Kinetics of the Pyrolysis of Trimethylarsine, Tristrifluoromethylarsine, and Related Compounds.

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A kinetic study of the pyrolysis of trimethyl- and tristrifluoromethylarsine has shown both reactions to be homogeneous and of the first order. They show little difference in activation energy. The main gaseous products are methane, from trimethylarsine, and hexafluoroethane from tristrifluoromethylarsine. Tentative reaction mechanisms based on primary steps involving the liberation of methyl or trifluoromethyl radicals are discussed. The decomposition of trispentafluoroethylarsine is kinetically similar to that of tristrifluoromethylarsine. Preliminary experiments show that the pyrolysis of tristrifluoromethylstibine yields a much higher proportion of unsaturated fluorocarbons.

IN the decomposition of simple alkyl-metallic and alkyl-metalloidal compounds the primary step is believed to be the formation of free alkyl radicals. The purpose of the investigation described below was to study kinetically the pyrolysis of trimethyl- and tristrifluoromethylarsine with a view to comparing the reactions of trifluoromethyl radicals with those of the more familiar methyl radicals. Some preliminary work on the pyrolysis of trispentafluoroethylarsine and tristrifluoromethylstibine is also described.

The products of the decomposition of trimethylarsine have not hitherto been examined, although those of the pyrolysis or photolysis of other metal alkyls are known. Table 1 summarises the relevant information for methyl derivatives of mercury, lead, tin, and silicon. The symbols (T) and (P) indicate that decomposition was respectively thermal or photochemical. In these reactions the composition of the products varies systematically with the decomposition temperature rather than with the nature of the atom to which the methyl radical is attached. At room temperature the main reaction is dimerisation to ethane but, as the temperature increases, hydrogen-abstraction reactions occur and ethane is progressively replaced by methane. Above 500° ethylene and hydrogen appear in larger quantities, the ethylene suffering polymerisation and decomposition reactions.

TABLE 1.

Decomp. temp.	Compound	Products (%)					Ref.
		CH_4	C_2H_6	C_2H_4	H_2	Higher hydrocarbons	
25°	$HgMe_2$ (P)	—	100	—	—	—	1
200	$HgMe_2$ (P)	5	93	—	—	—	1
265	$PbMe_4$ (T)	65	22	2	—	5	2
295	$PbMe_4$ (T)	69	23	2·5	—	4·5	2
302	$HgMe_2$ (T)	71	25	—	—	—	3
340	$PbMe_4$ (T)	86	12	2	0·5	2	2
348	$HgMe_2$ (T)	82	15	—	—	—	3
410	$AsMe_3$ (T)	90	4	2·5	1	2·5	—
485	$SnMe_4$ (T)	88	—	4	6	—	4
550	$PbMe_4$ (T)	29	19	26	22	—	2
659	$SiMe_4$ (T)	58	—	1·5	39	1	5

References: 1, Linnett and Thompson, *Trans. Faraday Soc.*, 1937, **33**, 501; Rebbert and Steacie, *Canad. J. Chem.*, 1953, **31**, 631. 2, Simons, McNance, and Hard, *J. Phys. Chem.*, 1932, **36**, 939. 3, Cunningham and Taylor, *J. Chem. Phys.*, 1938, **6**, 359. 4, Waring and Horton, *J. Amer. Chem. Soc.*, 1945, **67**, 540. 5, Helm and Mack, *ibid.*, 1937, **59**, 60.

Table 1 includes the products of the pyrolysis of trimethylarsine at 410°. The kinetic study of the decomposition of this compound was made at 410—450° and within this range the yields of methane and other products remain approximately the same, namely: methane, 90%; ethane, 4%; ethylene, 2·4%; propylene, 2%; hydrogen 1%. Small amounts of higher hydrocarbons are also formed, together with carbon. All of these products are believed to be derived directly or indirectly from methyl radicals, the reactions of which are fairly well established (see E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publ. Corp., New York, 1946).

If it is assumed that trimethylarsine first gives methyl radicals, the low yield of ethane indicates that dimerisation and the abstraction of a methyl radical from an undecomposed molecule of reactant ($CH_3\cdot + AsMe_3 = AsMe_2\cdot + C_2H_6$) are both unimportant. In the early stages of the reaction it is likely that methane may arise from the reaction :

$$CH_3\cdot + AsMe_3 = CH_4 + AsMe_2\cdot CH_2\cdot$$

The subsequent fate of the complex radical $AsMe_2\cdot CH_2\cdot$ is unknown.

At a later stage the abstraction of hydrogen from other hydrocarbons by methyl radicals may become important. The formation of ethylene and hydrogen may be explained by disproportionation reactions such as $2CH_3\cdot = C_2H_4 + H_2$ and $2CH_3\cdot = CH_4 + \cdot CH_2\cdot$, followed by dimerisation of the methylene radicals. Both of these reactions have been postulated by other authors (Helm and Mack, *J. Amer. Chem. Soc.*, 1937, **59**, 60; Waring and Horton, *ibid.*, 1945, **67**, 540) in order to account for the presence of these compounds in the products from the pyrolysis of other organometallic compounds in the same temperature range. Reaction of ethylene with methyl or methylene radicals could give higher saturated or unsaturated hydrocarbons. The decomposition of trimethylarsine in a silica vessel at 400—500° was homogeneous and of the first order with an activation energy of 54·6 kcal./mole. This may be identified with the dissociation energy of the arsenic–carbon bond if it is assumed that the activation energies of secondary reactions in the decomposition are small. A similar argument has been applied in interpreting the activation energies for the thermal decomposition of other alkyl-metallic compounds. The following are typical values : $PbEt_4$ at 245—275°, 36·9 kcal./mole (Meinert, *ibid.*, 1933, **55**, 979); $SiMe_4$ at 659—717°, 78·8 kcal./mole (Helm and Mack, *loc. cit.*); $SiEt_4$ at 520—600°, 50·0 kcal./mole (Waring, *Trans. Faraday Soc.*, 1940, **36**, 1142). These reactions were also of the first order and homogeneous.

The decomposition of tristrifluoromethylarsine in a silica vessel at 350—410° gave 60—90% of hexafluoroethane in the volatile reaction product, corresponding approximately with the reaction $As(CF_3)_3 = As + \frac{3}{2}C_2F_6$, though the pressure increase was somewhat greater than 50%. Up to 10% of perfluoropropane and perfluorobutane were also formed, but no unsaturated fluorocarbons were detected. Most of the residue of the volatile products was a mixture of silicon tetrafluoride and carbon dioxide. These gases made up about 10% of the volatile product from a fresh silica bulb but, with continued use of the bulb, the amount increased and was 20—30% in most of the quantitative runs. Analyses of the products at different stages showed that the proportion of silicon tetrafluoride and carbon dioxide did not vary appreciably during any particular run. These products increased the ratio of the final to the initial pressure. In spite of this complicating factor it was found that, when the total pressure increase was used as a measure of the extent of reaction, the rate constants did not vary appreciably for a given temperature despite considerable differences in the proportions of fluorocarbons and silicon tetrafluoride plus carbon dioxide.

The decomposition of tristrifluoromethylarsine was a first-order reaction and, for the range 350—410°, had an activation energy of 57·4 kcal./mole. If this is identified with the dissociation energy of the carbon–arsenic bond, it is clear that replacement of hydrogen by fluorine causes little change in the bond energy. The nature of the main product is compatible with a primary fission of the carbon–arsenic bond to give a trifluoromethyl radical. Hexafluoroethane could be formed either by dimerisation of trifluoromethyl radicals or by the reaction $CF_3\cdot + As(CF_3)_3 = C_2F_6 + \cdot As(CF_3)_2$. The analytical results show that disproportionation reactions such as $2CF_3\cdot = CF_4 + \cdot CF_2\cdot$ do not occur to a marked extent up to 400°, since no tetrafluoromethane was formed. This reaction predominates in this temperature range for alkyl radicals. There are indications that, in systems containing only fluoroalkyl fragments, carbon–fluorine bonds are not broken to a significant extent below 1000° (Steuenberg and Cady, *J. Amer. Chem. Soc.*, 1952, **74**, 4165). The absence of unsaturated fluorocarbons, particularly tetrafluoroethylene, in the products is probably linked with the absence of $\cdot CF_2\cdot$ radicals and the very small formation of tetrafluoromethane. An explanation of the production of perfluoropropane and perfluorobutane cannot be based on analogy with the reactions of alkyl radicals since, in the latter, the formation of higher hydrocarbons is always linked with that of unsaturated material.

Some light is thrown on the reaction mechanism by a series of experiments made in a platinum vessel which became available towards the end of the investigation. The result of substituting platinum for silica was to increase the rate constant by about 50%, though the reaction remained of the first order. The composition of the fluorocarbon fraction of the products was however greatly altered (Table 7). In a series of decompositions carried out in vessels of similar size and shape, at the same temperature and pressure (370/300 mm.), C_3 and higher fluorocarbons formed about 10% of the total fluorocarbon from reactions in a silica vessel, and about 37% in a platinum vessel. Arsenic trifluoride was also formed in appreciable amounts in platinum though it was not estimated quantitatively. Very little was formed in silica vessels. In platinum it is possible that $\cdot CF_2\cdot$ radicals may be produced by collision of $CF_3\cdot$ radicals with arsenic, held as arsenide on the platinum surface. If so, reactions such as :

$$\cdot CF_2\cdot + CF_3\cdot \longrightarrow C_2F_5\cdot \longrightarrow C_4F_{10} \text{ and } CF_3\cdot + C_2F_5\cdot \longrightarrow C_3F_8$$

at once became possible. Of these reactions the latter would be more probable, whereas in fact C_3F_8 and C_4F_{10} are found in approximately equal amounts. Small amounts of an inert white polymer, having the characteristics of polytetrafluoroethylene were found in the platinum reaction vessel. This supports the hypothesis that $\cdot CF_2\cdot$ radicals are formed. If monomeric C_2F_4 exists as an intermediate it too could react with $CF_3\cdot$ to give $C_3F_7\cdot$ and C_4F_{10}. In the silica vessel elementary arsenic sublimed rapidly into the delivery tube and was therefore not available to the same extent for the formation of $\cdot CF_2\cdot$ radicals. It is thus possible to form a qualitative picture of the reaction mechanism, though it is clear that side-reactions of this type will greatly complicate the kinetic analysis of the decomposition, particularly in platinum vessels.

The mechanism of formation of silicon tetrafluoride and carbon dioxide is unknown. Direct reaction between tristrifluoromethylarsine and silica is unlikely because the rate-determining step is homogeneous. The gases are probably formed by attack of trifluoromethyl radicals on silica, which is known to occur, even at lower temperatures.

The behaviour of trispentafluoroethylarsine is fundamentally similar. It decomposes at about 280° to give a mixture of fluorocarbons in which perfluorobutane predominates (76%), though the relative amount of higher fluorocarbons (16%) is rather greater than from tristrifluoromethylarsine and there is some unsaturated material in the less volatile fractions. This is not unexpected since the build-up of higher fluorocarbons can take place *via* $\cdot CF_2\cdot$ radicals without, in this case, fission of the strong carbon-fluorine bonds. No hexafluoroethane is produced, so it may be concluded that the disproportionation reaction ($C_2F_5\cdot + C_2F_5\cdot = C_2F_6 + C_2F_4$) does not take place. Silicon tetrafluoride, carbon dioxide, and carbon monoxide are also formed in small quantities. The activation energy of the decomposition is 48 kcal./mole, so that by making the same assumptions as in the case of tristrifluoromethylarsine, a significant weakening of the arsenic-carbon bond can be observed.

The preliminary experiments on the decomposition of tristrifluoromethylstibine at 180—220° show significant differences in the products. The volatile material contains small amounts of tetrafluoroethylene, perfluoro*cyclo*propane, and other unsaturated fluorocarbons containing four or more carbon atoms. Considerable amounts of antimony trifluoride and a polymer resembling polytetrafluoroethylene remained in the silica reaction vessel, and about the same proportion of silicon tetrafluoride and carbon dioxide was produced as in the experiments with tristrifluoromethylarsine. There is insufficient evidence for a detailed consideration of the reaction mechanism, but it is noteworthy that antimony is insufficiently volatile at the reaction temperature to sublime. This therefore raises the possibility of a reaction between trifluoromethyl radicals and antimony leading to the formation of $\cdot CF_2\cdot$, the further reactions of which would probably account for the relatively high yields of unsaturated fluorocarbons.

Experimental

Materials and Methods.—Trimethylarsine was prepared by a modification of the method of Dyke and Jones (*J.*, 1930, 2426). Dry redistilled methyl iodide (175 ml.) in dry *n*-butyl ether (300 ml.) was added from a dropping funnel (3 hr.) to magnesium turnings (60 g.) in *n*-butyl ether (300 ml.). The resulting solution (unfiltered) was treated with arsenic trichloride (75 ml.) in xylene (500 ml.), added dropwise ($2\frac{1}{2}$ hr.). The temperature was kept below 50° and dry nitrogen was passed. The ether layer was syphoned off, the residue extracted with further portions of ether, and the solution distilled. The fraction boiling below 90° was redistilled several times, the sample retained for the pyrolysis experiments (22·3 g.) having b. p. 50·1—50·3° (Found : *M*, 120. Calc. for C_3H_9As : *M*, 120·0). The purity of the sample was confirmed by infra-red spectroscopy.

Tristrifluoromethylarsine was prepared by the method of Brandt, Emeléus, and Haszeldine (*J.*, 1953, 2552). Iodo-compounds were removed by shaking with mercury. Repeated fractional distillation of the residue yielded spectroscopically pure tristrifluoromethylarsine (Found : *M*, 282. Calc. for C_3F_9As : *M*, 281·9).

Trispentafluoroethylarsine and *iodobispentafluoroethylarsine* were prepared by heating pentafluoroiodoethane (30 g.) and arsenic (40 g.) in a steel autoclave for 40 hr. at 230°. Unchanged pentafluoroiodoethane and decomposition products were removed by vacuum-fractionation, and the mixture of arsenicals was distilled at reduced pressure in a small column (Found : As, 17·6; F, 66·0; C_2F_5, 81·1%; *M*, 426; b. p. 96·3°. $C_6F_{15}As$ requires As, 17·4; F, 66·0; C_2F_5, 82·7%; *M*, 432. Found : As, 17·1; F, 42·5; C_2F_5, 54·7; I, 28·6%; *M*, 450; b. p. 120°. $C_2F_{10}IAs$ requires As, 17·1; F, 43·3; C_2F_5, 54·1; I, 28·8%; *M*, 440). Fluorine was estimated by titration in buffered solution with thorium nitrate, the fluoride solution being prepared by heating the arsenical with sodium in a Carius tube at 600°, followed by steam-distillation of the aqueous solution of sodium fluoride with 50% sulphuric acid. C_2F_5 was estimated by hydrolysis with 20% sodium hydroxide solution for 24 hr. at 50° : the pentafluoroethane produced quantitatively in this reaction was distilled and weighed. The solution of sodium arsenite resulting from the hydrolysis was used for the iodometric estimation of arsenic. Iodide was estimated as silver iodide.

The tristrifluoromethylstibine used was prepared by J. W. Dale by reaction of trifluoroiodomethane with antimony in a steel autoclave at 175—185°.

The horizontal tube furnace (5 cm. in diameter), used in the pyrolysis experiments, had 5 independently controlled heating coils. At 400° the variation in temperature along the axis over a length of 30 cm. was $<0·5°$. Overall temperatures were maintained, within $\pm 0·5°$ by manual control. Reaction vessels of silica and of platinum were used (length, 20—25 cm.; int. diam., 3 cm.; capacity, 170—180 ml.). These were connected to the manometric system by a long narrow tube fitted with a ground joint. The dead space was about 3 ml. Capillary manometers were used in pressure measurements. Mercury was used as the manometric fluid, it having been previously established that the reactants and their pyrolysis are unaffected by the presence of mercury in the system. An auxiliary vessel of 300-ml. volume was incorporated in the apparatus for measuring the reactants manometrically. Other attachments were a Töpler pump, a McLeod gauge, and a series of traps for removing reaction products for analysis. Temperatures were measured with a calibrated chromel–alumel thermocouple.

The gas to be decomposed was admitted to the previously evacuated auxiliary vessel, its temperature and pressure were measured, and a tap leading to the reaction vessel was opened for 10 sec. The course of the reaction was followed manometrically, this procedure being justified in each case by a series of analyses of the mixture present at various stages of the decomposition.

Analytical Methods.—The non-condensable gases found in the pyrolysis of trimethylarsine were removed with the Töpler pump and measured. At the same time condensable gases were separated in traps cooled in liquid nitrogen. The non-condensable gases, which contained only methane and hydrogen, were analysed in an Ambler apparatus. The condensable gases were passed through a trap cooled to −80° to remove unchanged arsenicals, pumped off with the Töpler pump, measured, and transferred to the gas-analysis apparatus. Unsaturated hydrocarbons were absorbed in oleum, and the small volume of saturated hydrocarbons remaining was burnt in oxygen to find the average C and H content. The results of these analyses were confirmed and amplified by a mass-spectrographic analysis for which the authors are indebted to Dr. Bradford of Imperial Chemical Industries Limited, Billingham Division.

The decomposition products from fluoroalkyl compounds were distilled into an auxiliary vessel fitted with a trap cooled in liquid air. Any non-condensable gases were removed with the Töpler pump and measured. The condensable material was then transferred to a molecular-weight bulb fitted with a cold finger for the determination of weight and average molecular weight. This material was further separated in the vacuum system. Unchanged reactant was removed by distillation through a trap cooled to a suitable temperature and the material was divided into two or more fractions by distillation. The acid gases (SiF_4, CO_2) were removed from the most volatile fraction by shaking them with 20% aqueous sodium hydroxide, the weight and molecular weight of the remaining fluorocarbons being measured after removal of water vapour. For confirmation of the identity of the fluorocarbons, infra-red spectra of the various fractions were observed. Comparison of the intensity of characteristic absorption bands of pure fluorocarbons with the intensity of the corresponding bands in the spectra of the mixture enables the composition of the mixture to be estimated. The average molecular weight was also used to estimate the composition of fractions in which only two components were present.

Decomposition of Trimethylarsine.—The reaction was studied between 400° and 460°. In three preliminary experiments, in which the reaction was not allowed to go to completion, it was established that there was an approximately linear relation between the pressure and the amount of unchanged arsenical. This justifies the use of pressure measurements as a means of following the reaction rate. Analyses for hydrogen and methane were made in twenty-one experiments where the reaction was taken to completion. Typical results are shown in Table 2. All volumes are reduced to N.T.P.: Δp is the ratio of the increase in pressure to the initial pressure.

TABLE 2.

Temp.	$AsMe_3$ taken (ml.)	Final vol. (ml.)	Vol. of CH_4 (ml.)	Vol. of H_2 (ml.)	Δp
400°	17·35	36·6	31·0	0·6	1·11
410	13·04	27·5	23·5	0·5	1·10
420	7·96	16·55	14·35	0·25	1·08
440	16·30	34·0	26·7	0·5	1·09
450	16·77	34·7	28·85	0·55	1·06
460	8·24	18·0	13·95	0·25	1·19

Complete analyses by combustion and absorption were carried out on the products from four runs in a silica vessel, with the results given in Table 3, where the volumes of products are also expressed in parentheses as a percentage of the total volatile products. The values given for ethane and ethylene include higher saturated and unsaturated hydrocarbons, respectively. The relative proportions of these as given by the mass-spectrographic analysis of the condensable fraction of the product from a run at 400°, after removal of most of the unchanged arsenical are: CH_4, 0·5; C_2H_4, 27; C_2H_6, 41·0; C_3H_6, 13·0; C_3H_8, 7·0; C_4H_8, 2·0; C_4H_{10}, 0·5; CO_2, 3·0; C_3H_9As, 6·0%. The carbon and hydrogen figures for the saturated hydrocarbons in this mixture are 2·17 and 6·3 respectively, compared with the average values of 2·1 and 6·2 obtained by combustion. The corresponding figures for the olefin fraction are 2·4 and 4·8. The proportion of olefin is 42%, compared with values between 32 and 39% obtained by absorption in oleum. The calculated value for the total products in Table 3 is based on the observed pressure increase in the reaction. The discrepancy between it and the observed value may be ascribed to operational losses in the analysis and to the presence in the bulb of polymeric material with an appreciable vapour pressure at the reaction temperature. The carbon and hydrogen balance on these runs shows a recovery of 90—95% of the hydrogen and 70—75% of the carbon. Some free carbon was deposited as a coherent layer in the reaction vessel. By using pressure measurements to determine rates the reaction was shown to be of the first order by observing the time

TABLE 3.

Temp.	410°	440°	440°	450°
Vol. (ml.) of: $AsMe_3$	16·95	15·15	8·5	16·30
H_2	0·5 (1·5)	0·5 (1·7)	0·3 (1·9)	0·3 (1·9)
CH_4	30·7 (91·1)	25·7 (87·1)	14·3 (88·4)	—
C_2H_6	1·7 (5·0)	2·2 (7·5)	0·9 (6·0)	—
C_2H_4	0·8 (2·4)	1·1 (3·7)	0·6 (3·7)	—
Total volatiles	33·7	29·5	16·1	30·1
Residual $AsMe_3$	0·8	0·75	0·45	0·75
Total products (obs.)	34·5	30·25	16·55	30·85
Total products (calc.)	35·0	31·95	18·30	33·25

for its quarter and half completion at different initial pressures (Table 4). Specific rate constants are also given.

In three experiments at 450° in the unpacked vessel rate constants of 7·23, 7·41, and 7·03 × 10^{-4} sec.$^{-1}$ were observed, while in a vessel packed with silica powder to give a 10—20-fold increase in surface the value was 6·85 × 10^{-4} sec.$^{-1}$. Similarly at 420° values were 1·32 and 1·31 × 10^{-4} (unpacked) and 1·35 and 1·35 × 10^{-4} (packed) sec.$^{-1}$. These runs were made at an initial pressure of 100 mm. There was no observable change in the products from reactions in packed vessels.

TABLE 4.

Temp.	Initial pressure (mm.)	$t_{\frac{1}{4}}$ (min.)	$t_{\frac{1}{2}}$ (min.)	Rate const. (10^{-4} sec.$^{-1}$)
450°	54·7	7·6	15·4	6·51
	57·2	7·3	16·3	6·86
	97·8	7·0	15·3	7·41
	100·0	6·8	15·9	7·23
	199·5	6·4	13·9	8·09
440	100·3	10·9	23·6	4·29
	101·8	10·3	24·0	4·38
	192·9	10·3	22·8	4·59

The activation energy for the reaction was calculated from initial rates (the first 10—15%) in the range 400—460° at an initial pressure of 100 mm. The results, summarised in Table 5, yield an activation energy of 54·6 ± 1·8 kcal./mole [$\log_{10} k = 12{\cdot}77 - (54{,}600/2{\cdot}303\boldsymbol{R}T)$]. The frequency factor is approx. 10^{-13} sec.$^{-1}$, a characteristic value for unimolecular bond dissociation processes.

TABLE 5.

Temp.	Rate constant (10^{-4} sec.$^{-1}$)	Temp.	Rate constant (10^{-4} sec.$^{-1}$)	Temp.	Rate constant (10^{-4} sec.$^{-1}$)
460°	11·2, 11·0	430°	2·275, 2·15, 2·24	410°	0·750, 0·791
450	7·23, 7·48, 7·03	420	1·32, 1·31	400	0·427, 0·420
440	4·29, 4·38				

Decomposition of tristrifluoromethylarsine.—The reaction was studied in the range 350—410° in silica and platinum reaction vessels. The main volatile product in silica was hexafluoroethane, but perfluoropropane and perfluorobutane, detected by examining the infra-red absorption spectra of the less volatile material, were present in approximately equimolecular quantities and constituted about 10% of the fluorocarbon mixture. Distillation of the relatively small quantities of product available proved inadequate for more accurate analysis. No unsaturated fluorocarbons could be detected and only a trace of carbon tetrafluoride was found. A considerable amount of silicon tetrafluoride and carbon dioxide was formed together with a little carbon monoxide. The silica surface became opaque and the rate of attack increased progressively in a series of runs, though this trend was checked by heating the vessel almost to its softening point before use. Table 6 gives typical analyses of the products from successive runs between 360° and 410°, illustrating the wide variation in the ratio, "acid gases": fluorocarbon, and also the effect of strongly heating the vessel (after the run marked with an asterisk). The last two runs were carried out in the presence of silica powder and gave a greatly enhanced proportion of acid gases.

TABLE 6.

Temp.	Total fluorocarbon (g.)	SiF_4 & CO_2 (acid gases) (g.)	$\frac{\text{Acid gases}}{\text{Fluorocarbon}}$	Temp.	Total fluorocarbon (g.)	SiF_4 & CO_2 (acid gases) (g.)	$\frac{\text{Acid gases}}{\text{Fluorocarbon}}$
400°	0·146	0·014	0·096	360°	0·046	0·026	0·570
„	0·123	0·020	0·149	„	0·041	0·024	0·586*
„	0·148	0·022	0·137	370	0·066	0·015	0·228
390	0·133	0·029	0·218	410	0·058	0·016	0·278
380	0·107	0·023	0·213	390	0·015	0·037	2·46
„	0·125	0·029	0·247	„	0·010	0·032	3·20
				400	0·274	0·118	0·480

More detailed analyses were carried out on the combined products from two runs in a silica vessel and from three runs in the platinum vessel, all at 370°. The considerable increase in the relative proportions of higher fluorocarbons is shown in Table 7.

The decomposition was shown to be a first-order reaction by determining the time for a quarter and the time for half the reaction with various initial pressures. The results are in Table 8, which includes the values of specific rate constants. These too were independant of the initial pressure.

An increase in surface area of 10—20 times caused an increase in the rate constant of about 25% (from 2·77 × 10^{-4} to 3·44 × 10^{-4} sec.$^{-1}$) while the ratio, acid gases : fluorocarbon, increased from 0·22 to 2·44. According to the method of calculation used by Geddes and Mack (*J. Amer. Chem. Soc.*, 1930, **52**, 4372) this indicates a degree of heterogeneity of not more than 1·5%, despite the very considerable difference in the composition of the products. It is also significant that, when the surface of the vessel was covered with carbon, silver, or with calcium fluoride, there was very little difference in the rate constant, which also remained substantially reproducible throughout a series of experiments in the silica vessel, during which the vessel became very badly etched (see Table 9).

TABLE 7.

Product	Silica vessel g.	Silica vessel %	Platinum vessel g.	Platinum vessel %
CF_4	0·002	0·5	0·004	1·0
C_2F_6	0·246	61·4	0·258	62·4
C_3F_8,C_4F_{10}	0·028	7·0	0·152	36·6
SiF_4,CO_2	0·118	29·4	—	—
CO	0·007	1·7	—	—
	0·401	100·0	0·414	100·0

TABLE 8.

Temp.	Initial press. (mm.)	$t_{\frac{1}{4}}$ (min.)	$t_{\frac{1}{2}}$ (min.)	Rate const. (10^{-4} sec.$^{-1}$)	Temp.	Initial press. (mm.)	$t_{\frac{1}{4}}$ (min.)	$t_{\frac{1}{2}}$ (min.)	Rate const. (10^{-4} sec.$^{-1}$)
400°	51·5	8·5	17·8	5·53	380°	98·0	29·8	80	1·15
,,	102·5	8·9	18·5	5·31	,,	100·1	27·7	74	1·62
,,	197·5	8·1	17·8	5·08	,,	189·3	31·8	83	1·39
390	99·0	16·3	38·5	2·78					
,,	102·4	16·5	35·9	2·75					
,,	193·7	16·2	39·5	2·61					

Specific rate constants were calculated from the mean rate of reaction during the first 10—15% of the decomposition. These values are given in Table 9. The initial pressure was approx. 100 mm. The activation energy in the range 350—410° derived from these values is 57·4 ± 2·9 kcal./mole and the specific rate constant (k) is expressed by the equation $\log_{10} k = 15{\cdot}41 - (57{,}400/2{\cdot}303\ \boldsymbol{R}T)$. The frequency factor is higher than normal for unimolecular bond dissociation processes.

TABLE 9.

Temp.	$\frac{\text{Acid gases}}{\text{Fluorocarbon}}$	Rate constant (10^{-4} sec.$^{-1}$)	Temp.	$\frac{\text{Acid gases}}{\text{Fluorocarbon}}$	Rate constant (10^{-4} sec.$^{-1}$)
410°	0·28	10·8	380°	0·21, 0·21	1·51, 1·62
407	0·25	7·51	370	0·45, 0·23	0·734, 0·708
400	0·28, 0·28, 0·15	5·31, 5·08, 5·35	360	0·56, 0·59	0·356, 0·345
390	0·22, 0·22	2·78, 2·75	350	—	1·63

Decomposition of Trispentafluoroethylarsine.—This compound decomposes at a convenient rate in the range 270—310° but the vapour pressure is too low for accurate kinetic measurements with the manometric system used. For analytical purposes a larger sample was sealed in a silica tube and heated for 12 hr. at 300°. Analysis of the product by distillation gave the following results: C_4F_{10}, 76%; higher fluorocarbons, 16%; SiF_4 and CO_2, 8%; CO, trace; CF_4, trace. Several fluorocarbons, saturated and unsaturated, are present in the less volatile fraction, but they were not identified as comparative infra-red data were not available.

In a preliminary study of the reaction rates the specific rate constants were determined for three decompositions at 280° with an initial pressure of about 25 mm. The values were 2·47, 2·27, and 2·33 × 10^{-4} sec.$^{-1}$. If the reaction is of the first order, as is the decomposition of tristrifluoromethylarsine, and has the same frequency factor (approx. 10^{15}), the activation energy is 48·0 kcal./mole.

Decomposition of Tristrifluoromethylstibine.—A convenient temperature range for studying this decomposition is 180—240°, though a complete kinetic study has not been made. Preliminary examination of the products of the reaction show that not more than 50% of the carbon and fluorine in the starting material appears in the volatile products, and of this material 75—80% is silicon tetrafluoride and carbon dioxide. The remaining fluorocarbon is mainly tetrafluoroethylene and perfluoro*cyclo*propane in approximately equimolecular quantities, and some higher olefinic fluorocarbons. No hexafluoroethane or other compound containing CF_3 groups is present. The remainder of the carbon and fluorine appears as antimony trifluoride and a white polymer which behaves like polytetrafluoroethylene (decomposes at 600° in silica, giving mainly tetrafluoroethylene, silicon tetrafluoride, and carbon dioxide).

The pressure–time curves show very considerable irregularities, including, usually, a point of maximum pressure which was followed by a gradual fall in pressure over a period of several hours. These irregularities make it impossible to obtain absolute values of rate constants.

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