mathscr{L}(C)$ to the heat of formation of CH_3X it is necessary to determine the sum of four bond-dissociation energies. The first of these $D(CH_3—X)$ is, however, well known from thermochemical studies and the last $D(C—H) = 3·47$ eV has been obtained spectroscopically.[12a] The problem thus reduces to the evaluation of the sum $D(CH_2—H) + D(CH—H) = D_2 + D_3$. The ionization potentials $I(\cdot CH)$ and $I(C)$ have already been established and thus $D_2 + D_3$ can be obtained by a single mass-spectrometric determination of either $A(\overset{+}{C}H)$ or $A(\overset{+}{C})$.

The mechanism proposed for the formation of the methine and carbon ions consistent with that previously proposed is

$$e + CH_3X \rightarrow \overset{+}{C}H_3X + 2e$$

$$\overset{+}{C}H_3X \rightarrow \overset{+}{C}H + H_2 + X\cdot \qquad (1)$$

$$\overset{+}{C}H_3X \rightarrow \overset{+}{C} + H_2 + X\cdot + H\cdot \qquad (1a)$$

or

$$\overset{+}{C}H_3X \rightarrow \overset{+}{C}H + HX + H\cdot \qquad (2)$$

$$CH_3X \rightarrow \overset{+}{C} + HX + 2H\cdot \qquad (2a)$$

depending on whether or not $D(H—H) > D(H—X)$. In the former case, eqn. (1), (1*a*) are appropriate, otherwise (2), (2*a*) are used. Accordingly $A(\overset{+}{C}H)$ and $A(\overset{+}{C})$ are related to $I(CH)$ and $I(C)$ by

$$A(\overset{+}{C}H) - I(\cdot CH) - D(CH_3—X) + F = D_2 + D_3 + E,$$

and

$$A(\overset{+}{C}) - I(C) - D(CH_3—X) - D(C—H) + F = D_2 + D_3 + E,$$

where $F = D(H—H)$ or $D(H—X)$ whichever is the greater and E represents the total excess energy, electronic, vibrational and kinetic. $D_2 + D_3 + E$ obtained from the measured potentials $A(\overset{+}{C}H)$ is constant. The values of this sum, obtained from the $A(\overset{+}{C})$ measurements are all of this magnitude and are, moreover, the same within the rather large limits of experimental error. This suggests that the mechanism chosen is applicable to all the compounds here studied.

The spectroscopically preferred value of $\mathscr{L}(C) = 7·386$ eV leads to a thermochemically derived value of $D_2 + D_3 = 9·09$ eV. Taking an average observed value of $D_2 + D_3 + E = 12·34$ eV, $E = 3·25$ eV is obtained.

The choice of an alternative mechanism in which $\overset{+}{\mathrm{CH}}$ or $\overset{+}{\mathrm{C}}$ and neutral atoms are obtained is inconsistent with the presently preferred value of $\mathscr{L}(\mathrm{C})$. In general, errors in the determination of appearance potentials lead to an over-estimate of these quantities. The present values are too small for this alternative decomposition.

The simplest interpretation of the presence of excess energy is that it is associated with a common step in the reactions giving $\overset{+}{\mathrm{CH}}$ and $\overset{+}{\mathrm{C}}$, when E may be expected to be constant. As already mentioned, the values of $D(\mathrm{CH_3—X})$ obtained by electron impact-induced dissociations are in good agreement with those obtained by other methods and hence for these $E \sim 0$.

Assuming the reaction

$$e + \mathrm{CH_3X} \rightarrow \overset{+}{\mathrm{CH_2}} + \mathrm{HX} + 2e,$$

which is consistent with the other members of the series,

$$A(\overset{+}{\mathrm{CH_2}}) - I(\mathrm{CH_2}) - D(\mathrm{CH_3—X}) + D(\mathrm{H—X}) = D(\mathrm{CH_2—H}) + E = D_2 + E.$$

The value of $I(\mathrm{CH_2})$ is known and the measured values of $A(\overset{+}{\mathrm{CH_2}})$ are 15·6,[5] 15·00 ± 0·02 eV, 14·60 ± 0·05 eV, 14·8 ± 0·4 eV,[5] 15·62 ± 0·04 eV,[11] and 15·07 ± 0·1 eV for the molecule $\mathrm{CH_3X}$ where X = H, Cl, Br, I, CN and OH. Consequently the quantity $D_2 + E = 4{\cdot}1$ eV, 4·15 eV, 4·12 eV, 3·86 eV, 4·19 eV and 4·19 eV which, omitting the value for $\mathrm{CH_3I}$ because of the larger experimental error gives an average of 4·15 eV.

Evidence as to the mechanism of the reaction,

$$\mathrm{CH_2Cl_2} + 2\,\mathrm{Na} \rightarrow \mathrm{CH_2} + 2\,\mathrm{NaCl},$$

obtained by Bawn and Dunning[13] has enabled Laidler and Casey[14] to derive $D(\mathrm{CH_2—H}) = 3{\cdot}9$ eV which is in good agreement with the above, and suggests that the present value of $I(\mathrm{CH_2})$ is not greatly in error. Thus $E \sim 0$ and the excess energy must be associated with the fragmentation which leads to the methine ion. One possibility is that this ion is obtained in an electronically excited state. The energy of the transition $\overset{+}{\mathrm{CH}}(X, {}^1\Sigma^+) \rightarrow (A, {}^1\Pi) = 2{\cdot}99$ eV which is in good agreement with the observed value of E. Although using a rather different mechanism, such a conclusion has previously been reached by Langer, Hipple and Stevenson[9] for the decomposition of methyl and methylene radicals. However, the electron configuration of the excited ion $K(2s\sigma)^2(2p\sigma)(2p\pi)\colon {}^1\Pi$ suggests that decomposition of the $\overset{+}{\mathrm{CH_3X}}$ ion has occurred in such a way as to break the two two-electron bonds in the ion but leave the single electron carbon-hydrogen bond intact—a seemingly unlikely occurrence. Alternatively the excess energy, vibrational or translational, may arise in the course of the rather extensive fragmentation of the molecule. This would be consistent with observation if this energy term was localized around one or more of the C—H bonds as these are common to all the molecules. Further substitutions of the hydrogens by halogens in the molecule may then alter the magnitude of E. This needs rather precise measurements of ionization potentials of the form $I(\mathrm{CHX})$ and $I(\cdot\mathrm{CX})$ and experiments upon these are continuing.

The electron-impact induced dissociation of $\mathrm{CH_2Cl_2}$ and $\mathrm{CHCl_3}$ have also been examined. Assuming the corresponding dissociative mechanism,

$$e + \mathrm{CH_2Cl_2} \rightarrow \overset{+}{\mathrm{CH}} + \mathrm{HCl} + \mathrm{Cl}\cdot + 2e,$$

$$A(\overset{+}{\mathrm{CH}}) = 21{\cdot}72 \pm 0{\cdot}04\ \mathrm{eV},$$

$$D(\mathrm{CH_2Cl—Cl}) + D(\mathrm{CH_2—Cl}) + D(\mathrm{CH—H}) + E = 15{\cdot}02\ \mathrm{eV}.$$

Combining $\mathscr{L}(\mathrm{C}) = 7{\cdot}386$ eV, $\Delta H_f(\mathrm{CH_2Cl_2}, g) = -\ 0{\cdot}91$ eV,[15] $D(\mathrm{H{-}H}) = 4{\cdot}52$,[15] and $D(\mathrm{Cl{-}Cl}) = 2{\cdot}476$ eV [7b], a thermochemically derived value for the sum of these bond-dissociation energies of 11·85 eV is obtained, whence $E = 3{\cdot}19$ eV. Chloroform, using the analogous mechanism, the experimentally determined $A(\overset{+}{\mathrm{C}}\mathrm{H}) = 22{\cdot}90 \pm 0{\cdot}04$ eV, and $\Delta H_f(\mathrm{CHCl_3}, g) = -\ 1{\cdot}06$ eV,[15] yields $E = 3{\cdot}30$ eV. In a similar way the values of $E = 3{\cdot}30 \pm 0{\cdot}10$ eV and $3{\cdot}37 \pm 0{\cdot}05$ eV are obtained from the measured appearance potentials $A(\overset{+}{\mathrm{C}}) = 25{\cdot}45 \pm 0{\cdot}1$ eV and $24{\cdot}62 \pm 0{\cdot}05$ eV of these compounds.

Similar measurements have been made upon $\mathrm{CH_2Br_2}$ and $\mathrm{CHBr_3}$ yielding $A(\overset{+}{\mathrm{C}}\mathrm{H}) = 21{\cdot}55 \pm 0{\cdot}05$ eV and $21{\cdot}70 \pm 0{\cdot}05$ eV, and $A(\overset{+}{\mathrm{C}}) = 24{\cdot}52 \pm 0{\cdot}05$eV and $23{\cdot}55 \pm 0{\cdot}05$ eV respectively. It has been pointed out by Cottrell,[7c] however, that the heats of formation of these compounds are " calculated " and not purely experimental quantities.

The ionization potentials of certain halogenomethyl radicals have been determined (table 2) and it is found that there is a progressive lowering of this value with the successive replacement of the hydrogen by chlorine as shown in the series $I(\cdot\mathrm{CH_3}) = 9{\cdot}95 \pm 0{\cdot}03$ eV,[10] $I(\cdot\mathrm{CH_2Cl}) = 9{\cdot}70 \pm 0{\cdot}09$ eV, $I(\cdot\mathrm{CHCl_2}) = 9{\cdot}54 \pm 0{\cdot}10$ eV, and $I(\cdot\mathrm{CCl_3}) = 8{\cdot}75 \pm 0{\cdot}05$ eV.[16] Replacement of hydrogen by bromine further lowers this energy $I(\cdot\mathrm{CH_2Br}) = 8{\cdot}34 \pm 0{\cdot}11$ eV and $I(\cdot\mathrm{CHBr_2}) = 8{\cdot}13 \pm 0{\cdot}16$ eV. A similar drop in value has previously been noticed for $I(\cdot\mathrm{CCl_3})$ and $I(\cdot\mathrm{CBr_3})$.[1] This weakening effect is also apparent in the dissociation energies of the carbon—hydrogen bonds; $\sim$ 1 eV less energy is required to break such a bond in $\mathrm{CH_2Cl_2}$ than in $\mathrm{CH_4}$.

Knowledge of $I(\cdot\mathrm{CH_2Cl})$ and $A(\overset{+}{\mathrm{C}}\mathrm{H_2Cl})$ leads to $D(\mathrm{CH_2Cl{-}Cl}) = 3{\cdot}19 \pm 0{\cdot}12$ eV. The probable value of $D(\mathrm{CH{-}H})$ is $\sim 5{\cdot}2$ eV and substitution of these into

$$D(\mathrm{CH_2Cl{-}Cl}) + D(\mathrm{CH_2{-}Cl}) + D(\mathrm{CH{-}H}) = 11{\cdot}83 \text{ eV},$$

yields $D(\mathrm{CH_2{-}Cl}) \sim 3{\cdot}5$ eV. This result in which the first two dissociation energies of methylene chloride are nearly the same is consistent with the results from methane, $\mathrm{CF_4}$ and $\mathrm{CBr_4}$, and suggests that the value of $I(\cdot\mathrm{CH_2Cl})$ is a fairly reliable one. This may also be confirmed by the measurement of the ionization potentials of the radicals mentioned above.

[1] Reed and Snedden, *Trans. Faraday Soc.*, 1958, **54,** 949.

[2] Morrison and Stanton, *J. Chem. Physics*, 1958, **28,** 9.

[3] Tanaka, Jursa and LeBlanc, *J. Chem. Physics*, 1957, **28,** 862.

[4] Reed, *Trans. Faraday Soc.*, 1956, **52,** 1195.

[5] Field and Franklin, *Electron Impact Phenomena and the Properties of Gaseous Ions* (New York, 1957, Academic Press Inc.), p. 246.

[6] McDowell and Warren, *Faraday Soc. Discussions*, 1951, **10,** 53.

[7] Cottrell, *The Strengths of Chemical Bonds* (London, Butterworths, 1954), (*a*) p. 90; (*b*) p. 171; (*c*) p. 251.

[8] Douglas and Herzberg, *Can. J. Research A*, 1942, **20,** 71.

[9] Langer, Hipple and Stevenson, *J. Chem. Physics*, 1954, **22,** 1836.

[10] Lossing, Ingold and Henderson, *J. Chem. Physics*, 1954, **22,** 621.

[11] McDowell and Warren, *Trans. Faraday Soc.*, 1952, **48,** 1084.

[12] Herzberg, *Molecular Spectra and Molecular Structure*: 1. *Spectra of Diatomic Molecules*, 2nd ed. (New York, 1950, van Nostrand), (*a*) p. 518; (*b*) p. 519.

[13] Bawn and Dunning, *Trans. Faraday Soc.*, 1939, **35,** 185.

[14] Laidler and Casey, *J. Chem. Physics*, 1949, **17,** 1087.

[15] *Selected Values of Chemical Thermodynamic Properties* (Nat. Bur. Stand., circ. 500, 1952).

[16] Farmer, Lossing, Henderson and Marsden, *J. Chem. Physics*, 1956, **24,** 348.