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Free Radicals by Mass Spectrometry. IX. Ionization Potentials of CF_3 and CCl_3 Radicals and Bond Dissociation Energies in Some Derivatives*

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The vertical ionization potentials of CF_3 and CCl_3 radicals, as measured by electron impact, are 10.10 ± 0.05 and 8.78 ± 0.05 v respectively. From the appearance potentials of the CF_3^+ and CCl_3^+ ions from derivatives, the heats of formation of CF_3 and CCl_3 radicals were found to be -117 ± 2 kcal/mole and $+13.4 \pm 3$ kcal/mole respectively, assuming that no excess energy was included in the appearance potentials. From this data and other heats of formation the following bond dissociation energies (in kcal/mole) have been evaluated:

$$D(CCl_3-H) = 88.9 \pm 3$$
$$D(CCl_3-F) = 102 \pm 7$$
$$D(CCl_3-Cl) = 67.9 \pm 3$$
$$D(CCl_3-Br) = 49.5 \pm 3$$

$$D(CF_3-H) = 103 \pm 4$$
$$D(CF_3-F) = 121 \pm 4$$
$$D(CF_3-Cl) = 83 \pm 3$$

INTRODUCTION

THE presence of CCl_3 radicals in a variety of reactions has been postulated by a number of authors,[1] and it appears to be well established that the radicals are quite stable at moderate temperatures. Values for the dissociation energies of the CCl_3-H, CCl_3-Cl, and CCl_3-Br bonds have been derived from kinetic data. From the results of Braunwarth and Schumacher[2] on the photobromination of chloroform, Szwarc has calculated[3] that $D(CCl_3-H) = 89 \pm 2$ kcal/mole. An upper limit of 70 kcal/mole for $D(CCl_3-Cl)$ has been quoted by Szwarc[3] from unpublished work of Miller and Willard on the bromination of CCl_4. No other values of $D(CCl_3-Cl)$ appear to have been published. A number of values for $D(CCl_3-Br)$ ranging from 45 to 57 kcal/mole are given in Szwarc's review,[3] but the most reliable value for this bond is probably that of 49.0 kcal/mole[4,5] obtained from pyrolysis data. No estimates of $D(CCl_3-F)$ appear to have been published.

The data available on CF_3-X bonds is much less complete, and the only value which has been reported is that of $D(CF_3-Br) = 64.5$ kcal/mole,[4,5] obtained from the pyrolysis of CF_3Br. Although the heats of formation of CF_4, CF_3H, and CF_3Cl are now available, values of $D(CF_3-X)$ in these compounds cannot be derived from the value for $D(CF_3-Br)$ since the heat of formation of CF_3Br is not known.

In view of the limited amount of data on CCl_3-X and CF_3-X bonds, it was thought that measurement of the ionization potentials of the radicals and the ap-

propriate appearance potentials might provide useful estimates of the bond dissociation energies from the relation[6]

$$D(R-X) \leqslant A(R^+) - I(R).$$

It should be noted that this relation holds only if there is no interference by negative ion formation.

PRODUCTION OF RADICALS

For the present purpose the simplest method of obtaining a high concentration of CCl_3 radicals would appear to be by the pyrolysis of CCl_3Br[4,5] in a flow system. However at the elevated temperature ($\sim 750°C$) required to decompose CCl_3Br completely in a contact time of about 0.001 sec, it was found that the decomposition did not proceed solely by

$$CCl_3Br \rightarrow CCl_3 + Br$$
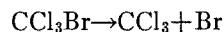
but in addition a proportion of the C–Cl bonds were broken. Attempts to prepare CCl_3I, which should dissociate at a lower temperature, resulted in a very impure product. It was found, however, that the thermal decomposition of chloropicrin resulted in a satisfactory yield of CCl_3 radicals either in a medium pressure reactor with 3 mm of helium[7] or in the low-pressure capillary reactor previously described.[8] In addition to CCl_3 radicals and the combination product C_2Cl_6, other products found were NO_2Cl, NO, $COCl_2$, C_2Cl_4, and Cl_2. These products suggest the presence of CCl_2 radicals as well, and low electron energy experiments indicated the presence of these radicals, but only at energies greater than $I(CCl_3)$. Without further work this identification cannot be regarded as unambiguous because of the possibility that the CCl_2^+ ions observed were produced from CCl_3 radicals by electron impact. The products may be accounted for by the following

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‡ Guest Worker.
[1] E. W. R. Steacie, *Atomic and Free Radical Reactions* (Reinhold Publishing Corporation, New York, 1954), second edition.
[2] V. Braunwarth and H.-J. Schumacher, Kolloid Z. **89**, 184 (1939).
[3] M. Szwarc, Chem. Revs. **47**, 75 (1950).
[4] A. H. Sehon and M. Szwarc, Proc. Roy. Soc. (London) **A209**, 110 (1951).
[5] M. Szwarc and A. H. Sehon, J. Chem. Phys. **19**, 656 (1951).
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[7] F. P. Lossing and A. W. Tickner, J. Chem. Phys. **20**, 907 (1952).
[8] J. B. Farmer and F. P. Lossing, Can. J. Chem. **33**, 861 (1955).

reactions:

$$CCl_3NO_2 \rightarrow CCl_3 + NO_2 \tag{1}$$

$$CCl_3NO_2 \rightarrow CCl_2 + NO_2Cl \tag{2}$$

$$CCl_3NO_2 \rightarrow COCl_2 + NO + Cl \tag{3}$$

$$2CCl_3 \rightarrow C_2Cl_6 \tag{4}$$

$$2CCl_2 \rightarrow C_2Cl_4 \tag{5}$$

$$2Cl \rightarrow Cl_2 \tag{6}$$

$$NO_2 \rightarrow NO + O. \tag{7}$$

Reaction (3) is the mode of decomposition proposed for the homogeneous decomposition by Steacie and Smith[9] and by Ashmore and Norrish.[10] The presence of Cl atoms was suggested by the latter to explain the action of chloropicrin as a sensitizer for the hydrogen-chlorine and hydrogen-oxygen reactions. Although the products shown in reactions (1)–(7) may have resulted from surface reactions even in the presence of 3 mm of helium, these results suggest that the sensitizing action of chloropicrin may be a result of the formation of CCl_3 and possibly CCl_2 radicals as well as Cl atoms. The relative rates of the three modes of decomposition, Eqs. (1)–(3) were not measured, but it was apparent from the size of the net peaks for CCl_3 radicals at 680°C that reaction (1) accounted for at least one-half of the chloropicrin decomposed. The only product which gave an interfering peak at mass 117 (CCl_3^{35}) was C_2Cl_6, and its contribution at this mass was determined from the ratio $CCl_3^+/C_2Cl_5^+$ measured on a pure sample of C_2Cl_6.

The production of a concentration of CF_3 radicals sufficient for ionization potential measurements proved to be much more difficult, chiefly because of the reaction between CF_3 and quartz at elevated temperatures to give SiF_4 and CO_2. Attempts to prepare CF_3 radicals from $Hg(CF_3)_2$ using the capillary reactor were unsuccessful for this reason. A coating of aquadag applied to the inside walls of the capillary reactor to reduce the action of CF_3 radicals on the quartz resulted in the formation of HF and products other than CF_3, possibly as a result of catalytic action. The use of $Hg(CF_3)_2$ in the medium pressure reactor was precluded by its low vapor pressure. A good yield of CF_3 radicals was finally obtained using hexafluoroazomethane (CF_3NNCF_3) carried in helium at 5 mm pressure in the medium pressure reactor. The presence of the large excess of helium evidently served to suppress the reaction of CF_3 radicals with the wall of the reactor by reducing the mean free path.

Since the parent peak of CF_3NNCF_3 at mass 166 was too small to be detected, it was difficult to determine the extent of decomposition of the CF_3NNCF_3 at a given temperature. Other peaks in the spectrum, such

as CF_3NN^+, were also found to be unsuitable for this purpose. The temperature at which the CF_3NNCF_3 was completely decomposed could be determined, although in an approximate manner, by observations of the height of the CF_3 radical peak, using low-energy electrons. It was found that this peak, which at low electron energy is a measure of the amount of CF_3 radicals, increased with temperature up to 950°C, was constant from 950° to 1050°C, and decreased slightly at higher temperatures. From this behavior it was concluded that at a temperature of about 1000°C the hexafluoro-azomethane was completely decomposed. At this temperature the combination product C_2F_6 was present in considerable amounts. The contribution of C_2F_6 to the mass 69 peak (CF_3) was determined from the ratio of $CF_3^+/C_2F_5^+$ measured on C_2F_6 added to the helium stream in the absence of CF_3NNCF_3.

IONIZATION POTENTIALS

CF_3

The method of measuring the ionization potential of the radicals was the same as that previously described.[11] The net peak height at mass 69 for the radical, using 50 v electrons, was determined from the total mass 69 peak at 1030°C by subtracting the contribution to mass 69 from C_2F_6 measured as described above. Krypton was then introduced into the gas stream at a rate sufficient to provide a mass 86 peak equal to the net mass 69 peak (about 180–200 cm). The ionization efficiency curves for mass 69 and mass 86 were then measured alternately until three pairs had been obtained. The logarithm of the ratio of the peak height at a given electron accelerating potential to the peak height at 50 v was plotted against the electron accelerating potential to give curves of the type shown previously.[11] The ionization potential of the radical was obtained from the voltage difference (δv) between the curves for CF_3 and for krypton by the method of extrapolated voltage differences.[12]

CCl_3

The method of measurement of $I(CCl_3)$ was the same as that described above. Owing to interference by CCl_2^+ in the region of mass 82–86, acetylene was used as a standard instead of krypton.

APPEARANCE POTENTIALS

In the case of dissociation processes involving the production of a halogen atom

$$CCl_4 + e \rightarrow CCl_3^+ + Cl + 2e$$

there is a possibility that an ion pair process

$$CCl_4 + e \rightarrow CCl_3^+ + Cl^- + e$$

may have a sufficient probability to cause the appear-

[9] E. W. R. Steacie and W. McF. Smith, J. Chem. Phys. **6**, 145 (1938) and Can. J. Res. **B16**, 222 (1938).
[10] P. G. Ashmore and R. G. W. Norrish, Proc. Roy. Soc. (London) **A204**, 34 (1950).

[11] Lossing, Ingold, and Henderson, J. Chem. Phys. **22**, 621 (1954).
[12] J. W. Warren, Nature **165**, 810 (1950).

ance potential to be lowered from that corresponding to the first process, by an amount which could approach the electron affinity of chlorine. Generally these processes have a small probability relative to positive ion production by the former process, but at low electron energies they may contribute significantly to the positive ion formation. In cases where this could happen a search was made for negative halogen ions. In no case were negative ions found in amounts greater than 1/1000 of the 50 v height for the positive ion. This does not mean that the ratio of production was necessarily this low since the collection efficiency for negative ions is generally lower than for positive ions. A very rough calibration for the relative collection efficiency was carried out by the method used by Marriott and Craggs.[13] The ratio O^-/O^+ with an electron energy of 35 v was found to be 1/90. From their data this gives a relative collection efficiency for negative ions of about 28% of that for positive ions, as compared to their value of about 50%. On this basis the limit for X^- production becomes 1/300. Since the appearance potential curves were measured down to 1/1000 of the 50 v positive ion peak, this amount of negative ions, if present, and if arising from ion pair formation, could cause a curvature at the lower end of the δ v vs I relation. Since this curvature was small (~ 0.1 v) in the cases for which the appearance potentials are used to calculate bond dissociation energies, it was assumed that negative ion formation did not seriously interfere with the measurements. It should be emphasized, however, that the calibration and the conclusions drawn from it are by no means rigorous.

CCl₃ Compounds

The relative abundance of the CCl_3^+ ion in the spectra of CCl_3H and CCl_3F is too small ($\sim 1\%$) to permit a precise measurement of the appearance potential. In CCl_4 and CCl_3Br the CCl_3^+ ion is in sufficient abundance and ionization efficiency curves were obtained which showed only a slight curvature at the foot as compared to the curve for the standard gas.

CF₃ Compounds

The abundance of CF_3^+ in the spectra of all the compounds studied was sufficiently large to permit measurement of the ionization efficiency curves. However, it was found that the ionization efficiency curves for CF_3^+ from CF_4 were not parallel to the curve for the standard gas, but had an appreciable extra curvature. For this reason it was difficult to evaluate $A(CF_3^+)$ from CF_4 from our data and no value is reported. Instead, the value of 15.44 ± 0.05 found by Warren and Craggs[14] was used to obtain the bond dissociation energy for CF_4.

The ionization efficiency curves for CF_3^+ from CF_3Cl, CF_3Br, and CF_3I, although appearing normal in shape, led to anomalous values for the bond dissociation energies, as discussed below.

MATERIALS

CF_3Br was prepared by reacting silver trifluoroacetate with gaseous bromine at 130°C. It was freed from CO and C_2F_6 and purified by several distillations at low pressure. The hexafluoroazomethane was a gift of Dr. J. R. Dacey of the Royal Military College, Kingston, and the $Hg(CF_3)_2$ a gift of Dr. V. H. Dibeler of the National Bureau of Standards, Washington. Other materials used were commercial products, purified if necessary by low pressure distillation.

RESULTS

Ionization Potentials

In Table I are given the individual and average values obtained for the ionization potentials of the CCl_3 and CF_3 radicals. The limits of error shown are estimated from the uncertainty in extrapolation of the δ v vs I curves. It is not surprising that $I(CCl_3)$ is less than $I(CH_3)$ since the substitution of Cl for H brings about an appreciable lowering of the ionization potential in chlorine-substituted methanes. From recent data $I(CH_4)=13.12\pm0.02$[15] and $I(CCl_4)=11.47\pm0.01$[16] from which $I(CH_4)-I(CCl_4)=1.65$ v. For comparison $I(CH_3)=9.95\pm0.03$ v[11] and hence $I(CH_3)-I(CCl_3)=1.17$ v.

The ionization potential of the CF_3 radical, 10.10 ± 0.05 v, is higher than that of CH_3 by only 0.15 v, an amount which seems surprisingly small in view of the high ionization potential of the fluorine atom (17.4 v). The ionization potential of CF_4 is not known, so no comparison can be made.

BOND DISSOCIATION ENERGIES FOR CCl₃ COMPOUNDS

The average values for the appearance potentials measured for CCl_3^+ from CCl_4 and CCl_3Br are listed in Table II, together with values for $D(CCl_3-Cl)$ and

TABLE I. Ionization potentials of CCl₃ and CF₃ radicals.

Radical	Individual values	Average
	Ionization potential (v)	
CCl₃	8.80	
	8.78	
	8.75	
	8.77	
	8.80	8.78±0.05
CF₃	10.10	
	10.07	
	10.12	10.10±0.05

[13] J. Marriott and J. D. Craggs, *Applied Mass Spectrometry* (Institute of Petroleum, London, 1954), p. 173.
[14] J. W. Warren and J. D. Craggs, *Mass Spectrometry* (Institute of Petroleum, London, 1952), p. 36.

[15] C. A. McDowell and J. W. Warren, Discussions Faraday Soc. 10, 53 (1951).
[16] K. Watanabe (private communication).

TABLE II. Appearance potentials, heats of formation, and bond dissociation energies
in kcal/mole for CCl_3 compounds.

Compound	$A(CCl_3^+)$ (ev)	$D(CCl_3-X)$ from $A(CCl_3^+)-I(CCl_3)$	ΔH_f (kcal/mole)	$D(CCl_3-X)$ from $\Delta H_f(CCl_3)$ and $\Delta H_f(CCl_3X)$	Other values of $D(CCl_3-X)$
CCl_3H	$\cdots$ a	$\cdots$	-24 b	88.9 ± 3	$89\ \pm2$ c
CCl_3F	$13.8\ \pm0.2$ d	$118\ \pm6$	$-70\ \pm4$ e	$102\ \pm7$	$\cdots$
CCl_4	$\begin{cases}11.67\pm0.1 & f \\ 11.83\pm0.05 & d\end{cases}$	68.3 ± 3	-25.5 b	$67.9\pm3^*$	$\leqslant70$ g
CCl_3Br	10.90 ± 0.1 f	48.9 ± 3	$-\ 9.4$ h	$49.5\pm3^*$	49.0 i
CCl_3	$\cdots$	$\cdots$	$+13.4\pm3$ j	$\cdots$	$\cdots$

a Low abundance.
b Reference 19.
c Reference 2,3.
d Reference 14.
e Reference 21.
f This work.
g Reference 3.
h Reference 20.
i Reference 4.
j Average of values derived from $A(CCl_3^+)$ from CCl_4 and CCl_3Br ($+14.0$ and $+12.8$ kcal/mole.)
* Denotes that these values are derived from those in column 3.

$D(CCl_3-Br)$ obtained from the relation

$$D(R-X)\leqslant A(R^+)-I(R).$$

A reliable value of the appearance potential of CCl_3^+ from CCl_3H could not be obtained since the CCl_3^+ ion is present to only about 1% of the largest peak. The same objection may be made to the value for $A(CCl_3^+)$ from CCl_3F reported by Warren and Craggs.[14]

The value for $A(CCl_3^+)$ from CCl_4, 11.67 ± 0.1 v, is in good agreement with that found by Warren and Craggs, but not with that of 12.3 v found by Baker and Tate.[17] The latter authors concluded from the near equality of the appearance potentials of CCl_3^+ and Cl^- that the process was

$$CCl_4+e\rightarrow CCl_3^++Cl^-+e.$$

If this interpretation is used, the presently reported value of $I(CCl_3)$ leads to $D(CCl_3-Cl)\sim169$ kcal/mole, using 88 kcal/mole for the electron affinity of chlorine.[18] This result is obviously much too high, and it is probable that the appearance potential does not correspond to a process of ion pair formation, but to the formation of a neutral chlorine atom. If the average of the Warren and Craggs value and the presently found value is taken, 11.75 ± 0.1 v, then $D(CCl_3-Cl)=68.3\pm3$ kcal/mole. Taken with $\Delta H_f CCl_4=-25.5$ kcal/mole and $\Delta H_f(Cl)=29.0$ kcal/mole,[19] this bond dissociation energy leads to a heat of formation of CCl_3 radicals of 14.0 ± 3 kcal/mole. The value $D(CCl_3-Br)=48.9\pm3$ kcal/mole, taken with $\Delta H_f CCl_3Br=-9.4$ kcal/mole[20] and $\Delta H_f(Br)=26.7$ kcal/mole,[19] leads to $\Delta H_f(CCl_3)=12.8\pm3$ kcal/mole. The average of these two, $\Delta H_f(CCl_3)=13.4\pm3$ kcal/mole, is given in Table II. Using this value and the heats of formation of CCl_3H[19] and CCl_3F,[21] the corresponding bond dissociation

energies were calculated and are given in Table II. $D(CCl_3-H)=88.9\pm3$ kcal/mole is in good agreement with the value of 89 ± 2 kcal/mole derived by Szwarc[3] from the data of Braunwarth and Schumacher.[2] The agreement between the value of $D(CCl_3-F)$ from the appearance potential and that from the heat of formation data is not good, but the absolute error in the appearance potential may be larger than given because of the smallness of the CCl_3^+ peak in the spectrum of CCl_3F.[14] It is of interest to compare the values for $D(CCl_3-F)$ with values for $D(CH_3-F)$ previously obtained, 107 ± 12 kcal[22] and 108 ± 5 kcal/mole.[23] It might be expected that $D(CCl_3-F)$ should be somewhat weaker than $D(CH_3-F)$ owing to repulsion by the chlorine atoms.

The dissociation energies for the CCl_3-Cl and CCl_3-Br bonds marked by an asterisk in the fifth column of Table II are derived from the values in the third column, through the average value of $\Delta H_f(CCl_3)$, and are not independent values. Although the value $D(CCl_3-Cl)\leqslant70$ kcal/mole[3] is probably rather uncertain, the agreement with the present result is satisfactory. The pyrolysis value[4,5] of $D(CCl_3-Br)=49.0$ kcal/mole is the same as the present data within experimental error.

BOND DISSOCIATION DATA FOR CF_3 COMPOUNDS

The data for bond dissociation energies of CF_3 compounds are by no means as straightforward as for the CCl_3 compounds, partly because of the lack of data on the heats of formation of CF_3Br and CF_3I, and partly because of uncertainties in the appearance potential data for CF_3Cl, CF_3Br, and CF_3I. The appearance potentials for CF_3^+ from these compounds, when combined with the value for $I(CF_3)$ lead to dissociation energy values which are quite evidently too low by an

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[22] Lossing, Ingold, and Henderson, J. Chem. Phys. 22, 1489 (1954).
[23] V. H. Dibeler and R. M. Reese, J. Research Natl. Bur. Standards 54, 127 (1955).

TABLE III. Appearance potentials, heats of formation, and bond dissociation energies for CF_3 compounds.

Compound	$A(CF_3^+)(v)$	$D(CF_3-X)$ from $A(CF_3^+)-I(CF_3)$ (kcal/mole)	ΔH_f (kcal/mole)	$D(CF_3-X)$ from $\Delta H_f(CF_3)$ and $\Delta H_f(CF_3X)$ (kcal/mole)	Other values of $D(CF_3-X)$ (kcal/mole)
CF_3H	14.53±0.05 a	102±2	−169 b	103±4*	...
CF_4	15.44±0.05 c	123±2	−220±2 d	121±4*	116.5 e
CF_3Cl	{13.06±0.05 a / 12.95±0.05 c}	...	−171±1 f	83±3	79.5±2 e
CF_3Br	(12.1 a)	...	...	...	64.5 g
CF_3I	$A(I^+)=12.9\pm0.15$	57±4	...	...	...
CF_3CH_3	14.0 h	90	...	...	117 h
CF_3CF_3	14.3 h	97	−303±2 f	69(?)	124 h
CF_3	...	...	−117±2 i	...	...

a This work.
b Reference 25.
c Reference 14.
d Reference 26.
e Reference 28.
f Reference 21.
g Reference 4.
h Reference 30.
i Average of values derived from $A(CF_3^+)$ from CF_3H and CF_4 (−118 and −115 kcal/mole).
* Denotes that these values are derived from those in column 3.

amount which approaches 1 v. A search for negative halogen ions at energies corresponding to these appearance potentials showed none present in a ratio greater than 1:300 of the positive ions as discussed above. These anomalous results are shown in brackets in Table III. The appearance potential of I^+ from CF_3I was measured, and combined with $I(I)=10.44$ v[24] leads to $D(CF_3-I)=57\pm4$ kcal/mole. This value is not greatly different from $D(CH_3-I)$.[22]

On the other hand, the appearance potentials for CF_3^+ from CF_4 and CF_3H given in Table III are consistent with the heats of formation of these compounds,[25,26] and lead to $D(CF_3-F)=123\pm2$ and $D(CF_3-H)=102\pm2$ kcal/mole. From these data and from $\Delta H_f(F)=18.3$ kcal/mole,[19,27] two values of the heat of formation of CF_3 are obtained, -118 ± 2 and -115 ± 2 kcal/mole. The average of these, 117 ± 2 kcal/mole, is in good agreement with a recent estimate of $\Delta H_f(CF_3)=-120.5$ kcal/mole, based on diffusion flame experiments.[28] In Table III are also given bond dissociation energies calculated from $\Delta H_f(CF_3)=-117\pm2$ kcal/mole and the heats of formation of CF_3H, CF_4, CF_3Cl, and C_2F_6. The agreement between these results and those of Rabinovitch and Reed is probably within the combined limits of error. Since the heat of formation of CF_3Br is not known, a thermochemical comparison cannot be made between the present data and the pyrolysis value of $D(CCl_3-Br)=64.5$ kcal/mole.[4,5]

By comparing the CF_3-H, CF_3-F, and CF_3-Cl bond with the corresponding CH_3-X bonds,[22] it is seen that the present results indicate that the $C-H$ and $C-Cl$ bonds are nearly the same in both cases, but the $C-F$ bond is considerably stronger in CF_4 than in CH_3F. The latter is consistent with the shortening of the $C-F$ bond distance in CF_4 attributed by Pauling[29] to resonance of the double-bond-ionic type.

The appearance potentials of CF_3^+ in CF_3-CH_3 and C_2F_6 reported by Dibeler, Reese, and Mohler[30] give $D(CF_3-CH_3)=90$ kcal/mole and $D(CF_3-CF_3)=97$ kcal/mole, using $I(CF_3)=10.10\pm0.05$ v. These estimates are considerably lower than those based on the same appearance potential data, but using a value of $I(CF_3)=8.9$ v derived[30] from $I(CH_3)=10.07$ v and $A(CH_3^+)$ from CF_3CH_3. The discrepancy between the derived and measured values for $I(CF_3)$ suggests that $A(CH_3^+)$ from CF_3CH_3 includes more than 1 v excess energy. The formation of CH_3^+ ions with kinetic energy from CF_3CH_3 has been reported.[31] All these values of the $C-C$ bonds seem rather high in comparison with $D(CH_3-CH_3)=83$ kcal/mole[1] and it is possible that $A(CF_3^+)$ from both compounds may also include an excess energy term.

On the other hand, the value $D(CF_3-CF_3)=69$ kcal/mole, derived from our heat of formation of CF_3 and the published heat of formation of C_2F_6, seems to be much too low. Since the value of $\Delta H_f(CF_3)=-117\pm2$ kcal/mole gives quite reasonable values for the dissociation energy of the other bonds, it appears quite possible that the reported value for the heat of formation of $C_2F_6(-303$ kcal/mole) may be in error by 10–20 kcal.

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