

### 424. The Thermal Decomposition of Tetrafluoroethylene.

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The thermal decomposition of tetrafluoroethylene at temperatures from 300° to 800° is described. Below 600° dimerization to octafluorocyclobutane, and the reverse reaction, are much faster than any of the other reactions taking place. Hexafluoropropene and octafluorobutenes are formed at 600–800°. At 800° hexafluoroethane and tars are also obtained. Vapour-pressure measurements for the major products are reported.

In the reaction, 2 tetrafluoroethylene  $\rightleftharpoons$  octafluorocyclobutane, the rate constant for the forward reaction, between 300° and 550°, is given by  $k = 10.3 \times 10^7 e^{-25,400/RT}$  l. mole<sup>-1</sup> sec.<sup>-1</sup> and that for the reverse reaction, between 520° and 590°, by  $k = 8.9 \times 10^{15} e^{-74,100/RT}$  sec.<sup>-1</sup>.  $\Delta H$  for the reaction at 527° (800° K) is  $-50.3$  kcal.

HARMON (U.S.P. 2,404,374) described the major products of the thermal decomposition of tetrafluoroethylene as octafluorocyclobutane and hexafluorocyclopropane; hexafluoropropene was probably wrongly assigned as hexafluorocyclopropane (Young and Murray, *J. Amer. Chem. Soc.*, 1948, **70**, 2814). In the present work quantitative measurements have been made of the rates of the two major reactions concerned in the decomposition. A range of products more extensive than that indicated by Harmon's account has been found.

While this work was in progress, Miller ("Preparation and Technology of Fluorine and Organic Fluorine Compounds," National Nuclear Energy Series, VII—I, 1951, Ch. 32) has reported on the pyrolysis of tetrafluoroethylene in a nickel tube packed with graphite, and Lacher, Tompkin, and Park (*J. Amer. Chem. Soc.*, 1952, **74**, 1693) have determined the activation energy for the dimerisation of tetrafluoroethylene.

#### EXPERIMENTAL

*Apparatus used for Pyrolysis.*—(a) *Flow method.* Tetrafluoroethylene from a cylinder was passed through an indicating wash-bottle containing water, a flow meter, a drying tube (CaCl<sub>2</sub>), and a trap at  $-12^\circ$  (the last removed stabilizer). A 60-c.c. cylindrical, silica vessel, internal diameter 21 mm., was used below 600°, and a 180-c.c. steel cylinder, internal diameter 34 mm., above 600°. Each vessel had capillary inlet and outlet tubes, and was heated in a tubular electric furnace, controlled to  $\pm 1^\circ$ . The condensable products were collected in two traps cooled in liquid nitrogen, and the non-condensable material was absorbed on activated charcoal in a trap cooled in liquid nitrogen. A glass-wool filter between the reaction vessel and the traps removed any polymer dust. Pressures on the inflow and outflow sides of each vessel were measured on mercury manometers. A mercury-vapour pump, backed by a rotary oil pump, was used to evacuate the apparatus up to and including the calcium chloride tube.

(b) *Static method.* Two vessels were used. The first was of Pyrex glass, 22 cm.  $\times$  4.5 cm. (volume 257.7 ml.), with a capillary inlet 30 cm. long and a coaxial thermocouple-well traversing practically its whole length and extending 22 cm. outside. The second was of steel and of similar but smaller capacity. Its internal surface had to be free from oxide scale, hence it was fabricated of cleaned steel tubing by brazing. It was fitted with a similar thermocouple-well and capillary inlet. Before use the metal vessel was freed from oxide by heating it at 700° and passing a stream of hydrogen through for several hours. A short capillary outlet provided for this purpose was then sealed by welding.

The furnace temperature was controlled by a Sunvic Energy Regulator, by the hand adjustment of which, the temperatures of the reaction vessels were kept within  $\pm 0.5^\circ$ . The chromel-alumel thermocouple was checked against a platinum/platinum-rhodium thermocouple of known reliability.

The vessels were connected by their capillary inlets to a capillary manometer and a two-way tap which led either to a gas reservoir for filling purposes, or to a series of traps for collection of the products. When the dimerization of tetrafluoroethylene was being followed, pressure changes were large and rapid, and readings were to the nearest 0.5 mm. against a scale. In the dissociation of octafluorocyclobutane the pressure changes were small and sufficiently slow to allow them to be measured by cathetometer to the nearest 0.1 mm.

**Starting Materials.**—(a) *Tetrafluoroethylene.* The gas, from a small cylinder, after passage through the purification system, contained: nitrogen, 1%; hydrogen chloride, 2.5%; and fluorinated ethanes and ethylenes, 3%. It was used in the flow experiments without further purification. For all experiments with the static method, the gas was purified by fractionation in a Podbielniak-type distillation column (Podbielniak, *Ind. Eng. Chem. Anal.*, 1931, **3**, 177), which was designed to fractionate up to 25 ml. A middle fraction of the tetrafluoroethylene had b. p.  $-76.5^\circ$  (Ruff and Bretschneider, *Z. anorg. Chem.*, 1933, **210**, 173, report b. p.  $-76.3^\circ$ ) (Found: *M*, 99.7, 100.0. Calc. for  $C_2F_4$ : *M*, 100.0).

(b) *Octafluorocyclobutane.* The crude tetrafluoroethylene was pyrolysed at  $600^\circ$  and the products were fractionated in the Podbielniak column. The middle portion of the octafluorocyclobutane fraction had b. p.  $-5.5^\circ$  (Found: *M*, 200.3. Calc. for  $C_4F_8$ : *M*, 200.0), and the infra-red spectrum showed no impurities.

**Handling of Products.**—(a) *Analysis.* The condensable gases were analysed by fractional distillation in a small Podbielniak type column designed to fractionate up to 5 ml. Yields were determined from the distillation curves in the usual manner.

A Toepler pump was used to transfer gases to a gas burette for measurement or to an Orsat-type of apparatus for analysis. Carbon monoxide was absorbed in acid cuprous chloride solution, and  $C_2$  and  $C_3$  olefins in a 10% solution of potassium bromide saturated with bromine. This reagent absorbed hexafluoropropene satisfactorily, but not  $C_4$  fluoro-olefins. The unsaturation of mixtures of  $C_4$  fluorocarbons was estimated by the semiquantitative potassium permanganate method described by Miller (*op. cit.*).

(b) *Physical properties.* Pure samples for the measurement of physical properties were prepared from the gases separated in the small distillation column either by vacuum fractionation or by redistillation, a middle fraction being taken in the centre of the relevant plateau.

Molecular weights of the condensable products were determined by condensing a known volume into a small bulb and weighing it; for the non-condensable gases the bulb was charged with a little activated charcoal. Vapour pressures were measured by means of an isoteniscope, a copper-constantan thermocouple standardized against an ethylene vapour-pressure thermometer being used for temperature measurement.

TABLE I

Temp.	Vessel	$C_2F_4$ , ml., passed per min.	Products, moles/100 moles of $C_2F_4$ passed								
			$CF_4$	$C_2F_4$	$C_2F_6$	$C_3F_6$	$C_4F_8$ cyclic	$C_4F_8$ , I *	$C_4F_8$ , II *	Liquids	
300°	Silica	19.3	—	94.6	—	—	—	2.7	—	—	—
400	"	23.2	—	59.2	—	—	—	20.4	—	—	—
500	"	19.4	—	13.5	—	—	—	43.3	—	—	—
600	"	18.6	—	2.4	—	5.2	—	41.7	approx. 0.1 ml. liquid †	—	—
									b. p. $> -5.5^\circ$		
700	"	19.0	carbon monoxide and silicon tetrafluoride formed								
400	Steel	59.2	—	59.6	—	—	—	20.1	—	—	—
600	"	66.7	—	5.6	—	4.6	—	39.5	approx. 0.1 ml. liquid †	—	—
									b. p. $> -5.5^\circ$		
700	"	60.5	—	—	—	20.5	—	9.4	21.8	—	2.9
800	"	62.4	trace	—	25.0	2.1	—	—	16.7	—	2.5 †

\* I, b. p.  $-1^\circ$  to  $+4.5^\circ$ ; II, b. p.  $+6^\circ$ .

† Per litre of tetrafluoroethylene passed.

‡ Also a tar condensed in the exit tube.

**The Thermal Decomposition of Tetrafluoroethylene.**—(a) *By the flow method.* In each run, about 1 l. of gas (at N.T.P.) was used; and the pressure in the reaction vessel was maintained at 1 atm. Except when the silica vessel was used at  $700^\circ$ , which led to the formation of much carbon monoxide, the non-condensable gases consisted entirely of the nitrogen impurity. The results obtained by fractionation of the condensable material collected are set out in Table I. A small amount of white polymer dust appeared in the exit tube during runs at  $500^\circ$  and  $600^\circ$ , and carbon was deposited on the walls of the vessel at  $800^\circ$ .

(b) *By the static method.* To ensure that the products formed did not result from the impurities present in the tetrafluoroethylene used in the flow method, the products of a number of runs made by the static method, pure tetrafluoroethylene being used, were collected and fractionated. Runs were carried out at  $500^\circ$  in the silica vessel and at  $700^\circ$  in the steel vessel, and the results showed that the impurities had no appreciable effect on the reactions, except possibly in being the cause of the trace of white polymer mentioned above.

**The Properties of the Reaction Products.**—The materials isolated by fractionation had the

properties described below. Equations for the vapour-pressure curves are given where these data do not appear in the literature.

(a) *Hexafluoroethane*.  $M$ ,  $137.1 \pm 1.0$  (Calc. for  $C_2F_6$ :  $M$ , 138); b. p.  $-79^\circ \pm 1^\circ$  (from column); m. p.  $-100.6^\circ \pm 1.0^\circ$  (v. p. curve), in close agreement with the b. p. ( $-78.3^\circ$ ) and m. p. ( $-100.7^\circ$ ) recorded by Ruff and Bretschneider (*loc. cit.*).

(b) *Hexafluoropropene*.  $M$ ,  $150.1 \pm 0.6$  (Calc. for  $C_3F_6$ :  $M$ , 150); b. p.  $-30.2^\circ \pm 1.0^\circ$  (v. p. curve); m. p.  $-155^\circ \pm 5^\circ$  (by observation). Henne and Waalkes (*J. Amer. Chem. Soc.*, 1946, 68, 496) give b. p.  $-29.4^\circ$ , m. p.  $-156.2^\circ$ . The vapour pressure between  $-45^\circ$  and  $-95^\circ$  is given by  $\log_{10} p_{\text{mm.}} = 7.90_8 - 1221/T$  ( $T$  in degrees abs.). The gas was slowly absorbed in the bromine reagent, and the permanganate titration showed one double bond per molecule. The infra-red spectrum agreed well with that published by Edgell (*J. Amer. Chem. Soc.*, 1948, 70, 2816) but gave evidence of the presence of  $< 1\%$  of octafluoropropane.

(c) *Octafluorocyclobutane*.  $M$ ,  $200.3 \pm 0.8$  (Calc. for  $C_4F_8$ :  $M$ , 200); b. p.  $-5.5^\circ \pm 0.5^\circ$  (v. p. curve); m. p.  $-38.7^\circ \pm 1.0^\circ$  (v. p. curve). Park, Benning, Downing, Laucius, and McHarnes (*Ind. Eng. Chem.*, 1947, 39, 354) gave b. p.  $-5^\circ$ , m. p.  $-40^\circ$ . The vapour pressure of the liquid between  $-38^\circ$  and  $-12^\circ$  is given by  $\log_{10} p_{\text{mm.}} = 7.72_4 - 1295/T$ , and for the solid between  $-50^\circ$  and  $-40^\circ$  by  $\log_{10} p_{\text{mm.}} = 8.93_7 - 1580/T$ .

(d) *Octafluorobutenes*. Material from both the flow run at  $700^\circ$  and the static runs at  $700^\circ$  furnished distillation curves with an inflection at  $-2^\circ$  followed by a gradual rise in the boiling point until a plateau was reached at  $6^\circ$ .

The material boiling between  $-2^\circ$  and  $+6^\circ$  from the static run was fractionated into two portions. The middle cut of the first portion, b. p. *ca.*  $0^\circ$ , had  $M$ , 202.4 and one double bond. Infra-red spectra indicated that this lower-boiling portion contained not more than a few units % of octafluorobut-1-ene and rather less of some other impurity. We believe it to be a moderately pure sample of an octafluorobutene. The middle cut of the second portion boiled at about  $4^\circ$ , had  $M$  202.6, and was unsaturated to a similar degree. Its infra-red spectrum indicated a mixture of octafluoro-but-1-ene and -but-2-ene. The observed molecular weights suggest that both portions contained some perfluorobutane. The absence of a plateau in the distillation curve shows that the unidentified octafluorobutene present is probably a mixture of *cis*- and *trans*-octafluorobut-2-ene. Henne and Newby (*J. Amer. Chem. Soc.*, 1948, 70, 130) found that a mixture of these two isomers boiled over the range  $0.4^\circ$  to  $3.0^\circ$ .

The material, b. p.  $6^\circ$ , proved to be identical with that obtained by pyrolysis at  $800^\circ$ ; it had  $M$ ,  $200.1 \pm 1.0$ ; b. p.  $5.7^\circ \pm 0.5^\circ$  (v. p. curve); m. p.  $-118^\circ \pm 5^\circ$  (by observation). The vapour pressure from  $-70^\circ$  to the b. p. is given by  $\log_{10} p_{\text{mm.}} = 8.31_6 - 1508/T$ . It did not react with the bromine reagent but the permanganate test indicated one double bond. This is undoubtedly the material (b. p.  $4.8^\circ$ ) characterized by Miller (*loc. cit.*) as octafluorobut-1-ene, which was his main product at  $700^\circ$ , and the predominant  $C_4$  compound in this temperature region in our experiments. An infra-red spectrum showed the absence of octafluorocyclobutane.

*The Rate of Dimerization of Tetrafluoroethylene.*—At  $300$ – $500^\circ$  the only product obtained on heating tetrafluoroethylene for a short time was the cyclic dimer. Further investigation showed that this was the only compound formed at  $500$ – $550^\circ$ ; thus the rate of dimerization of tetrafluoroethylene over the range  $300$ – $550^\circ$  could be followed by observing the pressure change in a closed system.

Pure tetrafluoroethylene was heated in the "Pyrex" vessel at temperatures between  $300^\circ$  and  $550^\circ$  and at initial pressures between 200 and 550 mm.; pressure-time readings were taken until the reaction was more than half complete. The velocity constants were determined by using formulæ, based on a second-order rate law, which allowed for the influence of dead space. If the reaction



occurs according to the law

$$-d(C_2F_4)/dt = k_1(C_2F_4)^2 \dots \dots \dots (2)$$

where  $(C_2F_4)$  is expressed in mole  $l^{-1}$ , and  $k_1$  in  $l. \text{ mole}^{-1} \text{ sec}^{-1}$ , and provided there are no other reactions occurring, then

$$k_1 t = \frac{760RT_1}{(1-b)[p_0 - (p_0 - p_t)(1-b)/(\frac{1}{2} - b)]} - \frac{760RT_1}{(1-b)p_0} \dots \dots (3)$$

Pressures are in mm.,  $p_t$  is the pressure after  $t$  secs.;  $b = T_1 V_2 / 2(T_2 V_1 + T_1 V_2)$ , where  $T_1$  is the temperature in degrees abs. in the reaction vessel of volume  $V_1$  l., and  $T_2$  the temperature

in the dead space of volume  $V_2$  l. If the second-order rate law is obeyed, the plot of  $t$  against  $1/[(p_0 - p_i)(1 - b)/(1/2 - b)]$  should be a straight line of slope  $760RT_1/k_1(1 - b)$ .

For runs at 450° and below, plots of the above function gave straight lines. At higher temperatures the last few points showed an upward deviation indicating a lower rate of pressure change for the later stages of the reaction than would accord with the presumed law. As no secondary reactions had been detected, it seemed possible that the deviations arose from the reverse reaction as we show below.



In calculating the rate constants, given in Table 2, the initial slopes of the graphs were used where there were deviations from a straight line. The plot of  $\log_{10}k_1$  against  $1/T$  gave a satisfactory straight line. Rate constants measured at 400°, 425°, and 450° in a vessel packed with small pieces of "Pyrex" glass agreed with those given in Table 2.

*The Dissociation of Octafluorocyclobutane.*—The pyrolysis of pure octafluorocyclobutane in the "Pyrex" vessel at 550° was accompanied by an increase in pressure; the rate of change decreased with time, suggesting an eventual condition of equilibrium. An adventitious subsequent pressure rise was shown by analysis to be due to the formation of silicon tetrafluoride and carbon monoxide from attack on the glass. There was, however, evidence that in the early stages the attack was small and that the initial slope of the pressure-time curve gave the rate of dissociation of octafluorocyclobutane. To exceed the temperature range and to confirm the above conclusion, it was essential to use a steel vessel, free from oxide scale.

TABLE 2

Temp. ....	300°	325°	350°	375°	400°	425°	450°	475°	500°	525°	550°
No. of runs .....	5	5	5	7	6	8	6	5	5	6	6
Mean $10^3k_1$ , l. mole <sup>-1</sup> sec <sup>-1</sup>	2.126	5.410	12.96	28.75	61.39	115.6	219.9	392.1	682.1	1147	1883

In the steel vessel, the pressure increased asymptotically to a virtually constant value after 10 min. at 550°, and after 1½ min. at 590°. This behaviour establishes the simplicity of the system under these conditions, as reactions other than (1) and (4) must be so slow that equilibrium is not measurably disturbed.

For those runs in which the equilibrium pressure was observed, the dissociation rate constant was calculated by three methods, reaction (4) being assumed to be of first order. (i)  $\log_{10}(2p_0 - p_i)$  was plotted against  $t$ , and since, owing to the occurrence of the reverse reaction, curves are obtained, the initial slopes were taken as corresponding to the rate of the forward reaction only and put equal to  $k_2/2.303$ . (ii) It was assumed that at equilibrium

$$k_2(2p_0 - p_e)/760RT = k_1'[(2p_0 - 2p_e)/760RT]^2 \dots \dots \dots (5)$$

where  $k_1' = \frac{1}{2}k_1$ , and  $p_e$  is the experimentally observed equilibrium pressure. (iii) The following integrated form of the rate equation for approach to equilibrium was used:

$$k_2 = \frac{(p_e - p_0)}{t(3p_0 - p_e)} \cdot 2.303 \log_{10} \frac{p_0(p_e - p_0) + (p_i - p_0)(2p_0 - p_e)}{p_0(p_e - p_i)} \dots \dots \dots (6)$$

The plot of the logarithmic term against  $t$  is a straight line provided that the assumed orders of reaction are correct; the slope of this line gives  $k_2$ .

Only (i) is applicable to the experiments in the "Pyrex" vessel, and the calculated rate constants are given in Table 3. (iii) gave straight-line graphs showing clearly that the dissociation is a first-order reaction. The agreement existing between all the methods at 550° confirms the applicability of (i) to the results in "Pyrex" (see Table 3). The poor concordance at 590° is probably due to the limit being reached in both the experimental method and the applicability of the assumptions implicit in the calculations.

The results obtained by (i) for each temperature were averaged;  $\log_{10}k_2$  plotted against  $1/T$  gave a straight line.

*Activation Energies and other Derived Properties.*—For reaction (1) the measurements of the forward rate give the energy of activation,  $E = 25.4$  kcal. By assuming the molecular diameter,  $\sigma = 1.33 \times 10^{-8} \sqrt[3]{v}$ , where  $v$  is the molar volume at the boiling point, and by expressing the rate constant as  $k_1 = PZe^{-E/RT}$ , where the terms have their usual significance, then the value  $P = 3.8 \times 10^{-4}$  is obtained. Similarly, for the reverse reaction (4),  $E = 74.1$  kcal., and in the equation  $k_2 = Ae^{-E/RT}$ ,  $A = 8.9 \times 10^{15}$  sec<sup>-1</sup>.

TABLE 3

Temp.	Vessel	Vel. const.,	Temp.	Vessel	Vel. const., $10^3k_2$ , sec. <sup>-1</sup> ,		
		$10^3k_2$ , sec. <sup>-1</sup> , method, (i)			method (i)	method (ii)	method (iii)
520°	Pyrex	3.52	550°	Steel	19.80	19.14	17.04
		3.50			18.60	18.72	18.56
		3.52			19.95	19.87	18.70
530	..	6.44	570	..	57.57	57.82	56.90
		6.71			59.29	58.41	55.42
		6.42			58.08	57.02	58.03
540	..	6.43	590	..	57.05	56.84	56.46
		10.94			142.0	172.8	175.3
		10.37			155.2	138.5	138.1
		10.36			175.0	175.5	176.3
550	..	10.51					
		18.94					
		19.54					
		19.13					
		19.52					

By use of the standard equations of the transition-state theory of reaction rates (Glasstone, Laidler, and Eyring, "The Theory of Rate Processes," McGraw Hill Book Co., New York, 1941) the following results are obtained (all at 800° abs.):

(i) forward reaction: the entropy of activation at a standard state of one atm. pressure,  $\Delta S_p^\ddagger = -38.4$  cal./degree; the heat of activation,  $\Delta H^\ddagger = 22.2$  kcal.:

(ii) reverse reaction:  $\Delta S^\ddagger = 10.6$  cal./degree;  $\Delta H^\ddagger = 72.6$  kcal. For the complete reaction,  $\Delta E$ , obtained by subtraction of the  $E$  values above, is  $-48.7$  kcal. From this,  $\Delta H = -50.3$  kcal. The standard entropy change for a standard state of one atm. pressure,  $\Delta S_p^\circ = -49.2$  cal./degree.

#### DISCUSSION

There is general agreement between our findings (Table 1) and those of Miller (*loc. cit.*) who used a reaction tube packed with graphite. He found only perfluorobut-1-ene in his butene fraction, however, did not prove the formation of hexafluoroethane, and obtained perfluoropropene at 550°.

At 300–550° there is a simple reversible dimerization of tetrafluoroethylene to octafluorocyclobutane. At 600°, and more so at 700°, perfluoropropene and perfluorobutenes are formed; this requires the transfer of a fluorine from one carbon atom to another, and the high temperature required to allow such reactions to proceed with speed is a demonstration of the high strength of carbon-fluorine bonds.

The mechanism by which perfluoropropene is formed is not known. Perfluorobutenes were always present when the fluoropropene was formed, so the reaction may be

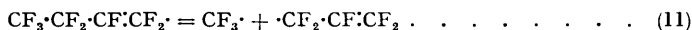


This does not account for Miller's observation that the compound was formed at 550° without butenes being formed. In his packed vessel the essential reaction must have been



but the reaction may have occurred on the graphite surfaces. It is known that  $CF_2$  free radicals initiate polymerisation of tetrafluoroethylene in the gas phase (Atkinson, *J.*, 1952, 2684). As, at 600° and 700°, we obtained no appreciable amount of solid or tar we doubt whether free radicals are present in the gas phase at these temperatures.

Below 800° the products have the formula  $(CF_2)_n$ , but at 800° a new mechanism operates since both saturated products of low molecular weight and highly unsaturated products of high molecular weight are formed. The rate of formation of octafluorobutene is undoubtedly fast at this temperature and the observed products are probably derived from the decomposition of this compound to free radicals:



The low yield of tetrafluoromethane shows that abstraction of fluorine, as in equation (12), is slow compared with the union of free radicals to form hexafluoroethane.



Our values for the rate constant of the dimerization reaction (1) give the equation  $k_1 = 10.3 \times 10^7 e^{-25,400/RT}$  l. mole<sup>-1</sup> sec.<sup>-1</sup>. Lacher, Tompkin, and Park (*loc. cit.*) found  $k_1 = 16.5 \times 10^7 e^{-26,299/RT}$  l. mole<sup>-1</sup> sec.<sup>-1</sup>. The *P* factor for reaction (1) is of the same order as that found by Pease for the dimerization of ethylene to butene (*J. Amer. Chem. Soc.*, 1931, **53**, 613).

The frequency factor for dissociation (4) is high, but this is true for other ring-opening reactions; for cyclopropane,  $A = 1.48 \times 10^{15}$  sec.<sup>-1</sup> (Chambers and Kistiakowsky, *J. Amer. Chem. Soc.*, 1934, **56**, 399), and for trioxymethylene,  $A = 1.43 \times 10^{16}$  sec.<sup>-1</sup> (Burnett and Bell, *Trans. Faraday Soc.*, 1938, **34**, 420). Corresponding with the high frequency factor, the entropy change, despite the loss of one vibrational term theoretically required, is positive and appreciable. The observed value of  $\Delta S^\ddagger$  may be explained by an open-chain activated state in which there is free rotation about the centre carbon-carbon bond.

No calorimetric data are available for comparison with the kinetically determined heat of dimerization of tetrafluoroethylene, nor have we found in the literature any reliable figures for any similar reaction.

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