

265. The Thermal Decomposition of Hexafluoroacetone.

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The thermal decomposition of hexafluoroacetone in a steel vessel at temperatures in the range 550—628° is described. At the lower temperatures a first-order reaction leading to the formation of hexafluoroethane and carbon monoxide predominates; this occurs as a result of a rearrangement rather than a free-radical mechanism. At the higher temperatures, a second first-order mode of decomposition to trifluoroacetyl fluoride and difluoromethylene becomes increasingly important and predominates at 600°; at this temperature, difluoromethylene radicals polymerise readily to octafluoroisobutene. Trifluoroacetyl fluoride is more stable than hexafluoroacetone, decomposing to carbonyl fluoride and difluoromethylene. Carbonyl fluoride decomposes by a heterogeneous process to yield mainly carbon monoxide.

FEW kinetic studies have been made of the thermal decomposition of completely fluorinated organic compounds, and those by Atkinson and Trenwith,¹ Atkinson and Atkinson,² Dresner, Mao, and Young,³ and Cady⁴ indicate that the products are usually appreciably different from those of the analogous hydrocarbons. As yet there is insufficient evidence to allow the mode of decomposition of a perfluoro-compound to be predicted with any certainty, but the present work shows that certain types of reaction appear to be common to quite different systems and so may be characteristic of many perfluoro-compounds.

The pyrolysis of hexafluoroacetone has been followed in a static system with a steel reaction vessel. The products and the rates of reaction show that there are two distinct modes of decomposition; the first is an initial splitting of the molecule into trifluoroacetyl fluoride and a difluoromethylene radical, and the second involves the rearrangement to hexafluoroethane and carbon monoxide which is predominant at lower temperatures. Rate constants for both processes have been determined and compared with available data for similar reactions of other perfluoro-molecules.

EXPERIMENTAL

Materials.—Hexafluoroacetone was prepared by permanganate oxidation of octafluoroisobutene.⁵ It was fractionated in a low-temperature (Podbielniak) distillation column, a middle cut being taken for use and stored in a blackened bulb at liquid-nitrogen temperature.

Carbonyl fluoride was prepared by the action of silver difluoride on carbon monoxide.⁶

The purity of these materials was checked by molecular-weight determinations and by their infrared spectra, which corresponded with those given by Simons.⁷

Apparatus.—This was of the conventional static type; a mild spun-steel reaction vessel (25 × 6.5 cm.) with a capillary inlet and a thermocouple well was joined to the glass part of the apparatus by a Fyffe coupling and Neoprene ring. It was heated in a tubular electric furnace kept to within $\pm 0.2^\circ$ of the required temperature by a "Sunvic" resistance-thermometer controller, type R.T.2. The temperature was measured by means of a chromel-alumel thermocouple and a Doran potentiometer. Evacuation of the apparatus was by a mercury-vapour pump backed by a rotary oil pump. A constant-volume mercury manometer⁸ was used to measure pressures in the reaction vessel. A two-way tap enabled it to be connected to either a storage bulb or a series of four collecting traps; the first three traps were empty and the last contained activated charcoal. The empty traps were connected to a small Podbielniak-type

¹ B. Atkinson and Trenwith, *J.*, 1953, 2082.

² B. Atkinson and V. Atkinson, *J.*, 1957, 2086.

³ Dresdner, Mao, and Young, *J. Org. Chem.*, 1959, **24**, 698.

⁴ Cady, *Proc. Chem. Soc.*, 1960, 133.

⁵ Morse, Ayscough, and Leitch, *Canad. J. Chem.*, 1955, **33**, 453.

⁶ Ruff and Miltschitzky, *Z. anorg. Chem.*, 1934, **221**, 154.

⁷ Simons, "Fluorine Chemistry," Academic Press Inc., New York, 1954, Vol. II.

⁸ Dodd and Robinson, "Experimental Inorganic Chemistry," Elsevier, Amsterdam, 1954, p. 122.

distillation column, and the charcoal trap to a gas burette which could be used as either a Töpler pump or a McLeod gauge.

Operation.—The reaction vessel was first heated to 700° with a stream of hydrogen passing through it to remove any oxide scale formed during welding. A capillary outlet provided for this purpose was subsequently sealed off. The vessel was then filled with hexafluoroacetone and left overnight at 600° to condition the surface.

The decomposition of hexafluoroacetone was followed by both the change of pressure with time and an analysis of the products after various periods of heating. Pressure–time measurements were made in the usual way, pressures being noted approximately every half-minute, and initial pressures were determined by extrapolation of the pressure–time curves to zero time. Between runs the reaction vessel was evacuated for at least 15 min. Results for duplicate runs showed good reproducibility. For analysis, five identical runs were made for each heating period and the products combined to give sufficient material for the distillations. The four collecting traps were cooled in liquid nitrogen, condensable products being frozen in the first three traps and non-condensable materials adsorbed on the activated charcoal. The condensable material was transferred to the low-temperature column and analysed by fractional distillation, individual fractions being identified by their b. p., molecular weight, and infrared spectrum. The non-condensable portion was transferred to the gas-burette by raising the temperature of the charcoal to 300°, and measured; its composition was ascertained by molecular-weight measurements and analysis by mass spectrometer.

RESULTS

The compounds identified in the products of pyrolysis of hexafluoroacetone were trifluoroacetyl fluoride, octafluoroisobutene, hexafluoroethane, carbonyl fluoride, and carbon monoxide; their amounts after various heating times at 600° are shown in Fig. 1. Carbonyl fluoride was present in measurable quantities only after the time required for about 50% decomposition. Rate measurements were made at temperatures between 550° and 628°. In the lower-temperature range pressure changes were very slow and just measurable manometrically, and at the higher were extremely rapid. At each temperature, the initial rates, given by the initial

TABLE 1. *Variation of first-order rate constant with pressure and temperature.**

Temp. p_0	550°		567°		576°		590°	
	$10^4(dp/dt)_0/p_0$	p_0	$10^4(dp/dt)_0/p_0$	p_0	$10^4(dp/dt)_0/p_0$	p_0	$10^4(dp/dt)_0/p_0$	p_0
31.5	0.635	55.5	1.207	55.5	1.891	51.0	3.920	
46.0	0.652	60.5	1.256	64.5	1.891	59.5	3.948	
62.0	0.645	65.0	1.246	71.5	1.790	69.5	3.960	
		76.0	1.210	75.5	1.880	77.5	3.935	
		84.0	1.202	85.5	1.905	84.0	3.868	
		90.5	1.214	94.5	1.820	94.0	3.710	
				103.0	1.748	102.0	3.871	
Mean	0.645		1.223		1.846		3.887	

Temp. p_0	596°		610°		628°	
	$10^4(dp/dt)_0/p_0$	p_0	$10^4(dp/dt)_0/p_0$	p_0	$10^4(dp/dt)_0/p_0$	p_0
54.5	5.685	42.5	11.76	46.0	26.96	
60.5	5.617	51.5	11.85	62.5	27.52	
70.0	5.712	61.0	11.96			
84.5	5.678	72.0	12.22			
96.0	5.830	79.0	11.65			
109.5	5.569	90.0	11.78			
Mean	5.682		11.87		27.24	

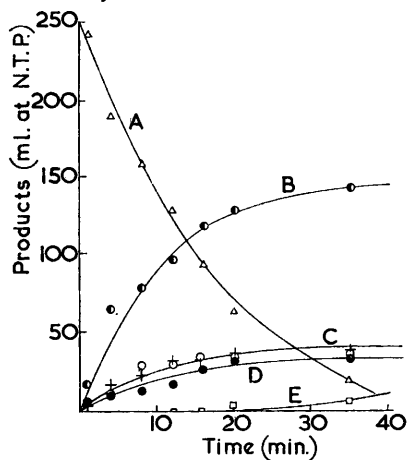
* Pressures (p_0) are in mm. of Hg. Rates $(dp/dt)_0$ are in mm. of Hg/sec.

slopes of the pressure–time curves, were determined for initial pressures of hexafluoroacetone between 30 and 110 mm. Plots of initial rate against pressure of hexafluoroacetone for every temperature gave straight lines passing through the origin and indicated that a first-order rate law applies to the decomposition under the experimental conditions. Values obtained for the

first-order rate constants at various pressures and temperatures are given in the Table. The Arrhenius plot of the rate constants is shown in Fig. 2. The points deviate from a straight line at the lower temperatures, the deviation increasing as the temperature falls. The temperature-dependence of the first-order rate constant is $k = 10^{16.6} \exp(-79,100/RT) \text{ sec.}^{-1}$ from the full line and $k' = 10^{9.6} \exp(-50,900/RT) \text{ sec.}^{-1}$ from the broken line.

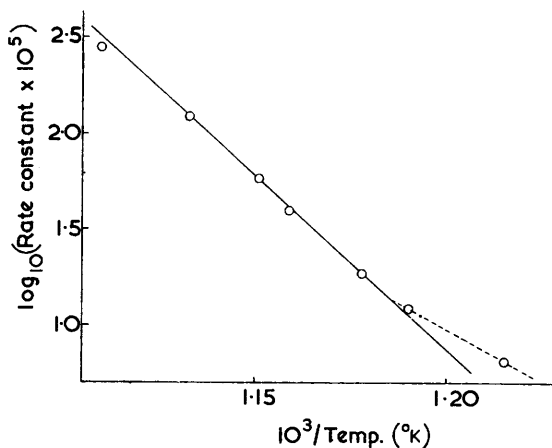
The decomposition of carbonyl fluoride was also investigated. There was no change in pressure when this compound was heated. At 600°, the products were carbon monoxide and a trace of silicon tetrafluoride. The rate of decomposition was followed between 554° and 600°. At the different temperatures a fixed amount was heated for varying times and the carbon monoxide was measured. Initial slopes of the curves for carbon monoxide formed against time were determined and graphs plotted of $d\text{CO}/dt$ against the initial pressures of carbonyl

FIG. 1. Products of pyrolysis of hexafluoroacetone at 600°.



A, $(\text{CF}_3)_2\text{CO}$. B, $\text{CF}_3\cdot\text{COF}$. C, CO and C_2F_6 (+ = CO, O = C_2F_6). D, C_4F_8 . E, COF_2 .

FIG. 2. Arrhenius plot of the rate constants for the decomposition of hexafluoroacetone.



fluoride. These were straight lines passing through the origin. An Arrhenius plot of the first-order rate constants derived from the slopes of these lines yielded the rate expression $k'' = 10^{13.3} \exp(-62,700/RT) \text{ sec.}^{-1}$.

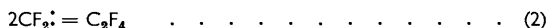
Some trifluoroacetyl fluoride, separated from combined products of pyrolysis by fractional distillation, was heated in the reaction vessel at 600°; it gave a very slow, steady increase in pressure with time. After 15 minutes' heating, the products consisted of carbonyl fluoride, octafluoroisobutene and carbon monoxide; there was some unchanged material. Even after being heated at 600° for >4 hours, some of the trifluoroacetyl fluoride remained undecomposed.

DISCUSSION

Trifluoroacetyl fluoride is the major product of pyrolysis of hexafluoroacetone at 600°. To account for its formation, it is suggested that a primary step in the decomposition is



followed by



Atkinson and Atkinson² have shown that at 650°, tetrafluoroethylene decomposes to give octafluoroisobutene, with octafluorocyclobutane and hexafluoropropene as intermediates. The tetrafluoroethylene and octafluorocyclobutane are rapidly consumed but the hexafluoropropene disappears much more slowly. The octafluoroisobutene formed in the hexafluoroacetone decomposition almost certainly results from the decomposition of

tetrafluoroethylene produced by reactions (1) and (2). As would be expected, it is always approximately one quarter of the amount of trifluoroacetyl fluoride formed. Of the intermediates, tetrafluoroethylene and octafluorocyclobutane could not be produced in measurable quantities because of their obvious instability at 600°. Hexafluoropropene, if formed, would have been separated in the hexafluoroacetone fraction because of the identity of boiling points; but since the latter must always be present in excess, it is understandable that the former was not detected from the infrared spectra.

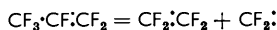
If the steps leading to the formation of octafluoroisobutene from difluoromethylene radicals are rapid compared with (1), the rate of the overall reaction



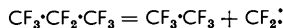
will equal that of reaction (1). The measured constant k is considered to be the rate constant for the reaction (3) because it applies between 576° and 628°. Since, in reaction (3), $-dCF_3 \cdot CO \cdot CF_3/dt = 4dp/dt$, the rate constant k_1 for (1) will be four times k ; hence $k_1 = 10^{17.2} \exp(-79,100/RT)$ sec.⁻¹.

Reaction (1) may be considered to occur by transfer of a fluorine atom from one carbon to the next and splitting-off of the remaining difluoromethylene group. (The high A factor seems to indicate two or more successive steps.)

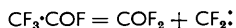
It is pertinent to consider other reactions which appear to involve a similar initial process. One such is the decomposition of hexafluoropropene for which the proposed primary step² is



This reaction has an activation energy of ≤ 75 kcal. mole⁻¹, significantly close to that found for (1). Steunenberg and Cady⁹ have suggested that a number of saturated fluoro-carbons may also decompose by a process with a similar initial step; thus, for instance, the products of decomposition of octafluoropropane indicate that the most likely primary step is



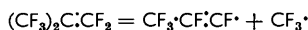
Although a detailed study of the decomposition of trifluoroacetyl fluoride has not been made, it seems reasonable to assume from the products that the initial step in the decomposition is



The apparently greater thermal stability of this compound than of hexafluoroacetone is analogous to the greater stability of hexafluoroethane than of octafluoropropane.⁹ By further analogy, perfluoroisobutene might be expected to decompose and to yield only perfluoro-olefins, following the initial reaction



In fact, it is comparatively stable at 600° and decomposes at higher temperatures to give one molecule of hexafluoroacetone for each molecule decomposing, the proposed initial reaction being



Another molecule which does not decompose in the expected manner is perfluorodiethyl ether, since no perfluoroethyl trifluoromethyl ether was found among the products.³ It is of interest that all the perfluoro-compounds which decompose readily by a process involving the initial step we have been considering possess three linked carbon atoms per molecule. Although there appears to be no theoretical significance in this, it would be of interest to see whether other similar fluoro-compounds exhibit the same behaviour.

⁹ Steunenberg and Cady, *J. Amer. Chem. Soc.*, 1952, **74**, 4165.

To account for the formation of hexafluoroethane and carbon monoxide from hexafluoroacetone it is suggested that there is a second mode of decomposition, namely:



This reaction is predominant at temperatures below 570° and the one to which the rate constant k' applies. Since for it $-\text{dCF}_3\cdot\text{CO}\cdot\text{CF}_3/\text{dt} = \text{dp}/\text{dt}$, k_4 equals k' . The reaction could occur by a chain mechanism with $\text{CF}_3\cdot$ and $\text{CO}\cdot\text{CF}_3\cdot$ radicals as intermediates, or by a rearrangement involving the formation of an activated complex with a three-membered carbon ring. The latter is preferred in view of the low A factor which indicates the negative entropy of activation associated with the formation of a cyclic intermediate. A somewhat similar rearrangement through a cyclic intermediate probably occurs in the decomposition of perfluoroethyl ether, where, as a primary step, the splitting of the molecule into carbonyl fluoride and octafluorobutane has been proposed.³

The thesis of two possible modes of decomposition of hexafluoroacetone can be tested in the following way. Since $\text{dCF}_3\cdot\text{COF}/\text{dt} = k_1[\text{CF}_3\cdot\text{CO}\cdot\text{CF}_3]$ and $\text{dCO}/\text{dt} = k_4[\text{CF}_3\cdot\text{CO}\cdot\text{CF}_3]$ it follows that $\text{dCO}/\text{dCF}_3\cdot\text{COF} = k_4/k_1$. The ratio of the rate constants at 600° is 0.29 and this agrees well with the 0.30 found for $\text{dCO}/\text{dCF}_3\cdot\text{COF}$ from the initial slopes of the appropriate curves in Fig. 1.

The fact that only carbon monoxide, silicon tetrafluoride, and unchanged material were present in the products of pyrolysis of carbonyl fluoride indicates the occurrence of some reaction with the surface of the vessel. This view is supported by the comparatively low energy of activation found, since the reaction must involve the initial splitting of a C-F bond, and this process requires¹⁰ an energy of about 116 kcal. mole⁻¹.

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¹⁰ Cottrell, "The Strengths of Chemical Bonds," Butterworths Scientific Publications, London, 1958.