Thermal Unimolecular Decomposition of 1,1,2,2-Tetrafluorocyclobutane

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The thermal decomposition of 1,1,2,2-tetrafluorocyclobutane has been studied in the gas phase in the temperature range $485-593^{\circ}$ C and at pressures around 5-9 Torr. There are two homogeneous first order decomposition pathways, one yielding 1,1-difluoroethylene (k_1) and the other ethylene and tetrafluoroethylene (k_2) . Arrhenius equations have been obtained for these processes viz.:

 $\log k_1/s^{-1} = 15.34 \pm 0.05 - (292.0 \pm 0.8 \text{ kJ mol}^{-1})/RT \ln 10$

 $\log k_2/s^{-1} = 15.27 \pm 0.06 - (308.1 \pm 0.9 \text{ kJ mol}^{-1})/RT \ln 10.$

The decomposition is almost certainly unimolecular and at the pressures studied the rate constants are close to their infinite pressure values. Rate constants were also determined from 22 to 0.01 Torr at 542.2 °C and the values obtained compared with those calculated using RRKM theory on the basis of various models. The energetics of the decomposition pathways are compared with cyclobutane and the fluorinated cyclobutanes.

The decompositions of cyclobutane and alkyl cyclobutanes are excellent examples of thermal unimolecular reactions and for this reason have been studied in detail.¹ Halogen substituted cyclobutanes have been little studied, though for many reasons they present a class of compounds of considerable mechanistic interest. We have recently reported work on 1,1-difluorocyclobutane² and the present study is a continuation of this programme.

EXPERIMENTAL

The apparatus has been described earlier.² 1,1,2,2-Tetrafluorocyclobutane was obtained from Columbia Organic Chemicals and purified by preparative gas chromatography using a 2 m×6 mm (i.d.) column packed with $\beta\beta^1$ oxydipropionitrile on Chromosorb P and operated at 30°C. Chromatographic analysis of the purified material on several different columns indicated that it was better than 99.9 % pure. The infrared spectrum and mass spectrum of the compound were in agreement with those reported in the literature.³ Tetrafluoroethylene was obtained by the pyrolysis of octafluorocyclobutane; ethylene and 1,1-difluoroethylene were commercial samples.

Analysis of decomposition products was by gas chromatography (Perkin Elmer F11; Hewlett Packard 3380 A integrator) using a $6.3 \text{ m} \times 2.2 \text{ mm}$ (i.d.) column packed with Poropak N and operated at 180° C.

RESULTS

Preliminary experiments carried out at 502.8° C (silica reaction vessel) revealed that the decomposition yielded ethylene, 1,1-difluoroethylene and perfluoroethylene. The ratio of ethylene to 1,1-difluoroethylene was constant, independent of percentage decomposition even for runs extending to well over 50 % conversion. The ratio of tetrafluoroethylene to ethylene remained constant provided the decomposition of the cyclobutane did not exceed 25 %. The ratio decreased slightly if decomposi-

tions extended appreciably beyond 25 %. Pressure changes, measured with an MKS Baratron, were found to be a quantitative monitor of the overall decomposition up to more than 25 % reaction. In various studies at 542.4°C runs were monitored both by pressure change and chromatographic analysis. For runs taken to ≈ 25 % decomposition the pressure measurements (corrected for ≈ 2 % dead space by the method of Robinson ⁴) showed strict first order behaviour and yielded a rate constant of $4.74 \times 10^{-4} \, \text{s}^{-1}$. Runs carried out at various initial pressures between 5 and 25 Torr and analysed by gas chromatography confirmed the strictly first order nature of the decomposition and yielded a mean value for the rate constant of $4.77 \pm 0.11 \times 10^{-4} \, \text{s}^{-1}$ in excellent agreement with the (probably more precise) value obtained by pressure measurements. In contradistinction to previous work on 1,1-difluorocyclobutane, no difficulty was experienced in conditioning the surface of the reaction vessel and reproducible results were obtained after a few preliminary pyrolyses.

From the information presented it appeared clear that the decomposition of 1,1,2,2-tetrafluorocyclobutane, certainly up to 25 %, could be represented by

$$F_{2}$$

$$F_{2$$

where both pathways were first-order processes.

A series of runs was carried out at 14 temperatures from 485 to 593°C. At each temperature the sum of the rate constants (k_1+k_2) was determined from pressure measurements using the Robinson procedure. In general, runs were not allowed to proceed to beyond a quarter lifetime, though a few were followed for over a half life to determine to what extent the changes in the ratio of tetrafluoroethylene to ethylene were reflected in the overall rate constant. Also, at each temperature several determinations of the ratio of ethylene to 1,1-difluoroethylene were carried out by gas chromatographic analysis for runs taken only to small overall decomposition. These yielded values of k_1/k_2 and hence allowed the calculation of the individual rate constants. The data so obtained are presented in table 1.

From the results presented in table 1, the following Arrhenius equations were obtained by the method of least squares; quoted error limits are one standard deviation.

$$\log (k_1 + k_2)/s^{-1} = 15.450 \pm 0.052 - 293.2 \pm 0.8 \text{ kJ mol}^{-1}/RT \ln 10$$
$$\log k_1/s^{-1} = 15.342 \pm 0.052 - 292.0 \pm 0.8 \text{ kJ mol}^{-1}/RT \ln 10$$
$$\log k_2/s^{-1} = 15.271 \pm 0.056 - 308.1 \pm 0.9 \text{ kJ mol}^{-1}/RT \ln 10.$$

A series of runs was carried out at 542.4°C in a vessel packed with silica tubes to increase its surface to volume ratio by a factor of 8 compared with the unpacked reaction vessel. The extent of reaction was monitored by gas chromatography and the overall rate constant obtained from a plot of the logarithm of the fraction of reactant remaining against time. A rate constant of $4.80 \times 10^{-4} \text{ s}^{-1}$ was obtained, which compares well with the values obtained for the unpacked vessel at this temperature, *viz.* $4.74 \times 10^{-4} \text{ s}^{-1}$ and $4.77 \times 10^{-4} \text{ s}^{-1}$ (by chromatographic and pressure measurements, respectively) and a value of $4.68 \times 10^{-4} \text{ s}^{-1}$ obtained from the Arrhenius

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equation. The close agreement suggests there can be no appreciable heterogeneous component of the reaction.

From the information already presented in this work and from the previous study on 1,1-difluorocyclobutane it seemed very probable that the reactions being observed are true unimolecular processes. At sufficiently low pressures the first order rate constant of any unimolecular reaction will become pressure dependent; the fall-off region. Again, simple calculations suggest that for a molecule of the complexity of tetrafluorocyclobutane, this pressure region should be experimentally accessible and so a number of runs were carried out at 542.2°C with initial pressures from 22 Torr down to 0.01 Torr. Rate constants were obtained by pressure measurements. Within experimental error the rate constants were found to be independent of pressure above 10 Torr (i.e., within 1 % of the infinite pressure value). In table 2 the values of the rate constants obtained at various pressures as a ratio of the infinite pressure value are presented.

temperature/°C	$(k_1+k_2)/10^{-4}\mathrm{s}^{-1}$	k_{1}/k_{2}	$k_1/10^{-4} \mathrm{s}^{-1}$	$k_2/10^{-5} \mathrm{s}^{-1}$
485.4	0.1829	15.16	0.1716	0.1132
495.0	0.3326	14.60	0.3113	0.2132
502.8	0.5295	14.03	0.4943	0.3523
510.5	0.8059	13.64	0.7509	0.5504
518.2	1.250	13.57	1.164	0.8575
526.2	1.913	13.25	1.779	1.343
534.1	2.927	12.85	2.716	2.113
542.0	4.460	12.57	4.131	3.287
549.8	6.883	12.14	6.359	5.238
557.9	10.45	11 .9 7	9.644	8.057
566.3	16.08	11.62	14.81	12.74
575.1	25.27	11.39	23.23	20.39
583.9	38.70	11.25	35.54	31.58
592.5	58.10	11.11	53.30	47.99

TABLE 1.—RATE CONSTANTS FOR DECOMPOSITION AT VARIOUS TEMPERATURES

(The rate data are quoted as obtained, without rounding, and as used in subsequent least squares analyses. The numbers of significant figures are not indicative of the precision of the constants. Multiple runs under the same conditions indicate an average precision of between 1 and 2 %.)

TABLE 2.—VALUES OF k/k_{∞} at various pressures and 542.2°C

pressure/Torr	22.0	12.2	9.43	8.86	7.26
k/k_{∞}	1.00	0.992	0.992	0.978	0.975
pressure/Torr	3.57	2.11	1.09	0.593	0.431
k/k_{∞}	0.943	0.920	0.880	0.820	0.783
pressure/Torr	0.219	0.157	0.089	0.088	0.062
k/k_{∞}	0.728	0.678	0.612	0.631	0.596
pressure/Torr	0.061	0.042	0.041	0.031	0.028
k/k_{∞}	0.587	0.516	0.531	0.557	0.563
pressure/Torr	0.0233	0.0202	0.0127	0.0121	0.0117
k/k_{∞}	0.499	0.470	0.495	0.490	0.479



log p/Torr

FIG. 1.—Curve (1) RRKM calculation, strong collision model, main channel only; curve (2) as for (1) but both channels considered; curve (3) step-ladder model, both channels, $\Delta E = 12 \text{ kJ mol}^{-1}$; curve (4) step-ladder model, both channels, $\Delta E = 24 \text{ kJ mol}^{-1}$.

Plots of some curves of $\log k/k_{\infty}$ against the logarithm of the pressure are shown in fig. 1. The curves were computed using the Rice-Ramsperger-Kassel-Marcus theory (RRKM) with input data given in Appendix A. Also shown in the figure are the experimental values reported in table 2.

DISCUSSION

Previous studies have shown that polyfluorinated cyclobutanes decompose with smaller rate constants than cyclobutane itself; their activation energies are correspondingly greater. The results reported here are fully consistent with this as shown by a comparison of results presented in table 3.

The rates at 500°C are calculated from the relevant Arrhenius equations. The table shows that the rate data and the activation energies fall into 3 groups and illustrates some remarkable features resulting from fluorine substitution. We have previously noted² that the decompositions of cyclobutane and 1,1-difluorocyclobutane have essentially the same "A" factors and hence probably very similar activated complexes and, therefore, that the difference in energies of activation must reflect differences in bond energies in the molecules. We also noted that this was consistent with the work of Rodgers and Ford 7 who report the carbon-carbon bond energy in 1,1,1-trifluoroethane as about 58 kJ mol⁻¹ higher than in ethane. Remembering that the decomposition of 1,1-difluorocyclobutane has a statistical factor twice that for the symmetrical (pathway) decomposition of 1,1,2,2-tetrafluorocyclobutane to 1,1-difluoroethylene, the fact that the two rates differ by little more than this factor implies a similar explanation for the energetics of decomposition. A comparison perhaps more relevant to cyclobutanes (than the trifluoroethane bond energy) shows that the carbon-carbon bond energy in polyfluoromethylene is 70 kJ mol⁻¹ greater than for the hydrocarbon.⁷⁻⁹ The similarity of the energies of activation for the two decompositions suggests that the bond energies of the participating carbon-carbon bonds are not significantly different (assuming, of course, the absence of compensating factors such as changes in ring strain).

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Of particular interest is the further rate reduction observed for the unsymmetrical fragmentation of 1,1,2,2-tetrafluorocyclobutane. The energetics of this decomposition pathway have a close resemblance to the decomposition of perfluorocyclobutane. Were the energetics identical, a factor of two in the rate constants would have been expected on symmetry grounds and it is rather surprising that the 1,1,2,2-tetrafluorocyclobutane decomposes more slowly than this. An intriguing (though perhaps rather speculative) possibility is that this is due to the more facile pathway "draining off" energised molecules so that the concentration of activated complexes, in transition state theory terms, is reduced below its equilibrium value.

reaction	$\log{(A/\mathrm{s}^{-1})}$	E/kJ mol ⁻¹	$k/10^{-5} \text{ s}^{-1}$ at 500°C	ref.
→ 2==	15.6	261.5	862	1
$\Box F^2 \rightarrow = + = \checkmark_F^F$	15.61	289.7	10.8	2
$ \begin{array}{c} & & F_2 \\ & & F_2 \\ & & F_2 \end{array} \rightarrow 2 = \begin{array}{c} & & F_2 \\ & & & F_2 \end{array} $	15.35	292.0	4.2	this work
$\Box_{F_2}^{F_2} \rightarrow = + \bigvee_{F \in F}^{F} F$	15.27	308.1	0.29	this work
$ \begin{array}{c} \mathbf{F_2} & \mathbf{F_2} \\ \mathbf{F_2} & \mathbf{F_2} \\ \mathbf{F_2} & \mathbf{F_2} \end{array} \xrightarrow{\mathbf{F}} \begin{array}{c} \mathbf{F} & \mathbf{F} \\ \mathbf{F} & \mathbf{F} \end{array} $	15.97	310.6	1.00	5, 6

TABLE 3.—DATA FOR VARIOUS CYCLOBUTANES

Central to an understanding of the mechanisms by which fluorinated cyclobutanes decompose is a rationale for the origin of the difference between the high and low values of the observed energies of activation. With the information available, two features characteristic of the high and low energy decompositions emerge. The first concerns the strengths of those bonds undergoing fragmentation and activation energies. The decomposition pathways which occur with the lower activation energies of $\approx 290 \text{ kJ mol}^{-1}$ involve cleavage of one unusually strong carbon–carbon bond and another whose energy probably is only a little greater than those in cyclobutane itself. In contrast the decomposition pathways characterised by the high energy of activation of $\approx 309 \text{ kJ mol}^{-1}$ require that two exceptionally strong carbon–carbon bonds be broken.

The second point of interest is the relation between the energies of activation and the heats of reaction for the two groups. Since heats of formation ¹⁰ and π bond energies ^{9, 11} are known for the olefin products, qualitative and, in some cases, quantitative estimates of ΔH for the fragmentation process are possible (see Appendix

B). An analysis of this sort shows that the two higher energy fragmentations leading to tetrafluoroethylene are very appreciably more endothermic than the lower energy decompositions leading to difluoroethylene. Thermochemical estimates show that for 1,1,2,2-tetrafluorocyclobutane the value for ΔH for the symmetrical cleavage is some 67 kJ mol⁻¹ less than for the unsymmetrical fragmentation. A similar calculation based on the estimate of the π bond energy of 1,1-difluoroethylene leads to a difference in the enthalpy changes for the decomposition of 1,1-difluorocyclobutane of at least 90 kJ mol⁻¹. In a related fashion it can be shown that the values of ΔH within the high and low groups are similar.

pressure/Torr	SC	WC(1)	WC(2)
∞	12.6	12.6	12.6
31.6	12.7	12.7	12.9
10	12.8	12.9	13.3
3.16	13.0	13.3	13.9
1.0	13.6	14.0	1 4.9
0.316	14.4	15.0	16.4
0.1	15.6	16.6	18.5
0.0316	17.4	18.7	21.3
0.01	19.8	21.6	25.3

TABLE 4.—CALCULATED RATE CONSTANT RATIOS AS A FUNCTION OF MODEL AND PRESSURE (815 K)

SC, Strong collision hypothesis. WC(1), Step-ladder model, $\Delta E = 24 \text{ kJ mol}^{-1}$. WC(2), Step-ladder model, $\Delta E = 12 \text{ kJ mol}^{-1}$.

In our earlier study on the pyrolysis of 1,1-difluorocyclobutane we noted the formation of 2-fluorobuta-1,3-diene by an HF elimination reaction. Much of this pathway was surface catalysed but there did appear to be a homogeneous component with first order behaviour over a limited temperature range. The data were not sufficiently extensive to yield a satisfactory Arrhenius plot but if an A factor of \approx 10¹⁴ s⁻¹ is assumed then this homogeneous elimination must have an energy of activation of $\approx 276 \text{ kJ mol}^{-1}$. A similar elimination pathway has not been observed in the present work. If even as little as 1 % of the decomposition had proceeded by HF elimination the trifluorobutadiene would have been easily observed. Assuming the same A factor as for the difluorocompound we can set a lower bound for the HF elimination for the energy of activation of 293 kJ mol⁻¹. The significantly different behaviour may be related to the different thermochemistries; thus it has been shown ¹² that fluorine substituents increase the strength of β carbon-hydrogen bonds and this effect is probably absent or at least much reduced for γ carbonhydrogen bonds. This suggests the possibility that the HF elimination observed for 1,1-difluorocyclobutane occurs via a 1,3-transannular process in preference to a 1,2 process.

The RRKM curve (1) for 1,1,2,2-tetrafluorocyclobutane shown in the figure was calculated assuming the strong collision hypothesis and also related only to the major (lower energy of activation) pathway. Curve (2) also assumes the strong collision hypothesis but is a more realistic calculation in that both reaction channels are considered. The difference in the two curves arises from the fact that the higher

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energy of activation channel (k_2) falls off faster at low pressures than the major channel (k_1) . This is perhaps more clearly illustrated by a calculation of the values of k_1/k_2 as a function of pressure. These values are shown in table 4.

The fact that the theoretical curves (1) and (2) lie to the left of the plotted experimental points, *i.e.*, experimentally fall-off is observed at higher pressures than the theoretical predictions, is by no means unusual in thermal unimolecular reaction studies and has been observed in many systems. It almost certainly results from a failure of the strong collision hypothesis in its original form. In most systems studied a small displacement along the pressure axis is all that is needed to bring the experimental and calculated curves into coincidence. This is equivalent to a modification of the strong collision hypothesis in the sense that only one in x collisions stabilise the energised molecule (where x > 1) and in the other collisions no energy loss (Of course one can formally produce exactly the same effect by arbitrarily occurs. reducing the values used for the collision diameter of the molecules involved, but this often leads to unrealistically small values.) An alternative modification is to allow intermolecular energy exchange to occur on every collision made by an energised molecule but to postulate that the average amount transferred is not necessarily sufficient to reduce the energy content below the critical value (though it will increase its lifetime). Models of this kind not only move the theoretical curve to higher pressures but also affect its shape. Unfortunately, for thermal systems, it is doubtful whether the available experimental data are sufficiently accurate to allow a choice between these modifications.

In fig. 1, curve 3 is computed on the basis of the two reaction channels and on the assumption that energy transfer occurs in steps (stepladder model) of 1000 cm⁻¹ or $\approx 12 \text{ kJ mol}^{-1}$. As can be seen, the theoretical curve now lies appreciably to the right of the experimental points. Interestingly, though not unexpectedly, the values of k_1/k_2 as a function of pressure are model dependent and the values for this model are shown in table 4. Finally, curve (4) is computed in the same way as for curve (3) but using a step size of 2000 cm⁻¹ or $\approx 24 \text{ kJ mol}^{-1}$. This curve gives a reasonable fit between theory and experiment and while a closer fit could probably be obtained with a slightly greater step size, it is doubtful whether there is any justification for attempting such "fine tuning". Indeed, the experimental data below ≈ 0.05 Torr show very considerable scatter and make any conclusions that rely on data in this region suspect.

Inspection of table 4 suggests that a direct experimental determination of the values of k_1/k_2 as a function of pressure (and also in fact as a function of pressure at different temperatures) may well be a better test of collisional deactivation models than the total fall-off curve. Unfortunately, in the present work values of the overall rate constant (k_1+k_2) were determined in the low pressure region by pressure measurements alone and so the required values are not available. (A redesigned apparatus is being built to enable the required information to be measured with high accuracy.)

Despite the limitations of the results outlined above, one important fact does emerge that concerns the extent of fall-off for 1,1,2,2-tetrafluorocyclobutane at any particular pressure compared with cyclobutane. For cyclobutane p_{\pm} (the pressure at which $k/k_{\infty} = 0.5$) occurs at ≈ 0.2 Torr compared with 0.02 Torr for the fluorinated molecule. Even this comparison is not strictly valid since the results refer to appreciably different temperatures and correction for this would increase the relative value for cyclobutane and hence increase the difference between the two compounds. This decrease in the value of p_{\pm} with fluorine substitution of hydrogen is exactly in line with theoretical expectations and is a result of the lower vibrational

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frequencies of C—F as against C—H bonds leading to a greater density of states at a given energy for the fluorinated molecule.

Finally we note that in most of the present work initial reactant pressures of around 8 Torr were used; at these pressures the reaction was probably $\approx 2 \%$ into the fall-off region. This is unlikely to have produced a measurable difference in the reported E_a compared with the infinite pressure value but could lead to an A_{∞} value perhaps 0.01 log units greater than the reported A factor.

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- ¹ C. T. Genaux, F. Kern and W. D. Walters, J. Amer. Chem. Soc., 1953, 74, 6169; R. W. Carr and W. D. Walters, J. Phys. Chem., 1963, 67, 1370; R. E. Wellman and W. D. Walters, J. Amer. Chem. Soc., 1957, 79, 1542; S. M. Kellner and W. D. Walters, J. Phys. Chem., 1961, 65, 466; H. R. Gerberich and W. D. Walters, J. Amer. Chem. Soc., 1961, 83, 4884, 3935.
- ² R. T. Conlin and H. M. Frey, J.C.S. Faraday I, 1979, 75, 2556.
- ³ J. R. Durig and W. C. Harris, Spectrochim. Acta., 1971, 27A, 619.
- ⁴ P. J. Robinson, Trans. Faraday Soc., 1965, 61, 1655.
- ⁵ J. N. Butler, J. Amer. Chem. Soc., 1962, 84, 1393.
- ⁶ B. Atkinson and A. B. Trenwith, J. Chem. Phys., 1952, 20, 754.
- ⁷ A. S. Rodgers and W. G. F. Ford, Int. J. Chem. Kinetics, 1973, 5, 965.
- ⁸ D. M. Golden and S. W. Benson, Chem. Rev., 1969, 69, 125.
- ⁹ E.-Chung Wu and A. S. Rodgers, J. Amer. Chem. Soc., 1976, 98, 6112.
- ¹⁰ J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds* (Academic Press, N.Y., 1970).
- ¹¹ J. M. Pickard and A. S. Rodgers, J. Amer. Chem. Soc., 1977, 99, 695.
- ¹² J. M. Pickard and A. S. Rodgers, J. Amer. Chem. Soc., 1977, 99, 691.
- ¹³ D. R. Stull, E. F. Westrum and G. C. Sinke, *The Chemical Thermodynamics of Organic Compounds* (Wiley, N.Y., 1969).

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APPENDIX A

RRKM CALCULATIONS

Vibrational assignments (cm⁻¹), degeneracies in brackets were appropriate.

ENERGISED MOLECULE

3039, 2984, 2981 (2), 1454, 1425, 1352, 1300, 1240, 1220 (2), 1181, 1122, 1055, 988, 947, 912, 905, 734, 666, 606 (2), 510, 465, 420, 360, 322, 264, 200, 90.

ACTIVATED COMPLEX (1) (major decomposition channel)

3039, 2984, 2981 (2), 1454, 1425, 1352, 1300, 1240, 1220 (2), 1181, 1122, 1055, 988, 947, 912, 905, 734, 666, 606 (2), 510, 210, 170, 120, 90, 70, 50.

ACTIVATED COMPLEX (2) (minor decomposition channel)

3039, 2984, 2981 (2), 1454, 1425, 1352, 1300, 1240, 1220 (2), 1181, 1122, 1055, 988, 947, 912, 905, 734, 666, 606 (2), 510, 200, 170, 130, 90, 80, 50.

For both channels: path degeneracy = 1. collision diameter 5.5 Å.

Ratio of rotational partition functions taken as unity.

For major channel: Marcus $E_0 = 284730 \text{ J mol}^{-1}$.

For minor channel: Marcus $E_0 = 300 830 \text{ J mol}^{-1}$.

(2)

(3)

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APPENDIX B

[Where necessary thermochemical data have been obtained from ref. (11)-(13).]

SAMPLE THERMOCHEMICAL CALCULATIONS

ILLUSTRATION FOR CYCLOBUTANE DECOMPOSITION

$$\Delta H_{\rm r}^{\circ} = 2 \mathrm{DH}^{\circ}(-\mathrm{CH}_2 - \mathrm{CH}_2 - \mathrm{CH}_2) - E_{\rm s} - 2 \mathrm{D}\pi^{\circ}(\mathrm{CH}_2 - \mathrm{CH}_2)$$
(1)

$$\Delta H_{\mathbf{f}}^{\mathbf{o}} = 2\Delta H_{\mathbf{f}}(C_2H_4) - \Delta H_{\mathbf{f}}(\Box)$$

$$\Delta H_{\mathbf{f}}^{\mathbf{o}} = E_1 - E_2$$



From eqn (1) $\Delta H_{\rm s}^{\rm o} = 2(341) - 109.6 - 2(247.3) = 77.8 \, \rm kJ \, mol^{-1}$.

From eqn (2) $\Delta H_r^{\circ} = 104.6 - 26.8 = 77.8 \text{ kJ mol}^{-1}$.

From eqn (3) $77.8 = 261.5 - E_2$; hence $E_2 = 183.7$ kJ mol⁻¹.

Note E_2 is the strain energy and $D\pi^{\circ}$ is the π bond energy in ethylene.

Note also that eqn (3) requires the value of E_2 at constant pressure, *i.e.*, $E_2(p)$. If the constant concentration value is required then $E_2(p) = E_2(c) - RT$. All data refer to 298 K though some experimental values of E_1 have not been adjusted since the corrections are small.

calculation for 1,1,2,2-tetrafluorocyclobutane (to 1,1-difluoroethylene)

$$\Delta H_{\rm r}^{\circ} = DH^{\circ}(-CH_2-CH_2-) + DH^{\circ}(-CF_2-CF_2-) - E_{\rm s} - 2D\pi^{\circ}(CF_2-CH_2) \quad (1)$$

= 341+374-110-2(263)

= 79 kJ mol⁻¹ (This value has an uncertainty of at least 10 kJ mol⁻¹.) $\Delta H_{\rm f}^{\rm o} = 2\Delta H_{\rm f}({\rm CF}_2 = {\rm CH}_2) - \Delta H_{\rm f}(\Box_{\rm F}^{\rm F_2})$ (2)

$$79 = 2(-337) - \Delta H_{f}(\Box_{F_{2}}^{F_{2}})$$

$$\Delta H_{f}(\Box_{F_{2}}^{F_{2}}) = -753 \text{ kJ mol}^{-1}$$

$$\Delta H_{r}^{\circ} = E_{1} - E_{2}.$$
(3)

To estimate E_2 we assume that for all olefin dimerisations it can be related to that of ethylene when corrections are made for π bond strengths; hence

 $E_2 = E_2$ (ethylene dimerisation)+ $[2D^{\circ}\pi^{\circ}(\text{olefin reactant}) - 2D\pi^{\circ}(C_2H_4)]$

Thus for 1,1,2,2-tetrafluorocyclobutane

$$E_2 = 183 + [2(263) - 2(247)]$$

= 215 kJ mol⁻¹,

which gives

 $E_1 = 294 \text{ kJ mol}^{-1}$ (experimental value 292 kJ mol⁻¹).

The primary weakness of our method is that it regards E_2 as a function of only the π bond energies and ignores the possibility that the extent of σ bond formation for any olefin dimerisation will also differ from that of ethylene. Nevertheless the above calculations

(the extremely close agreement is, of course, fortuitous) suggests that the procedure has some merit and in cases where the model fails one should look for mechanistic differences between ethylene and other olefin dimerisations.

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From eqn type (2) we obtain $\Delta H_r^{\circ} = 148 \text{ kJ mol}^{-1}$ hence substituting into eqn (1) $DH^{\circ}(-CH_2-CF_2-) = 362 \text{ kJ mol}^{-1}$ and from eqn (3) $E_1 = 303 \text{ kJ mol}^{-1}$ (experimental value 308 kJ mol}^{-1}).

CALCULATION FOR THERMAL DECOMPOSITION OF 1,1-DIFLUOROCYCLOBUTANE

From eqn (1) $\Delta H_r^\circ = 83 \text{ kJ mol}^{-1}$.

From eqn (2) $\Delta H_{\rm f}^{\rm o} = -368 \, \rm kJ \, mol^{-1}$.

From eqn (3) $E_1 = 282 \text{ kJ mol}^{-1}$ (experimental value 290 kJ mol⁻¹).

Finally we use this calculation procedure for the decomposition of octafluorocyclobutane :

From eqn (1) $\Delta H_{\rm f}^{\circ} = 2DH^{\circ}(-CF_2-CF_2--)-E_{\rm s}-2D\pi^{\circ}(C_2F_4)$ = 2(374.5)-109.6-2(219) = 201 kJ mol⁻¹ (observed \approx 209 kJ mol⁻¹). From eqn (2) $\Delta H_{\rm f} = -1519$ kJ mol⁻¹ (observed ≈ -1527 kJ mol⁻¹). From eqn (3) 201 = $E_1 - 126(E_2)$ *i.e.*, $E_1 = 327$ kJ mol⁻¹ (observed = 310 kJ mol⁻¹).

For this compound there is a relatively large discrepancy between E_1 calculated and observed and indeed a similarly large discrepancy between E_2 calculated here and the observed value of 100 ± 5 kJ mol⁻¹. The discrepancy suggests that the balance between σ bond cleavage and π bond formation of octafluorocyclobutane decomposition is quite different from that in cyclobutane decomposition. This is the most extreme case considered. Since for the fluorocarbon system the σ bonds are strong and the π bonds weak relative to the hydrocarbon analogue, this discrepancy implies that the transition state for dimerisation of C₂F₄ or fragmentation of ocatafluorocyclobutane involves significantly more σ bonding and less π bonding than the transition state for cyclobutane.