The Thermal Decomposition of Perfluorocyclopropane
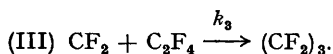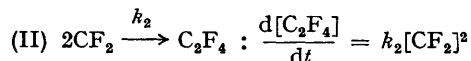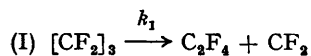
By B. Atkinson and D. McKeagan

(Chemistry Department, Imperial College of Science and Technology, London, S.W.7)

We have found that perfluorocyclopropane decomposes thermally to tetrafluoroethylene and difluoromethylene. The fluorocarbon is much less stable than cyclopropane.

Perfluorocyclopropane was prepared by the mercury-photosensitized reaction of tetrafluoroethylene[1] and purified by gas–solid chromatography. Reaction products were separated by gas–solid chromatography and identified by infrared spectra. At 276° the sole product at 70% decomposition of perfluorocyclopropane is tetrafluoroethylene: the amount of perfluoropropene formed, if any, was less than 0·1%. At 375° octafluorocyclobutane is formed in significant amounts through the dimerization of tetrafluoroethylene. In quantitative studies of the reaction at 253—276° a pressure transducer was used in recording pressure changes and the material balance was checked by terminal analysis. The stoicheiometric reaction is $2C_3F_6 \rightarrow 3C_2F_4$. The variation of initial rate with initial pressure indicates a unit order of reaction, but the rate during a run decreases at a higher order because of the vital influence of tetrafluoroethylene on the

rate. Pressure–time curves can be fitted quantitatively to an integrated rate equation derived from the following mechanism,

$$(\text{I}) \quad [CF_2]_3 \xrightarrow{k_1} C_2F_4 + CF_2$$

$$(\text{II}) \quad 2CF_2 \xrightarrow{k_2} C_2F_4 \; : \; \frac{d[C_2F_4]}{dt} = k_2[CF_2]^2$$

$$(\text{III}) \quad CF_2 + C_2F_4 \xrightarrow{k_3} (CF_2)_3.$$

The fitting process involved a graphical integration of the differential rate equation.

$$k_1 c_r + \frac{dc_r}{dt} - (c_{r_0} - c_r) - \left(\frac{9 k_3^2}{8 k_2} \frac{dc_r}{dt} \right)^{\frac{1}{2}} = 0$$

where c_r is the molar concentration of reactant. Accurate values of k_1 were obtained, but we hope to reduce the present error ($\pm 10\%$) in $k_3/k_2^{\frac{1}{2}}$ by using a computer, and the ranges of temperature and pressure covered are being extended in current work.

The presence of CF_2 in the reaction mixture has been confirmed by performing the reaction in the presence of perfluoropropene and ethylene. With perfluoropropene present a substance giving the $6\cdot6\mu$ and $11\cdot9\mu$ absorption bands expected for perfluoromethylcyclopropane[2] is formed. The same substance is formed when the mercury-photosensitized reaction of tetrafluoroethylene is performed in the presence of perfluoropropene. With ethylene present small amounts of a substance believed to be 1,1-difluorocyclopropane are formed. The poor yield indicates that CF_2 does not add to ethylene as rapidly as it does to tetrafluoroethylene, or that the activated $CF_2C_2H_4$ initially formed

is unstable at the temperature and pressure of the experiment.

Experiments at 253—276° gave $k_1 = 10^{13\cdot25}$ exp$(-38,600/RT)$ sec.$^{-1}$, no variation with pressure being detected in the range 2—16 cm. Values of $k_3/k_2^{\frac{1}{2}}$ in the above temperature range were combined with the value of $1\cdot1 \times 10^{-2\cdot8}$ at 30° from the mercury-photosensitized reaction of tetrafluoroethylene[1] to obtain the expression $k_3/k_2^{\frac{1}{2}} = 10^{2\cdot8}$ $T^{\frac{1}{2}}$ exp$(-7900/RT)$ M$^{-\frac{1}{2}}$sec.$^{-\frac{1}{2}}$ There is possible error of ± 1 kcal. in the activation energy. With the value of $k_2 = 10^{6\cdot57}$ $T^{\frac{1}{2}}$ exp$(-1200/RT)$ M^{-1}sec.$^{-1}$ found by Dalby[3] we obtain $k_3 = 10^{6\cdot09}$ $T^{\frac{1}{2}}$ exp$(-8500/RT)$ M^{-1}sec.$^{-1}$ Combination of k_1 and k_3 gives for $[CF_2]_3 \to CF_2 + C_2F_4$, $\Delta H_1 \approx 31$ kcal.

For the reaction $(CH_2)_3 \to CH_3CH{=}CH_2$, $k = 10^{15\cdot3}$ exp$(-65,084/RT)$sec.$^{-1}$ [4] and similar constants have been found for methylcyclopropane,[5] dimethylcyclopropane,[6] and monofluorocyclopropane.[7] For the isomerization of 1,1,2,2-tetrafluorocyclopropane,[8] $k = 10^{15\cdot27}$ exp$(-48,480/RT)$sec.$^{-1}$ Reaction (I) above has a lower activation energy and a "normal" pre-exponential factor.

Using ΔH_f for C_2F_4 $(-152$ kcal.$)$[9] and CF_2 $(\gg -40$ kcal.$)$[10] and the above value for ΔH_1 we obtain for perfluorocyclopropane $-\Delta H_f$ $\leqslant 223$ kcal. With ΔH_f for perfluoropropene $(-259$ kcal.$)$[9] this gives $[CF_2]_3 \to CF_3CF{=}CF_2$, $-\Delta H \geqslant 36$ kcal. This figure is very high in comparison with $[CH_2]_3 \to CH_3CH{=}CH_2$, $\Delta H = -7\cdot8$ kcal. The high heat of isomerization of the fluorocarbon is probably associated with repulsion between the comparatively bulky fluorine atoms.

[1] B. Atkinson, *J. Chem. Soc.*, 1952, 2684.
[2] R. A. Mitsch, *J. Heterocyclic Chem.*, 1964, **1**, 271.
[3] F. W. Dalby, *J. Chem. Phys.*, 1964, **41**, 2297.
[4] W. E. Falconer, T. F. Hunter, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1961, 609.
[5] J. P. Chesick, *J. Amer. Chem. Soc.*, 1960, **82**, 3277.
[6] M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 1959, 3953.
[7] F. Casas, J. A. Kerr, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1964, 3655.
[8] F. P. Herbert, J. A. Kerr and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1965, 5710.
[9] C. R. Patrick, *Adv. Fluorine Chem.*, 1961, **2**, 27.
[10] J. P. Simons, *Nature*, 1965, **205**, 1308.