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SOME ASPECTS OF THE THERMOCHEMISTRY AND THERMODYNAMICS OF FLUOROCARBONS

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Abstract—The thermochemistry of some simple fluoro-compounds is discussed, and it is shown that the heats of formation of tetrafluoroethylene and of some 1:1-difluoroethylenes are anomalously low, suggesting a weakening of the double bond in these compounds as compared with that in more familiar ethylenes. This fact is shown to account for the high thermal stability of octafluoro*cyclo*butane and of polytetrafluoroethylene.

The considerable interest in fluorine-containing compounds, which is due in part to their high thermal stability, is backed by very little systematic thermodynamic data. It is the purpose of this paper to draw attention to some features of the information available.

The primary quantity to be determined is the bond-energy term for the C–F bond, and this can be derived from the heat of formation of carbon tetrafluoride. Several determinations have been made of the heat of formation of carbon tetrafluoride and the results are tabulated in Table 1. The more recent and more reliable

TABLE 1. HEAT OF FORMATION OF CARBON TETRAFLUORIDE

Value (kcal/mole)	Method of determination	Literature reference
−184	(Unspecified)	1
−162	Reaction of F_2 with charcoal (reaction did not proceed to completion)	2
−229 (corrected to graphite)	Fusion of K with CF_4	3, 4
−220·4	Reaction with F_2 with CH_4	5
−212·7	From heats of reactions: $C_2F_4 - 2O_2 \rightarrow CO_2 + CF_4$	6
−217·1	$C_2F_4 + 2H_2 \rightarrow 2C + 4HF$	7
−218·3	Combustion of Teflon–oil mixture	8
−218	Fusion of K with CF_4	9

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[1] G. Glockler, *Fluorine Chemistry* (Edited by J. H. Simons). Academic Press, New York (1950).
[2] H. von Wartenburg and R. Schutte, *Z. Anorg. Chem.* **211**, 222 (1933).
[3] H. von Wartenburg, *Z. Anorg. Chem.* **258**, 356 (1949).
[4] H. von Wartenburg, *Nachr. Ges. Wiss. Göttingen* 57 (1946).
[5] R. S. Jessup, R. E. McCoskey and R. A. Nelson, *J. Amer. Chem. Soc.* **77**, 244 (1955).
[6] H. C. Duus, *Industr. Engng. Chem.* **47**, 1445 (1955).
[7] G. A. Neugebauer and J. L. Margrave, *J. Phys. Chem.* **60**, 1318 (1956).
[8] D. W. Scott, W. D. Good and G. Waddington, *J. Amer. Chem. Soc.* **77**, 245 (1955).
[9] F. W. Kirkbride and F. G. Davidson, *Nature, Lond.* **174**, 79 (1954).

values lie in the range $\Delta H_f\,(CF_4, g)$ −210 to −230 kcal/mole, and the value −218 kcal/mole seems to be a reasonable average for our purposes.

The controversy concerning the value of the heat of atomisation of carbon makes it impossible to calculate heats of atomisation and bond-energy terms that are universally acceptable. We have thought it advisable to duplicate many of our calculations by using the two more widely accepted values for the heat of atomisation of carbon, namely

$$L_c = 171{\cdot}7 \text{ kcal}^{10} \text{ (symbol } \alpha)$$
$$L_c = 138 \text{ kcal}^{11} \text{ (symbol } \beta)$$

Using these values, and the more recent value for heat of dissociation of fluorine, namely $D(F\text{–}F) = 36{\cdot}6$ kcal/mole,[10] we obtain, respectively:

$$\alpha H_a\,(CF_4) = 463 \text{ kcal/mole}; \quad \bar{B}\,(C\text{–}F) = 116 \text{ kcal}$$
$$\beta H_a\,(CF_4) = 430 \text{ kcal/mole}; \quad \bar{B}\,(C\text{–}F) = 107{\cdot}5 \text{ kcal}$$

Owing to their acceptance of other values for $\Delta H_f\,(CF_4)$, previous authors have reported different values of $\bar{B}\,(C\text{–}F)$. Thus Glockler[1] reports $\bar{B}\,(C\text{–}F) = 110$ kcal (α) and Cottrell[11] quotes $\bar{B}\,(C\text{–}F) = 94$ kcal (β), whereas Sidgwick[12] gives $\bar{B}\,(C\text{–}F) = 117{\cdot}4$ kcal (α). Long[13] uses the value $\Delta H_f\,(CF_4) = -229$ kcal,[3] but uses the old value $D\,(F\text{–}F) = 62$ kcal/mole.[14]

Sidgwick notes that his value of $\bar{B}\,(C\text{–}F)$ from $\Delta H_f\,(CF_4)$ is much higher than that observed in compounds containing less fluorine, for which he gives the value $\bar{B}\,(C\text{–}F) = 103{\cdot}4$ kcal. That the increase of $\bar{B}\,(C\text{–}F)$ with progressive fluorination is a real effect is suggested by the following considerations. The difference in the heats of formation ($\Delta H_f\,(RF)$ and $\Delta H_f\,(RH)$) of two compounds differing only in substitution of a fluorine atom for a hydrogen atom is dependent chiefly on the difference in bond energy terms, namely:

$$\begin{aligned}\Delta &= \Delta H_f\,(R\text{–}F) - \Delta H_f\,(RH)\\ &= \bar{B}\,(C\text{–}F) - \bar{B}\,(C\text{–}H) - \tfrac{1}{2}[D\,(F\text{–}F) - D\,(H\text{–}H)]\end{aligned}$$

Using data taken from a National Bureau of Standards circular,[10] we have calculated Δ for the cases tabulated in Table 2. The relationship for Δ applies strictly only when the heats of formation refer to the gas phase. We have not attempted to correct the available heats of formation to those for the gas phase, since insufficient information is available to enable this to be done easily or precisely. We consider that the errors that arise from ignoring this correction are very much smaller than the discrepancies in Δ. For these reasons we have not corrected data for both members of a pair of substances to the same state. An error of 2–3 kcal may arise in Δ from comparing solid and liquid substances.

Our results show that for the introduction of one fluorine atom into a hydrocarbon $\Delta \simeq -40$ kcal, whereas for the introduction of a second fluorine atom on to the same carbon atom $\Delta \simeq -50$ kcal. This indicates that the mean C–F bond energy in a difluoro compound is about 10 kcal greater than that in a monofluoro compound and that, whereas the former quantity is about 105 kcal, the latter must be about

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[10] National Bureau of Standards, Circular 500 (1952).

[11] T. L. Cottrell, *Strengths of Chemical Bonds*. Butterworths, London (1954).

[12] N. V. Sidgwick, *Chemical Elements and their Compounds* Vol. II. Oxford University Press (1950).

[13] L. H. Long, *Quart. Rev. Chem. Soc.* 7, 134 (1953).

[14] H. von Wartenburg, G. Sprenger and J. Taylor, *Z. Phys. Chem., Bodenstein Festband* 61 (1935).

TABLE 2

Pair of substances	States (l = liquid c = solid)	Heats of formation[10] (kcal/mole)	Δ (kcal)
(a) Hydrocarbon and monofluoro compounds—			
CH_3COOH	l	$-116{\cdot}4$	$-44{\cdot}5$*
CH_2FCOOH	c	$-160{\cdot}9$	
CH_3CH_2OH	l	$-66{\cdot}4$	$-43{\cdot}3$
CH_2FCH_2OH	l	$-109{\cdot}7$	
CH_3CONH_2	c	$-76{\cdot}6$	$-39{\cdot}7$
CH_2FCONH_2	c	$-116{\cdot}3$	
(b) Monofluoro and difluoro compounds—			
CH_2FCOOH	c	$-160{\cdot}9$	$+26$†
CHF_2COOH	l	$-134{\cdot}4$	
CH_2FCONH_2	c	$-116{\cdot}3$	$-48{\cdot}7$
CF_2HCONH_2	c	$-165{\cdot}0$	
CH_2FCH_2OH	l	$-109{\cdot}7$	$-51{\cdot}7$
CF_2HCH_2OH	l	$-161{\cdot}4$	

* This value may be high by about 2 kcal, owing to our neglecting the differing states of the two substances.

† We consider that the value $\Delta H_f\,(CHF_2COOH)$ is incorrect, since the value of Δ that involves this quantity is so much out of keeping with the other estimates. This supposition is supported by the inconsistency of the following set of equations:

$$\begin{aligned} \Delta H_f\,(CH_3CONH_2) - \Delta H_f\,(CH_3COOH) &= +40 \text{ kcal} \\ \Delta H_f\,(CH_2FCONH_2) - \Delta H_f\,(CH_2FCOOH) &= +45 \text{ kcal} \\ \Delta H_f\,(CHF_2CONH_2) - \Delta H_f\,(CHF_2COOH) &= -30 \text{ kcal} \end{aligned}$$

115 kcal. Thus no appreciable difference in the bond energy appears to result from the introduction of the third and fourth fluorine atoms. These observations are in keeping with the shortening of the C–F bond in fluoromethanes noted by Pauling.[15]

In passing it is interesting to note that the results reported by Kirkbride and Davidson[9] for the heats of formation of chlorofluoromethanes, when plotted against flourine content, with the exception of the values for ΔH_f (CF_2Cl_2), lie close to a straight line, which also passes through the values for $\Delta H_f\,(CCl_4)$ and our selected value for $\Delta H_f\,(CF_4)$. This suggests that the C–F and C–Cl bond energy terms are nearly constant throughout the series, and that $\bar{B}\,(\text{C–Cl}) \simeq 77{\cdot}5$ kcal, as in simple chlorocompounds.

We can now consider the C–C bond-energy term in fluorocarbons. Kirkbride and Davidson[9] give for the heat of formation of hexafluoroethane $\Delta H_f = -303$ kcal/mole. Hence the heat of atomisation is:

$$\alpha H_a\,(C_2F_6) = 756 \text{ kcal/mole}$$

$$\beta H_a\,(C_2F_6) = 689 \text{ kcal/mole}$$

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[15] L. Pauling, *Nature of the Chemical Bond*. Cornell University Press, New York (1945).

Using the values of $\bar{B}$ (C–F) obtained from H_a (CF_4), we have:

$$\alpha\bar{B}\,(\text{C–C}) = 61 \text{ kcal}; \quad \beta\bar{B}\,(\text{C–C}) = 44 \text{ kcal}$$

When compared with the values for hydrocarbons (α, $\bar{B}$ (C–C) = 83 kcal[16]; β, $\bar{B}$ (C–C) = 66 kcal[11]), these values appear very low. However the data for hydrocarbons[17] do not show a constant increment for each methylene group until hydrocarbons containing more than six carbon atoms are reached. The discrepancies in the C–H and C–C bond-energy terms involved are small, and, although a similar effect may occur in the fluorocarbon series, we do not consider that this will account for the present large disparity. We therefore suggest that the value for ΔH_f (C_2F_6) is low. Our suggestion has some support from the value for $\bar{B}$ (C–C) that we obtain as described below from the heat of formation of polytetrafluoroethylene.

The literature values for the heat of formation of polytetrafluoroethylene are —193·5[8] and $\rightleftharpoons$199·9[6] kcal/mole C_2F_4. The latter value of the heat of formation of the polymer was determined on the basis of ΔH_f (CF_4) = —212·7 kcal/mole. We have recalculated this quantity directly from the results of the combustion given by Duus,[6] using ΔH_f (CF_4) = —218 kcal/mole, and we obtained ΔH_f (C_2F_4; polymer (c)) = —202·8 kcal/mole C_2F_4. This value is derived from data for a reaction at constant volume. The correction to constant pressure increases numerically the value by about 0·6 kcal/mole C_2F_4. Duus[6] found that the heat of formation of the heat-treated polymer had a (numerically) lower heat of formation as instanced by the value recalculated from his results on the basis outline above, namely ΔH_f (C_2F_4; polymer, (c) heat treated) = —200·9 kcal/ mole C_2F_4. This differs from that for the untreated polymer by about 2 kcal. The difference is the latent heat of fusion, since the fusion process is not reversed easily on cooling. We shall use a value:

$$\Delta H_f\,(C_2F_4;\ \text{polymer},\ (c);\ \text{heat-treated}) = 196 \pm 5 \text{ kcal/mole } C_2F_4.$$

The published data for the heats of vaporisation of perfluoropentane[18] and perfluoroheptane[19] give for the increment (assumed constant) for the heat of vaporisation of linear perfluorocarbons at 25° the value 1·08 kcal/CF_2 group (which value is slightly smaller than that for hydrocarbons, 1·18 kcal/CH_2 group[20]). We may write therefore:

$$\Delta H_f\,(C_2F_4;\ \text{polymer},\ g) = -194 \text{ kcal/mole}$$

whence:

$$\alpha H_a\,(C_2F_4;\ \text{polymer}) = 611 \pm 5 \text{ kcal/mole}$$

$$\beta H_a\,(C_2F_4;\ \text{polymer}) = 544 \pm 5 \text{ kcal/mole}$$

Since:

$$H_a\,(C_2F_4;\ \text{polymer}) = 2\bar{B}\,(\text{C–C}) + 4\bar{B}\,(\text{C–F})$$

we have, using our value of $\bar{B}$ (C–F) from H_a (CF_4):

$$\alpha\bar{B}\,(\text{C–C}) = 74 \text{ kcal}$$

$$\beta\bar{B}\,(\text{C–C}) = 57 \text{ kcal}$$

These values are about 10 kcal less than those that are found in hydrocarbons. In view of the small uncertainties in the heats of formation of the polymer, and of the

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[16] G. E. Coates and L. E. Sutton, *J. Chem. Soc.* 1187 (1948).

[17] E. J. Prosen and F. D. Rossini, *J. Res. Nat. Bur. Stand.* **34**, 263 (1945).

[18] J. H. Simons and R. D. Dunlap, *J. Chem. Phys.* **18**, 335 (1950).

[19] G. D. Oliver and J. W. Grisard, *J. Amer. Chem. Soc.* **73**, 1688 (1951).

[20] F. S. Dainton, T. R. E. Devlin and P. A. Small, *Trans. Faraday Soc.* **51**, 1710 (1955).

uncertainty of equating $\bar{B}$(C–F) in the polymer to $\bar{B}$(C–F) in carbon tetrafluoride, we must conclude that $\bar{B}$(C–C) in fluorocarbons is close to, but probably smaller than, $\bar{B}$(C–C) in hydrocarbons. It is difficult to reconcile this observation with the mass-spectrometric estimates of 97 to 124 kcal/mole[21] for the dissociation energy, $D(CF_3\text{–}CF_3)$, in hexafluoroethane, which are abnormally high when compared with D(C–C) values in hydrocarbons (about 80–87 kcal/mole[22]).

Three values are available for the heat of formation of tetrafluoroethylene, namely, −151·3,[6] −162,[9] and −151·7 kcal/mole.[7] The first value is associated with $\Delta H_f(CF_4) = -212{\cdot}7$ kcal/mole and comes from the heat of hydrogenation of tetrafluoroethylene. Using the data of Duus[6] for the combustion of tetrafluoroethylene, we find, assuming $\Delta H_f(CF_4) = -218$kc al/mole, that $\Delta H_f(C_2F_4) = -155$ kcal/mole.

We shall use the value $\Delta H_f(C_2F_4) = -152$ kcal/mole, which is close to the value (−151·7 kcal/mole) obtained in the most recent and most careful determination.[7] We have for the heat of atomisation:

$$\alpha H_a(C_2F_4) = 569 \text{ kcal/mole}$$

$$\beta H_a(C_2F_4) = 501 \text{ kcal/mole}$$

If we again use the value of $\bar{B}$(C–F) obtained from $H_a(CF_4)$ we can find $\bar{B}$(C=C). For comparison we tabulate (Table 3) also the values of $\bar{B}$(C=C) derived from $H_a(C_2H_4)$ and $H_a(CH_4)$, and $H_a(C_2Cl_4)$ and $H_a(CCl_4)$, using heats of formation given by the National Bureau of Standards.[10] Values are rounded to the nearest kcal.

TABLE 3. THERMOCHEMICAL DATA FOR LOW-SUBSTITUTED ETHYLENES

Compound	ΔH_f (kcal/mole)	$\bar{B}$(C-X)	$\bar{B}$(C=C)* (kcal) (x: L_c = 171·7 kcal)
C_2H_4	+12·5	98·8	142
C_2Cl_4	−3	78	149
C_2F_4	−152	116	105

* Similar differences arise when L_c is taken as 138 kcal.

These figures demonstrate an anomaly in the heat of formation of tetrafluoroethylene, which may conveniently be measured by the low value of $\bar{B}$(C=C) obtained for this compound when compared with other olefines. We shall show that this is of considerable importance in determining the properties of this compound, and that in particular it accounts for the high thermal stability of polytetrafluoroethylene and of perfluoro*cyclo*butane.

The weakness of the C=C bond in tetrafluoroethylene is also demonstrated by the ability of excited mercury atoms (Hg^3P_1) to dissociate the compound into two CF_2 radicals.[23] This requires that the dissociation energy of the double bond, $D(CF_2\text{=}CF_2)$ is equal to, or less than, the energy associated with the energy of

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[21] J. B. Farmer, I. H. S. Henderson, F. P. Lossing and D. G. H. Marsden, *J. Chem. Phys.* **24**, 348 (1955).

[22] M. Szwarc, *Chem. Rev.* **47**, 75 (1950).

[23] B. Atkinson, *J. Chem. Soc.* 2684 (1952).

excitation, that is 112 kcal/mole. This compares with the value of at least 130 kcal/mole required for the dissociation of the C=C bond in ethylene (see Cottrell[11]). Bond-dissociation energies are not simply related to average bond-energy terms. In any case the latter are dependent on the value used for the heat of atomisation of graphite. Clearly, however, changes in the one quantity must correspond to similar changes in the other. Bond-energy terms obtained by using $L_c = 171{\cdot}7$ kcal are closer to the observed bond-dissociation energies than are those obtained by using $L_c = 138$ kcal.

Weakening of olefinic double bonds seems to be associated with the presence of $=\mathrm{CF_2}$ grouping. This is demonstrated by the values in Table 4, which are calculated from heats of formation of a number of compounds containing this grouping. The values of $\bar{B}$ (C=C) have been derived by using the bond-energy terms used previously.

TABLE 4. THERMOCHEMICAL DATA FOR FLUOROETHYLENES

Compound	ΔH_f (kcal/mole)	Literature reference	Heats of atomisation* (kcal/mole) (α: $L_c = 171{\cdot}7$)	$\bar{B}$ (C=C) (kcal/mole)
$\mathrm{CF_2{=}CFCl}$	−126	9	553	127
$\mathrm{CF_2{=}CH_2}$	−77·5	7	561	131
$\mathrm{CF_3CF{=}CF_2}$	−259†	6	884	114‡

* Similar differences arise when L_c is taken as 138 kcal.

† Calculated from Duus's result:[6]

$$\mathrm{C_2F_4}\,(g) \rightarrow \tfrac{2}{3}\mathrm{C_3F_6}\,(g) + 20{\cdot}2 \text{ kcal},$$

using $\Delta H_f\,(\mathrm{C_2F_4}) = -152$ kcal/mole.

‡ Calculated by using $\bar{B}$ (C–C) = 74 kcal, as estimated from polytetrafluoroethylene. This quantity may therefore be low by about 5 kcal.

The values of $\bar{B}$ (C=C) in these compounds lie about midway between that in tetrafluoroethylene and those found in other compounds.

In a series of papers by Lacher, Park and co-workers[24-27] the heats of bromination, chlorination and hydrobromination of a number of fluorinated olefines have been reported, and these differ markedly from those obtained with normal olefines. The authors observe that their results indicate anomalous bond-energy terms in the compounds concerned. This is demonstrated by the analysis of the results shown in Tables 5, 6, 7 and 8, in which the heats of saturation of the compounds are compared with the heats of saturation of ethylene. The heats of addition to tetrafluoroethylene are greater than those to ethylene and tetrachloroethylene by about 15–16 kcal/mole for all cases for which data are available. The heats of addition to chlorotrifluoroethylene are about 8 kcal/mole greater than those to ethylene. For other compounds containing the $=\mathrm{CF_2}$ group the difference seems to be about 4–5 kcal/mole. These differences between the heats of addition parallel the differences between

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[24] J. R. Lacher, J. J. McKinley, C. M. Snow, L. Michel, G. Nelson and J. D. Park, *J. Amer. Chem. Soc.* **71**, 1330 (1949); J. R. Lacher, J. J. McKinley, C. Walden, K. Lea and J. D. Park, *J. Amer. Chem. Soc.* **71**, 1334 (1949).

[25] J. R. Lacher, K. Lea, C. Walden, G. G. Olson and J. D. Park, *J. Amer. Chem. Soc.* **72**, 3231 (1950).

[26] J. R. Lacher, L. Casali and J. D. Park, *J. Phys. Chem.* **60**, 608 (1956).

[27] J. R. Lacher, A. Kianpour and J. D. Park, *J. Phys. Chem.* **61**, 584 (1957).

TABLE 5. HEATS OF ADDITION TO $CF_2{=}CF_2$ AND $CH_2{=}CH_2$ (kcal/mole)

Compound	Additive		
	HBr	Br_2	Cl_2
$CF_2{=}CF_2$	−32·99[25]	−38·48[26]	−57·32[24]
$CH_2{=}CH_2$	−16·8*	−23·8*	−41·5*†
Difference	16·2	14·6	15·8

* Here and elsewhere in these Tables heats of addition to ethylene are calculated from data given by the National Bureau of Standards[10] (T = 25°).

† It is interesting to note that the heat of chlorination of tetrachloroethylene is −41·1 kcal/mole.[10]

‡ These heats of addition were determined at about 90–130°. As elsewhere in this paper, no attempt has been made to correct the thermochemical data to a standard temperature. This is insufficient data to enable this to be done easily, but the correction involved is much smaller than the anomalies to be demonstrated.

TABLE 6. HEATS OF ADDITION TO $CF_2{=}CFCl$ AND $CH_2{=}CH_2$ (kcal/mole)

Compound	Additive		
	HBr	Br_2	Cl_2
$CF_2{=}CFCl$	−26·07[25]	−31·61[26]	−48·83[24]
$CH_2{=}CH_2$	−16·8	−23·8	−41·5
Difference	9·3	7·8	7·3

TABLE 7. HEATS OF ADDITION TO CF_2CCl_2 AND $CH_2{=}CH_2$ (kcal/mole)

Compound	Additive	
	HBr	Cl_2
$CF_2{=}CCl_2$	−22·05[25]	−41·08[24]
$CH_2{=}CH_2$	−16·8	−41·5
Difference	5·2	—

TABLE 8. HEATS OF CHLORINATION OF FLUORINATED OLEFINES

Compound	Heat of chlorination (kcal/mole)	Heat of chlorination of olefine − heat of chlorination of ethylene
$CF_3CF{=}CF_2$	−47·15[24]	−5·7
$C_2F_5CF{=}CF_2$	−44·97[27]	−3·5
$C_3F_7CF{=}CF_2$	−45·64[27]	−4·1
$(CF_3)_2C{=}CF_2$	−42·22[27]	+0·7

the bond-energy terms calculated above, but unfortunately there is no quantitative agreement. The smallness of these differences compared with the differences between the bond-energy terms may result in part from low values of $\bar{B}$(C–C) in highly fluorinated compounds, consistent with the trends shown by the single bond-energy terms we have calculated. Since heats of addition to olefines can be measured with greater accuracy than can heats of formation, the former provide a more reliable indication of bond-energy differences.

The C═C bond length in tetrafluoroethylene[28] is 1·31 Å, which is slightly shorter than that in ethylene[29] (1·33 Å). This shortening, which is significant, would normally be accompanied by an increase in binding energy. The C═C bond force constants in ethylene[30] and tetrafluoroethylene[31] are, respectively, 9·6 and 9·2 × 10^5 dyn/cm. This suggests that the bond orders in the two compounds are about the same. The effects observed may be explained by supposing that the fluorine atoms withdraw electrons from the carbon atoms. One result of the reduction of electron density around the carbon atoms will be an increased repulsion between their nuclei, thus weakening the bond between them. Overlapping of the orbitals constituting the double bond may be made more difficult, and the slight shortening of the bond may be the means of correcting for this.

The C═C bond length in vinylidene fluoride[28] (1·31 Å) is about the same as that in tetrafluoroethylene. If the same effect persists in the $=CF_2$ structure, then a weakening of the C═C bond in this compound may arise in a manner similar to tetrafluoroethylene.

The partial transfer of electrons to the C–F bonds must also take place in saturated perfluoro structures, and may in a similar manner reduce the strengths of the C–C bonds.

We will now turn our attention to the stability of perfluoro*cyclo*butane and polytetrafluoromethylene. *cyclo*Butanes decompose primarily to ethylenes on heating, so that in discussing their stability we are concerned with equilibria of the type.

$$cyclo\text{-}C_4F_8 \rightleftharpoons 2C_2F_4$$

This equilibrium has been studied by Atkinson and Trenwith[32] in the temperature range 300-550°. The measured heat of reaction, −50·3 kcal/mole, compares well with that of −49·4 kcal/mole given by the results of Duus.[6] The experimental value of the entropy change (at 550°) is −49·2 e.u./mole, which compares with the value of −47·6 e.u./mole (at 298·2°K), calculated from the standard entropy of tetrafluoroethylene reported by Mann *et al.*[33] and that for perfluoro*cyclo*butane (the value of Furukawa *et al.*[34] for 261°K corrected to 298·2°K by using the specific heat data of Masi[35]). The corresponding quantities for the hydrocarbon series are −18·7 kcal/mole and −41·5 e.u./mole.[20] The heats of formation of partly fluorinated *cyclo*butanes from the corresponding ethylenes will have values intermediate between those quoted above, and this fact will be reflected in lower thermal stability of these

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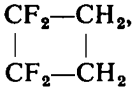
[28] I. L. Karle and J. Karle, *J. Chem. Phys.* **18**, 963 (1950).
[29] L. Pauling and L. O. Brockway, *J. Amer. Chem. Soc.* **59**, 1223 (1937).
[30] G. Herzberg, *Infra-red and the Raman Spectra.* Van Nostrand, New York (1945).
[31] Y. Morino, K. Kuchitsi and T. Shimanouchi, *J. Chem. Phys.* **20**, 726 (1952).
[32] B. Atkinson and A. B. Trenwith, *J. Chem. Soc.* 2082 (1953).
[33] D. E. Mann, N. Acquista and E. K. Plyler, *J. Res. Nat. Bur. Stand.* **52**, 67 (1954).
[34] G. T. Furukawa, R. E. McCoskey and M. L. Reilly, *J. Res. Nat. Bur. Stand.* **52**, 11 (1954).
[35] J. F. Masi, *J. Amer. Chem. Soc.* **75**, 5082 (1953).

butanes. We can predict that a compound of the form



$$\begin{array}{c} CF_2\text{—}CH_2 \\ |\quad\quad| \\ CF_2\text{—}CH_2 \end{array}$$

which may be prepared from ethylene and tetrafluoroethylene, will prefer to decompose into $CF_2{=}CH_2$.

Polytetrafluoroethylene decomposes almost exclusively to tetrafluoroethylene.[36] Other compounds detected in the decomposition products, particularly at higher pressures and temperatures, are products of subsequent reactions of the monomer. Results we have discussed give us for the heat of polymerisation of tetrafluoroethylene:

$$\begin{aligned} \Delta H_{gc} &= \Delta H_f\,(\text{polymer, virgin}) = \Delta H_f\,(\text{monomer}) \\ &= -198 - (-152) = -46 \text{ kcal}/C_2F_4 \text{ mole unit} \end{aligned}$$

The entropy of polytetrafluoroethylene cannot be specified at standard temperature (25°) on account of the second-order phase transition that takes place over the temperature range −20° to 40°. We shall, therefore, use the value at 340°K. The calorimetric entropy of the polymer at this temperature is[37] 28·95 e.u./C_2F_4 mole unit. We shall make no correction for the zero-point entropy, since this is likely to be small. Since the entropy of tetrafluoroethylene (1 atm) is 74·1 e.u./mole,[33] the entropy of polymerisation is:

$$\begin{aligned} \Delta S_{gc} &= 28{\cdot}95 - 74{\cdot}1 \\ &= -45{\cdot}1 \text{ e.u.}/C_2F_4 \text{ mole unit} \end{aligned}$$

Dainton and Ivin[38] have shown that the "crucial temperature," T_c, at which a polymer is in equilibrium with 1 atm pressure of its monomer, may with reasonable accuracy be predicted by using the expression:

$$T_c = \Delta H_{gc}/\Delta S_{gc}$$

in which the quantities are those at standard temperature. We may equally well use thermodynamic quantities at any other temperature. We have then:

$$T_c = 46{,}000/45{\cdot}1 \quad \text{or} \quad 1020°\text{K}$$

A more reasonable (but arbitrary) measure of polymer stability is the temperature at which a small pressure, say 10^{-2} atm (7·6 mm) of monomer will be supported over the polymer. Our entropy change would then be:

$$\begin{aligned} \Delta S_{gc}' &= \Delta S_{gc} + R \ln p \\ &= \Delta S_{gc} + R \ln 10^{-2} \\ &= -54{\cdot}3 \text{ e.u.}/C_2F_4 \text{ mole unit} \end{aligned}$$

Hence

$$T_c' = 850°\text{K} \quad \text{or} \quad \text{about } 580°\text{C}$$

In kinetic studies of the depolymerisation of polytetrafluoroethylene pressures of about 6 mm of monomer have been generated over the polymer[36] at 513°. Although this observation may have been made on a non-equilibrium system, we think it more likely that the discrepancy between this experimental observation and our calculated

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[36] S. L. Madorsky, V. E. Hart, S. Straus and V. A. Sedlak, *J. Res. Nat. Bur. Stand.* **51**, 327 (1953).

[37] G. T. Furukawa, R. E. McCoskey and G. T. King, *J. Res. Nat. Bur. Stand.* **49**, 273 (1952).

[38] F. S. Dainton and K. J. Ivin, *Trans. Faraday Soc.* **46**, 331 (1950).

estimate is due to the incorrectness of our thermochemical data. There is some doubt about the correct value of ΔH_p. Indeed we have already observed that the heats of chlorination, bromination and hydrobromination of tetrafluoroethylene are about 16 kcal/mole greater than those for ethylene. A disparity of the same order is found when the heats of dimerisation of the two ethylenes are compared. Thus it would seem reasonable to suppose that the heat of polymerisation of tetrafluoroethylene would exceed that of ethylene by about the same amount. Using the value for ethylene of $\Delta H_{gc} = -24{\cdot}7$ kcal/mole,[20] we would estimate for tetrafluoroethylene $\Delta H_{gc} = -41$ kcal/mole, which is somewhat lower than the value used above. Nevertheless, we suggest that the polymer owes its high thermal stability to its unusually large heat of polymerisation. (Heats of polymerisation of most other olefines lie between -15 and -25 kcal/mole.) The polymeric radicals once formed by the moderately frequent rupture of bonds at about 400° and above, decompose in accord with their thermodynamic instability.

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