208. *The Thermal Decomposition of Octadeuterocyclobutane and Octafluorocyclobutane.*

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The high-pressure rate constant for the decomposition of [$^2H_8$]*cyclo*butane at 443° is greater than that for ordinary *cyclo*butane and the fall-off of the rate constant takes place at a slightly higher pressure for the deuterated species. The decomposition of octafluoro*cyclo*butane is shown to be a complex process unsuitable for testing theories of unimolecular reactions.

Slater [1] has pointed out that his theory of unimolecular reactions leads to the expectation that an isotope effect should be observable in the thermal decompositions of *cyclo*propane and *cyclo*butane. We have studied the pressure dependence of the rate constant for the thermal decomposition of [$^2H_8$]*cyclo*butane, and in an attempt to gain more information about the nature of the isotope effect, we have also studied the decomposition of octafluoro*cyclo*butane on the (mistaken) supposition that the substitution of fluorine for hydrogen might only be accompanied by a large pseudo-isotope effect.

EXPERIMENTAL

*Thermal Decomposition of Octadeutero*cyclo*butane.*—A sample of [$^2H_8$]*cyclo*butane of 99·7% isotopic purity was kindly given to us by Dr. D. G. Rea; after bulb-to-bulb distillation, mass-spectrometric analysis confirmed the deuterium content of the material, and showed that no impurities were present. The details of apparatus and procedure are identical with those already described for the parallel study on normal *cyclo*butane [2] except that, owing to the rather greater rate constant in the present experiments and the limited amount of substance available, the temperature of the reaction vessel used was 442·6° instead of about 448°. Ten runs taken to about 30% decomposition were performed, covering the pressure range 1·25—0·005 cm., and extrapolation of k against $1/p$ led to the value $k_\infty(C_4D_8) = 5{\cdot}5 \times 10^{-4}$ sec.$^{-1}$ at 442·6° as compared with $k_\infty(C_4H_8) = 2{\cdot}6 \times 10^{-4}$ sec.$^{-1}$ calculated for the same temperature. The individual results are plotted in the Figure showing the variation of log k/k_∞ with log p for [$^2H_8$]*cyclo*butane together with that for ordinary *cyclo*butane; the fall-off is shifted very slightly to higher pressures upon deuteration of the molecule.

*Thermal Decomposition of Octafluoro*cyclo*butane.*—Octafluoro*cyclo*butane was prepared by heating tetrafluoroethylene in a Pyrex vessel for about 30 hr. at 330°; at this temperature, the equilibrium $2C_2F_4 \rightleftharpoons C_4F_8$ lies well to the right.[3] The dimer was purified by low-temperature fractional distillation. Experiments were carried out in a 1-l. spherical Pyrex reaction vessel kept by thermostat at 530°, the course of the reaction being studied by pressure measurement and by analysis of the products. The behaviour of the system varied markedly according to conditions, *e.g.*, pressure, presence of impurities and ageing of the reaction vessel, and the most important effects are dealt with in the following five sections:

(i) In an unaged vessel a very rapid reaction took place in which the pressure of the system doubled in about 1—1½ min. and then remained approximately constant; the vessel could be aged by leaving tetrafluoroethylene in it overnight, but the effect was immediately reversed upon the admission of air. If during the progress of rapid decomposition the mixture was frozen out with liquid nitrogen and then allowed to evaporate, a 30% decrease in pressure was observed and a thin layer of polymer was formed in the cold part of the system; this is consistent either with the presence of long-lived free radicals in the mixture, or with the presence of hydrogen fluoride or oxygen (originating from the walls) which are known to polymerize tetrafluoroethylene under suitable conditions.

(ii) Atkinson and Trenwith reported a first-order rate constant for the decomposition of octafluoro*cyclo*butane of about 6×10^{-5} sec.$^{-1}$ at 530° in the pressure range 35—45 cm. Our experiments at this temperature and at 30 cm. initial pressure (p_0) were in excellent agreement with these results: equilibrium was reached in about 10 min., and mass-spectral analysis of the equilibrium mixture confirmed that, apart from traces of carbon monoxide and silicon tetrafluoride, only octafluoro*cyclo*butane and tetrafluoroethylene were present; on the basis of

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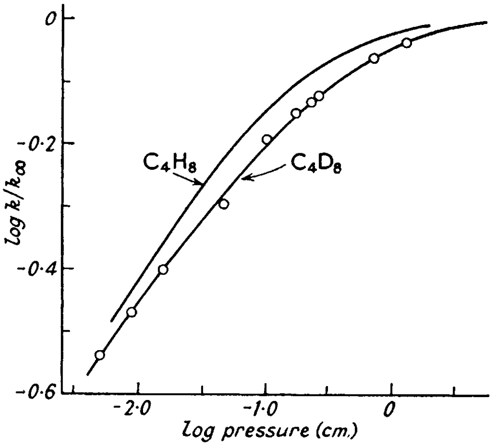
[1] Slater, *Phil. Trans.*, 1953, *A*, **246**, 57.

[2] Pritchard, Sowden, and Trotman-Dickenson, *Proc. Roy. Soc.*, 1953, *A*, **218**, 416.

[3] Atkinson and Trenwith, *J.*, 1953, 2082.

Atkinson and Trenwith's interpretation of a first-order decomposition opposed by a second-order dimerization, we obtained the first-order rate constant of 3×10^{-5} sec.$^{-1}$. If, however, the equilibrium mixture remained in the vessel, there was a very gradual increase in pressure, having a zero-order rate constant of 0·01 cm. min.$^{-1}$ to a final pressure of $9{\cdot}6p_0$. The final equilibrium mixture was shown by mass-spectrometric analysis to consist mainly of silicon tetrafluoride and carbon monoxide, some water (which can only arise from hydroxyl ions in the glass), and a trace of tetrafluoroethylene; volatile boron compounds were also shown to be present in the mixture by rapidly pumping out the contents of the vessel into a trap containing water and applying the standard qualitative tests for boron.

(iii) A series of runs were made covering the pressure range 30—0·03 cm., but no decrease in the rate constant was detected—in fact, it apparently increased. At the lower pressures the condition of equilibrium became less apparent and often there was only an inflection in the p–t curve before the steady rise to $9{\cdot}6p_0$ became dominant; in those cases where the first equilibrium could be detected with reasonable certainty, the following apparent first-order constants were obtained :



The dependence of the rate of decomposition of cyclo*butane and* [$^2H_8$]cyclo*butane on pressure.*

p_0 (cm.)	31·55	5·0	1·0	0·16	0·08	0·03
k (sec.$^{-1}$) $\times 10^5$	3	10	15	120	237	330

It is clear that the decomposition of octafluoro*cyclo*butane is not a simple unimolecular process, and the following additional experiments were therefore performed.

(iv) In a run with 1 cm. of octafluoro*cyclo*butane and 1·8 cm. of water, the approach to the first equilibrium was unaffected, but the rate of the zero-order pressure rise was *decreased* by a factor of 10 and the final pressure (after allowance for the added water) was only $8{\cdot}9p_0$ instead of $9{\cdot}6p_0$, demonstrating that water, both in the solid and in the vapour phase, is fundamentally involved in the zero-order process.

(v) Several runs were carried out in the presence of about 10% of toluene : the general behaviour of the p–t curve remained unchanged except that during the first 10 min. the pressure varied in a periodic manner; the number and positions of the pressure maxima and minima were quite reproducible from one run to another. Mass-spectrometric analysis of the mixture showed it to contain a very large number of partially fluorinated hydrocarbons, up to and including a mass number of 225, strongly indicative of a complex free-radical process.

Discussion.—It is not an easy matter to correlate the results for octadeutero*cyclo*butane with Slater's theory, which is dependent on a complete vibrational analysis of both molecules and the suitable choice of a critical co-ordinate. One can say, however, that if the critical energy of activation for both molecules is the same,* the critical co-ordinate is neither a C–H nor an H–H distance, because the theory would then predict $k_\infty(C_4H_8)/k_\infty(C_4D_8) \approx \sqrt{2}$ in both cases, as opposed to the ratio of $\frac{1}{2}$ actually found; our observations are, however, consistent with Slater's theory in that the *higher* value

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* We are unable now to undertake experiments which would be sufficiently accurate to detect a small difference in the activation energies for the decomposition of these molecules.

of k_∞ is associated with the fall-off taking place at a *higher* pressure than for the normal molecule.

The octafluoro*cyclo*butane experiments show that, even allowing for the complication of handling fluorocarbons in a glass system, the thermal decomposition of octafluoro*cyclo*butane is not a simple unimolecular reaction and thus not suitable for energy-transfer studies. We are not prepared to speculate upon the nature of the reactions taking place, but it seems likely that the initial decomposition proceeds by fission of a C–C bond; the best estimate for the C–C dissociation energy in *cyclo*butane is 74 kcal./mole,[4, *] and whilst *cyclo*butane itself decomposes by a non-radical mechanism having an activation energy of 62·8 kcal./mole, the decomposition of octafluoro*cyclo*butane has an activation energy of 74·1 kcal./mole and is attended by obvious free-radical effects.

In conclusion we acknowledge the help received from Drs. R. G. Sowden and A. F. Trotman-Dickenson through their collaboration in the early stages of the octafluoro*cyclo*butane work, and from Dr. J. C. Robb who carried out the mass-spectrometric analyses; also, we are greatly indebted to Dr. D. G. Rea for his generous gift of the sample of octadeutero*cyclo*butane. This work was carried out whilst one of us (B. F. G.) was in receipt of a D.S.I.R. maintenance grant.

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[*] The derivation of this value has been critised by Seubold [5] but Dr. Seubold has agreed with us in personal correspondence that his criticism is invalid.

[4] Pritchard and Trotman-Dickenson, *Chem. and Ind.*, 1954, 1064.

[5] Seubold, *ibid.*, p. 1389.