508. *The Mercury-photosensitised Reactions of Tetrafluoroethylene.*

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The main products of the mercury-photosensitised reactions of tetrafluoroethylene at 30° have been identified as hexafluoro*cyclo*propane and polytetrafluoroethylene. The variations of rates of formation of these products with pressure of tetrafluoroethylene and with intensity of light have been studied. Some observations on the effects of polymer dust and hexafluoro*cyclo*propane on the rates of reaction are discussed.

Over the pressure range 1—35 cm. the quantum efficiency of formation of hexafluoro*cyclo*propane increases with increasing pressure. At 5 cm. the quantum efficiency is almost independent of intensity but at higher pressures an increase in intensity was found to lower the quantum efficiency.

It is shown that the experimental results are fairly well represented by a mechanism involving scission of tetrafluoroethylene into difluoromethylene, followed by addition of the free radicals to tetrafluoroethylene to form hexafluoro*cyclo*propane or to initiate polymerisation. A high proportion of the free radicals recombine either in the gas phase or at the walls.

The reaction of tetrafluoroethylene is contrasted with the mercury-photosensitised reactions of ethylene.

Absorption of the 2537-Å mercury resonance line by mercury vapour in the presence of tetrafluoroethylene is accompanied by polymerisation of the fluorocarbon and a decrease in the total pressure (Atkinson, *Nature*, 1949, **163**, 291). This reaction is interesting both as a mercury-photosensitised reaction and as one involving fluorocarbon free radicals. It may be compared and contrasted with the mercury-photosensitised reactions of ethylene at ordinary temperatures in which free-radical formation is only a secondary process and initially there is a pressure rise (Le Roy and Steacie, *J. Chem. Phys.*, 1941, **9**, 829).

The obvious product of the reactions of tetrafluoroethylene is a white polymer. Owing to the low quantum efficiency at high light intensities, the reactions in the experiments described here were always fairly slow and only comparatively small amounts of products could be produced. Hexafluoro*cyclo*propane, the main product of the primary reactions, has been separated by vacuum fractionation, but the volatile higher fluorocarbons formed have not been identified. When the percentage conversion was low the yield of volatile products other than hexafluoro*cyclo*propane was negligible.

Although some useful information could be obtained simply by measuring pressure changes, it was clear that polymer and hexafluoro*cyclo*propane were not formed in any universally constant ratio and that the separate rates of formation of these products must be measured. An attempt was made to follow the formation of hexafluoro*cyclo*propane by gas analysis, advantage being taken of the olefinic properties of tetrafluoroethylene. It was found that a solution of mercuric sulphate in diluted sulphuric acid, an excellent absorbing reagent for ethylene (Francis and Lukasiewicz, *Ind. Eng. Chem. Anal.*, 1945, **17**, 703), does not react with tetrafluoroethylene. A concentrated solution of bromine in aqueous potassium bromide was found to be a satisfactory reagent in that it did not react with hexafluoro*cyclo*propane but absorbed tetrafluoroethylene. When the gas mixture was to be irradiated again after analysis the alternative methods, vapour-density determination by direct weighing, and vacuum fractionation, were used.

For a complete interpretation of the results of rate measurements on mercury-photosensitised reactions it is essential to know the intensity both of the light absorbed and of that re-emitted as fluorescence radiation. There is a gas pressure above which little error is involved in assuming that quenching of fluorescence is complete, this pressure being related to the quenching cross-section of the gas molecule concerned. As the quenching cross-section for tetrafluoroethylene and Hg^3P_1 atoms is not known, it was necessary to measure the intensity of fluorescence radiation over a range of pressures. These measurements served also as a means of calculating approximate figures for the intensity of light quenched in the region of incomplete quenching.

Approximate measurements of quantum yield have been made. To obtain a parallel beam suitable for thermopile measurements much of the lamp intensity had to be sacrificed and percentage error of measurements was consequently high. The method adopted to measure higher intensities made use of Le Roy and Steacie's value of 0·37 for the quantum efficiency of the mercury-photosensitised reaction of ethylene (*loc. cit.*).

The experimental results show the mercury-photosensitised reactions of tetrafluoroethylene to be complex. Further work will be required to test and extend the theories given here.

EXPERIMENTAL

Apparatus.—The fractionating line was of conventional design and consisted of four 30-c.c. traps joined in series and individually joined to the main vacuum line. A branch of the main line terminated in the section shown in Fig. 1. This included the reaction tube *A*, a small trap, *B*, used in filling the reaction tube, a spoon gauge, taps for adjusting the air pressure on the exterior of the gauge, and two wide-bore mercury manometers. Movements of the spoon-gauge pointer were magnified 25 times by projection. The apparatus was evacuated by a single-stage mercury-diffusion pump backed by a Cenco " Hyvac " rotary oil pump, the vacuum being checked by a tilting McLeod gauge.

In the quantitative experiments the reaction tubes used were Pyrex cylinders, internal diameter 4·3 cm., with silica windows sealed to the flanged ends. One tube was 2·2 cm. long and the other 11·6 cm. long. The tubes were attached at a standard cone-socket joint as indicated in Fig. 1, the axis being vertical to reduce deposition of polymer on the front window. The thermostat surrounding the tubes was filled with distilled water to a level 1 cm. above the top window. After each experiment the top window was detached and polymer was removed by wiping with a soft cloth. For the preparation of polymer in greater quantity a 560-ml. bulb made in two parts was used. The upper part was a large Pyrex bulb with a tap attached. The lower part, a silica tube 2·5 cm. in diameter, 15 cm. long, was joined to the upper at a cone-and-socket joint sealed with picein.

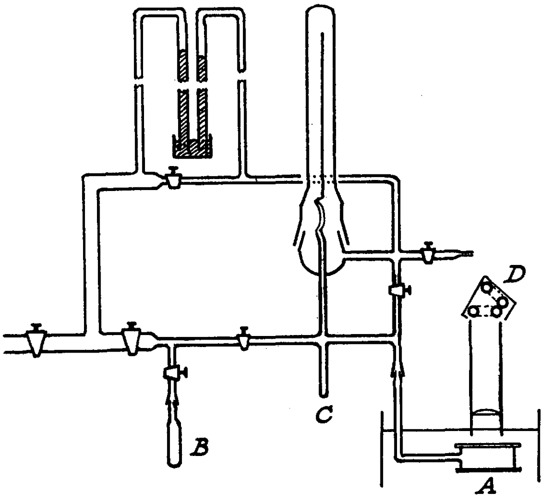
A 150-watt low-pressure mercury lamp with its tube bent to an upturned U was used throughout. The arrangement for the group of experiments F 2—11 is shown in Fig. 1. An aluminium shield *D* was placed round the tubes of the lamp, and a 2·5-cm. diameter brass tube fitted into a hole in the shield. At 7·5 cm. from the lamp the brass tube held a 7·5-cm. focallength lens. The lower end of the tube dipped just below the surface of the water of the thermostat. In the group of experiments K 1—9 the lamp was fixed with the U tubes vertical and the base of the U tubes just above the surface of the water. The water served as a filter to absorb the mercury 1849-Å line. The lamp was always switched on at least 30 minutes before the light shutter was removed.

Low-temperature measurements were by a copper–constantan thermocouple calibrated by making measurements of the vapour pressure of pure ethylene. Manometer levels were measured to ±0·005 cm. by cathetometer.

For light-intensity measurements a Kipp surface thermopile calibrated by the National Physical Laboratory was used. The e.m.f. of the thermopile was measured by potentiometer.

Determination of Unsaturated Gases.—A bubble of gas was brought to atmospheric pressure over mercury and pushed into a capillary tube containing concentrated sodium sulphate solution. The length of the bubble under atmospheric pressure was measured. It was then transferred to a 1-c.c. bulb containing a 25% solution of bromine in 23% aqueous potassium bromide. When the reaction was complete, the bubble was passed back to the standard section of capillary tube or to a second, narrower standard section and measured. A correction for the vapour pressure of the bromine derivative was applied.

FIG. 1.



Weighing of Gases.—A 10-ml. bulb fitted with a vacuum tap and a standard joint was evacuated and weighed to 0·1 mg. against a counterpoise. The gas was condensed into the bulb and the bulb was weighed again. If the gas was to be returned to the reaction tube, the bulb was attached at position *B* (Fig. 1), and the gas was condensed into tube *C*. For both reaction tubes the volume of tube plus gauge was measured by filling with tetrafluoroethylene to a measured pressure and weighing the gas. These volumes were then used as standard volumes for vapour-density determinations.

Tetrafluoroethylene.—A small cylinder of the gas was kindly provided by the Ministry of Supply. After a simple fractionation, the gas still contained 2% of saturated impurity. It was therefore purified by an adaptation of the bromination method used by Ruff and Bretschneider for separating tetrafluoroethylene from hexafluoroethane (*Z. anorg. Chem.*, 1933, **210**, 173). The gas was bubbled into bromine water in contact with excess of bromine, the unchanged bromine was destroyed by potassium hydroxide, and the dibromotetrafluoroethylene was separated and distilled. The product was dropped into a suspension of zinc dust in glacial acetic acid, 20 ml. of the halide being added during 4½ hours. The gas evolved was collected in a trap cooled in liquid air. It was purified by distillation from a trap at −135° to one at −196° with rejection of head and tail portions, the process being repeated until the gas was at least 99·75% unsaturated gas. The vapour pressure of the product was within experimental error in agreement with the figures given by Ruff and Bretschneider (*loc. cit.*) and the b. p. (by extrapolation) was −76·4° (Ruff, −76·3°).

Ethylene.—Anæsthetic grade ethylene was purified by a vacuum-distillation procedure similar to that described above for tetrafluoroethylene. The product was 100% unsaturated gas.

Reaction Products.—A series of experiments were performed in which the 560-c.c. bulb described above was filled with tetrafluoroethylene and a small amount of mercury was condensed in it by cooling the silica tube in liquid nitrogen. The tetrafluoroethylene was allowed to vaporise and the lamp was placed at the side of the tube and left on for 24 hours. The pressure decreased at a rate that increased with time during the first few hours and a white powder was deposited. A saturated gas was formed and this was isolated by fractionation, traps at −100°, −135°, and −196° being used. The third fraction was pure tetrafluoroethylene. The portion retained at −100° was a mixture and will be referred to below as higher fluorocarbons. Only small amounts of this mixture were obtained and attempts to separate it into pure substances were unsuccessful. Table 1 summarises the results of an attempted separation of one sample. A larger quantity of gas was retained at −135°. This fraction had the following properties: *M* (from vapour density) 150·5 ± 1, b. p. −33° ± 1°, vapour pressure $\log_{10} p_{\text{mm.}} = 7{\cdot}746 - 1168/T$ above −80°; a point of inflexion in the vapour pressure curve at −80° corresponded to the observed m. p. The gas did not react with bromine solution. From its molecular weight this substance can only be hexafluoropropene or hexafluoro*cyclo*propane (both *M*, 150). Hexafluoropropene reacts readily with bromine solution of the concentration used here and its m. p. is −156·5° (Young and Murray, *J. Amer. Chem. Soc.*, 1948, **70**, 2814). Therefore the compound described above is hexafluoro*cyclo*propane.

TABLE 1. *Attempted separation of mixture of higher fluorocarbons.*

Fraction	Wt., mg.	*M*	Probable carbon number	Fraction	Wt., mg.	*M*	Probable carbon number
1	1·87	—	C_{11} or higher	5	1·11	316 ± 50	C_7—C_8
2	—	—	About C_{11}	6	1·21	301 ± 50	C_4—C_7
3	2·57	—	C_9—C_{11}	7 *	<0·6	—	C_3—C_6
4	0·71	436 ± 60	C_9—C_{10}				

* This does not include the major portion of C_3F_6, weight 22 mg.

The above conclusions concerning the gaseous products are illustrated by the following analysis of gas remaining at the end of experiment K 5, in which the pressure decreased from 35·035 to 30·46 cm.: collected at −196°, *M*, 100·4 (C_2F_4, *M*, 100), amount equivalent to 27·345 cm. in reaction tube; collected at −135°, *M*, 151·3 ± 1, equivalent to 3·09 cm.; collected at −110°, equivalent to 0·025 cm. in the reaction tube.

The white solid deposited in the 560-c.c. bulb in good quantity both as dust and as a film on the silica was insoluble in all reagents tested. It was completely attacked by fusion with sodium peroxide and glucose in a Parr bomb but was inert to less vigorous reagents. On heating, it became glassy at 320—340° and decomposed at about 500°. The products of decomposition were tetrafluoroethylene and in much smaller amount a substance of molecular weight 154 ± 10 (Calc. for C_3F_6: *M*, 150). In accord with the material balance for the photochemical reaction, and the nature of the products of decomposition, micro-analysis of the polymer gave figures for carbon content in the range 24·8 ± 1% (Calc. for CF_2: C, 24%). The *X*-ray diffraction pattern of the powder showed a main ring at 4·9 Å.

The above details may be compared with a description of polytetrafluoroethylene (Teflon) given by Hanford and Joyce (*J. Amer. Chem. Soc.*, 1946, **68**, 2082) and Renfrew and Lewis (*Ind. Eng. Chem.*, 1946, **38**, 870). This product of the catalysed polymerisation of tetrafluoroethylene undergoes a phase transition at 327° and decomposes to tetrafluoroethylene and hexafluoropropene at temperatures above 450°. Its *X*-ray diffraction photograph has a main ring corresponding to a spacing of 4·86 Å. Molten alkali metals attack the polymer but it is otherwise unreactive. The material from the photochemical reaction is obviously very similar to this. Hanford and Joyce designate their product as a linear polymer. A polymer of chain length of the order of 26 monomer units melts at 220° (Raal and Danby, *J.*, 1950, 1596). The polymers described above must have a distinctly higher chain length.

Relative Quantity of Products.—Data in Table 2 show that under a wide variety of conditions the yield of higher fluorocarbons is small. The first few figures refer to conditions and time intervals in which only a comparatively small amount of polymer accumulates in the reaction zone. At low pressures there was a marked predominance of polymer. On using long reaction times and the large reaction bulb, which favoured accumulation of polymer in the reaction zone, there was a very marked predominance of polymer formation. In the fifth and the sixth experiment in Table 2 the rate of pressure decrease was found to increase with time, this increase being actually an increase in the rate of polymer formation. The abnormal rate of polymer formation, which led to a preponderance of polymer in the products, was associated with the presence of polymer in the reaction zone.

TABLE 2. *Relative amounts of products.*

(*a*, 11·6-cm. tube; *b*, 560-c.c. bulb.)

Tube	Initial pressure, cm.	Pressure decrease, cm.	C_2F_4 consumed, cm.	C_2F_4 (%) consumed to form : polymer	C_3F_6	higher fluorocarbons
a	35·035	0·82	1·22	50·2	49·1	0·7
a	18·005	0·62	1·22	24·9	73·5	1·6
a	3·555	0·31	0·39	70·5	29·5	trace
a	1·145	0·46	0·51	84·8	15·2	trace
b	33·30	1·17	1·36	79	21	trace
b	29·36	17·53	18·39	93·0	6·4	0·6
b	12·90	11·0	11·49	92·5	5·7	1·8

Measurement of Light Intensity by Thermopile.—An arrangement of light source and reaction tube similar to that shown in Fig. 1 was used. The thermostat was removed and a short Pyrex cylinder was sealed to the top of the reaction tube and filled with water to a depth of 1 cm. The thermopile was placed immediately below the lower window of the reaction tube.

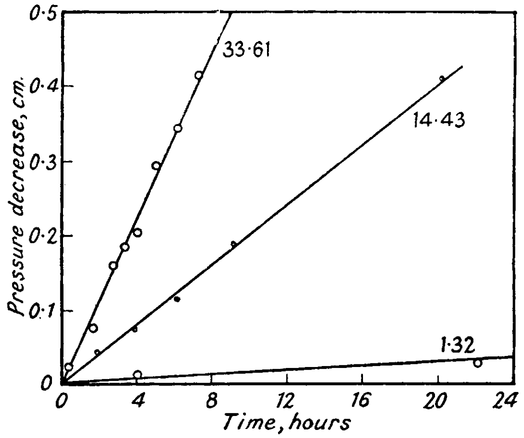


FIG. 2. *Pressure–time curves for low-intensity irradiation; initial pressures (in cm.) are marked on the curves.*

To obtain a figure for the intensity of ultra-violet light and to eliminate the effect of variable dark e.m.f., readings were taken alternately with and without a sheet of glass in the beam and at intervals of 3 minutes. Successive readings of the same type were averaged and subtracted from the intervening reading. The intensity of ultra-violet light was measured with the tube empty and with the tube containing mercury vapour and mercury vapour plus gas.

With mercury vapour present, the measured intensity included fluorescence radiation as well as unabsorbed light. The reduction caused by the addition of gas was due to quenching and reached a maximum on the addition of sufficient gas to give complete quenching. When the tube contained tetrafluoroethylene the time of exposure to ultra-violet light was sufficient to cause noticeable deposition of polymer on the lower window. In a series of measurements with increasing pressures of gas it was necessary to correct the later readings for loss in trans-

TABLE 3. *Quenching of fluorescence by tetrafluoroethylene.*

Tube length, 2·2 cm.		Tube length, 11·6 cm.	
Pressure of C_2F_4, cm.	Fraction of fluorescence quenched	Pressure of C_2F_4, cm.	Fraction of fluorescence quenched
2·5	0·67	1·9	0·5
9·2	1·0	6·0	0·82
28·2	1·0	9·5	0·89
		12·4	1·0

mission due to the deposition of polymer. Figures for the fraction of fluorescence radiation quenched are given in Table 3 and show that at 10 cm. pressure of tetrafluoroethylene quenching was virtually complete.

The total amount of light absorbed when quenching was complete was estimated from the intensity measurements and the area of the light beam. The value obtained was for the equilibrium vapour pressure of mercury at 20°. In a separate experiment in which a photocell was used for intensity measurements the variation of light absorption with mercury vapour pressure was measured. The light absorbed in the reaction tube at 29·7° was then calculated. Results for experiments F 8 and 11 given in an earlier note (*loc. cit.*) were calculated before the photo-cell measurements were made and revised figures are now given.

Quenching by hexafluoro*cyclo*propane was found to be slightly more efficient than by tetrafluoroethylene. Hexafluoro*cyclo*propane does not absorb the 2537-Å line.

The absorption spectrum of tetrafluoroethylene in the range 2100—4000 Å was photographed, 7 cm. pressure of gas being used in a 30-cm. tube. No evidence of absorption was obtained.

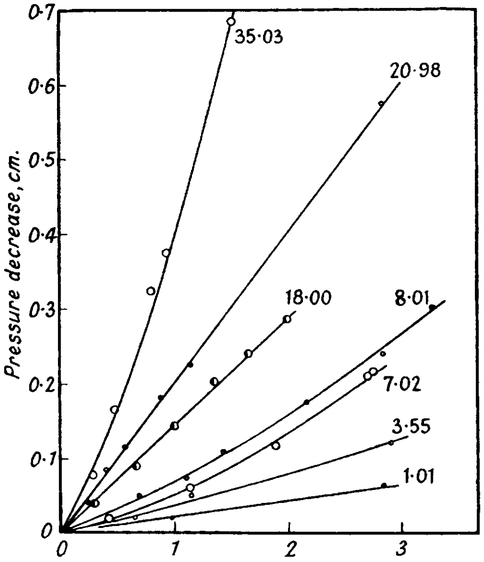


FIG. 3. *Pressure–time curves for medium-intensity irradiation; initial pressures (in cm.) are marked on the curves.*

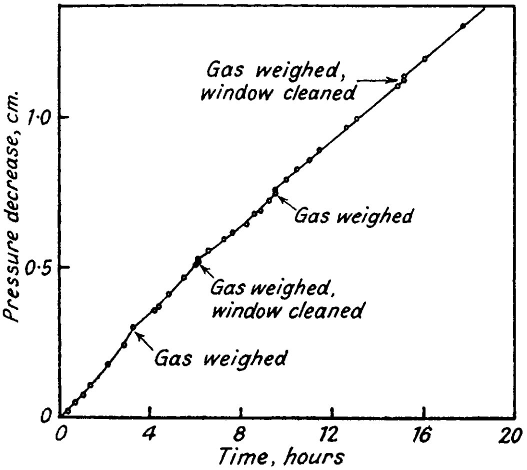


FIG. 4. *Pressure–time curve showing the effect of interrupting the reaction when the rate is increasing with time. (Initial pressure, 8·01 cm.).*

Ethylene Actinometer.—According to Le Roy and Steacie (*loc. cit.*), at an ethylene pressure of 1·3 cm. and a temperature of 25°, the mercury-photosensitised reaction of ethylene is, in the initial stages, almost exclusively

$$C_2H_4 + Hg^3P_1 = C_2H_4^* + Hg^1S_0 \qquad (1)$$

$$C_2H_4^* = H_2 + C_2H_2 \qquad (2)$$

Quenching is complete and the quantum efficiency of acetylene formation is 0·37.

The following method was used for measuring the absorbed intensity in the circumstances of experiments K 1—9. The mercury-photosensitised reaction of ethylene was followed until sufficient points had been obtained for the initial rate of pressure increased to be measured. This was assumed to be equal to the rate of acetylene formation and the intensity was calculated by using the value of 0·37 for the quantum efficiency.

This method is not highly accurate. Allen and Gunning (*J. Chem. Phys.*, 1948, **16**, 634) have reported that some polymerisation takes place even in the early stages of the reaction, and more recently Darwent (*ibid.*, 1951, **19**, 258) has given evidence that the reaction is partly heterogeneous.

Rate Measurements.—All measurements were made at 29·8° with a drop of mercury in the tube. Curves showing the change of pressure with time in several experiments are given in Figs. 2 and 3. In the absence of mercury there was no pressure change. With a low light intensity constant rates were obtained but several curves at the higher intensity show some increase of rate with time, this effect being observed at intial pressures of 35 and 8 but not at 18 cm. The initial rates increase with increasing pressure.

When the rate of reaction increased with time the initial rate of formation of the two main products could not be calculated from an analysis made during the run without making some assumption about the cause of the increase in rate. To discover the cause, experiments were performed in which analyses were made at intervals. As shown in Fig. 4 it was found that the effect of interrupting the reaction when the rate was increasing was to restore the rate to its initial value. In Fig. 5 a run frequently interrupted is compared with one infrequently interrupted. The values for C_3F_6 are in the normal relationship, being higher for the experiment at the higher initial pressure, and decreasing as the window becomes cloudy and the pressure decreases. The polymer figures are close at first but subsequently higher in the experiment with few interruptions. The observed increase in rate is therefore an increase in the rate of polymer formation. Initial rates of formation of C_3F_6 were assumed to be steady at least for the first few hours of any run and the initial rates of polymer formation were calculated from the overall initial rate and the rate of C_3F_6 formation. If no measurable quantity of higher fluorocarbons was separated at the first interruption the formation of these products was neglected. Figures for the initial rates are given in Table 4.

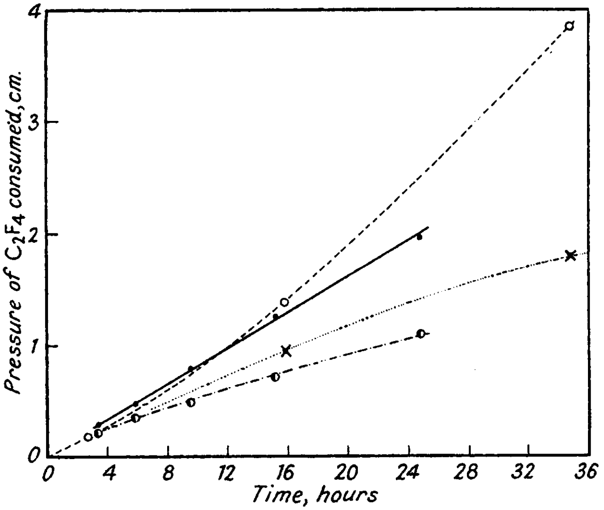


FIG. 5. *The influence of interruptions on the yields of hexafluoro*cyclo*propane and polymer*:

K. 1, initial pressure 7·02 cm.; polymer ○, C_3F_6 ×.
K. 6, initial pressure 8·01 cm.; polymer ◐, C_3F_6 ●.

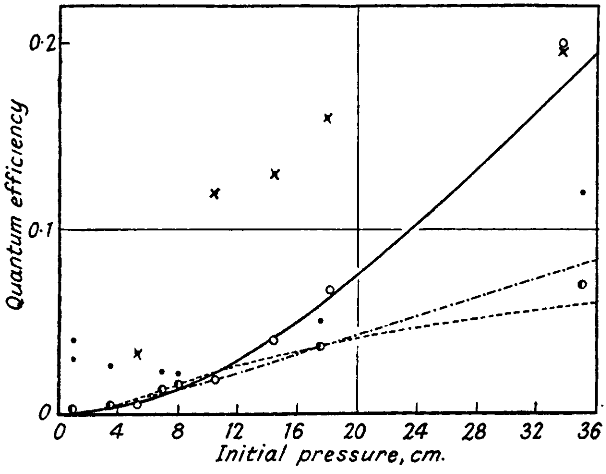


FIG. 6. *Quantum efficiencies*: $\eta_{C_3F_6}$, *F group* ○, *K group* ◐; ϕ, *F group* ×, *K group* ●. *Theoretical curves, second-order recombination: F group* ——, *K group* —·—; *third-order, K group* — — —.

TABLE 4. *Initial rates of reaction.*

F, short reaction tube, 53·04 c.c.; G and K, long tube, 180·4 c.c. Light absorbed for complete quenching: F, 2·02 × 10^{18}; G, 2·8 × 10^{18}; K, 1·04 × 10^{20} quanta per hour.

Expt.	Initial pressure, cm.	Pressure decrease, cm./h.	Rate of consumption of C_2F_4, cm./h.: forming C_3F_6	forming polymer	Expt.	Initial pressure, cm.	Pressure decrease, cm./h.	Rate of consumption of C_2F_4, cm./h.: forming C_3F_6	forming polymer
F.2	1·325	0·0012	—	—	G.3	14·925	0·011	—	—
F.4	0·395	*	—	—	K.3	1·010	0·023	0·007	0·021
F.5	1·075	0·0013	—	—	K.7	1·145	0·034	0·008	0·032
F.7	5·050	0·004	0·002	0·003	K.2	3·555	0·040	0·021	0·033
F.8	10·435	0·016	0·007	0·014	K.1	7·025	0·056	0·065	0·034
F.9	14·430	0·020	0·016	0·015	K.6	8·015	0·062	0·082	0·035
F.10	18·195	0·028	0·026	0·019	K.9	18·005	0·165	0·205	0·093
F.11	33·610	0·050	0·079	0·024	K.5	35·035	0·33	0·367	0·208

* Not measurable.

Quantum Efficiencies.—The reaction forming hexafluoro*cyclo*propane must be of the type

$$\mathrm{Hg}^* + C_2F_4 = \mathrm{Hg} + C_2F_4^* \tag{3}$$

$$C_2F_4^* + 2C_2F_4 = 2C_3F_6 \tag{4}$$

one excited atom causing at maximum efficiency the formation of two molecules of hexafluoro*cyclo*propane. To make the expressed quantum efficiency $\eta_{C_3F_6}$ a true measure of the efficiency it has been calculated as the number of molecules consumed to form C_3F_6 divided by three times the number of quanta absorbed.

The efficiency of initiation of polymer chains cannot be calculated; ϕ is the number of molecules of C_2F_4 polymerised divided by the number of quanta absorbed.

The results for the F and K groups of experiments are plotted in Fig. 6. In the region of incomplete quenching the light absorbed has been estimated from the results of the thermopile measurements described above.

*Effect of Hexafluoro*cyclo*propane.*—The following figures show that under the conditions of the K group of experiments decomposition of pure hexafluoro*cyclo*propane is slight: initial pressure, 1·54 cm.; time of irradiation, 17 hours 40 minutes; final pressure, 1·52 cm.; C_2F_4 formed, 0·03 cm.; C_3F_6 consumed, 0·05 cm.; C_3F_6 polymerised, 0·03 cm. Figures given in Table 5 show that hexafluoro*cyclo*propane has a noticeable effect on the reaction of tetrafluoroethylene when present in quantity. Pressure–time curves are straighter in the presence of hexafluoro*cyclo*propane (see Fig. 4).

TABLE 5. *Rates of reaction in the presence of hexafluoro*cyclo*propane.*

Expt.	Initial pressures, cm.: C_2F_4	C_3F_6	Rates of consumption of C_2F_4, cm./h.: to give C_3F_6	to give polymer	Rates for C_2F_4 alone, cm./h.: to give C_3F_6	to give polymer
K.9	13·950	2·275	0·14	0·041	0·152	0·062
K.6	6·725	0·535	0·082	0·038	0·058	0·033
K.6	6·050	0·840	0·073	0·043	0·050	0·032
K.8	3·820	1·975	0·021	0·053	0·025	0·027
K.8	3·465	2·040	0·016	0·048	0·020	0·027

Mechanism of the Reaction.—The products of the reaction are compounds built from CF_2 groups, as is the reactant. Rupture of carbon–fluorine bonds would lead to products containing CF_3 groups and to consumption of mercury and may be ruled out, for the reaction has in some experiments been maintained by mercury vapour alone. The two possible primary reactions are

$$C_2F_4 + \mathrm{Hg}^{3}P_{1} = C_2F_4^* + \mathrm{Hg}^{1}S_{0} \tag{5}$$

$$C_2F_4 + \mathrm{Hg}^{3}P_{1} = 2CF_2 + \mathrm{Hg}^{1}S_{0} \tag{6}$$

This assumes, as is usually assumed for the ethylene reaction, that the mercury atoms are quenched directly to the ground state. Reaction (5) could be followed by

$$C_2F_4^* = 2CF_2 \tag{7}$$

$$C_2F_4^* + C_2F_4 = 2C_2F_4 \tag{8}$$

$$C_2F_4^* + C_2F_4 = C_3F_6 + CF_2 \tag{9}$$

$$C_2F_4^* + C_2F_4 = C_4F_8 \tag{10}$$

The last of these reactions could yield C_3F_6 only by a reaction of the type

$$C_4F_8{}^* + C_2F_4 = 2C_3F_6 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (11)$$

As C_4F_8 is not in evidence in the products, it is doubtful whether (10) occurs at all. Even if it did, the competing deactivation reactions would only permit a low yield of C_3F_6 by (11). Reactions (8) and (9) occurring alone would give quantum yields lying between two limits, one twice the other. No such restriction has been found.

Fairly good representation of the experimental results is given by mechanisms involving a scission of tetrafluoroethylene into difluoromethylene. In connection with these mechanisms, the possibility that excited tetrafluoroethylene molecules are deactivated by reaction (8) must be considered. This reaction cannot be of over-riding importance in the pressure range studied, for although quantum yields up to 0·2 have been found the efficiency is not decreasing with increasing pressure. The major variations of $\eta_{C_3F_6}$ are obviously determined by reactions other than (8) and it will be disregarded in the treatment below. This, of necessity, leaves completely unresolved whether the primary reaction is (5) or (6).

The reaction scheme that follows from the scission of tetrafluoroethylene into difluoromethylene is as follows. By (5) and (7) or (6)

$$C_2F_4 = 2CF_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (12)$$

$$CF_2 + C_2F_4 = C_3F_6{}^* \text{ or } {-}C_3F_6{-}\text{; rate} = k_1[CF_2][C_2F_4] \quad (13)$$

$$C_3F_6{}^* \text{ or } {-}C_3F_6{-} + C_2F_4 = C_3F_6 + C_2F_4 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (14)$$

$$C_3F_6{}^* \text{ or } {-}C_3F_6{-} + C_2F_4 = {-}C_5F_{10}{-} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (15)$$

$${-}C_5F_{10}{-} + C_2F_4 = {-}C_7F_{14}{-}\text{, etc.} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (16)$$

$$CF_2 + CF_2 + C_2F_4 = 2C_2F_4 \qquad -d[CF_2]/dt = 2k_2[CF_2]^2[C_2F_4] \quad . \; . \quad (17)$$

or

$$CF_2 + CF_2 = C_2F_4 \qquad -d[CF_2]/dt = 2k_2'[CF_2]^2 \quad . \; . \; . \; . \quad (18)$$

$$CF_2 + CF_2 = C_2F_4 \text{ (at the walls)} \qquad -d[CF_2]/dt = k_3(CF_2)/[C_2F_4] \quad . \; . \; . \quad (19)$$

As the weight yield of polymer is of the same order as the weight yield of hexafluoro*cyclo*propane, (15) must be slow compared with (14). Application of the usual stationary state method gives the following alternative expressions for the quantum yield, three-body recombination of radicals being assumed :

$$\eta_{C_3F_6} = \frac{k_1{}^2}{8k_2Q}\left[\sqrt{\left([C_2F_4] + \frac{k_3}{k_1[C_2F_4]}\right)^2 + \frac{16Qk_2[C_2F_4]}{k_1}} - \left([C_2F_4] + \frac{k_3}{k_1[C_2F_4]}\right)\right] \quad (20)$$

and, second-order recombination being assumed :

$$\eta_{C_3F_6} = \frac{k_1{}^2[C_2F_4]}{8k_2'Q}\left[\sqrt{\left([C_2F_4] + \frac{k_3}{k_1[C_2F_4]}\right)^2 + \frac{16Qk_2'}{k_1{}^2}} - \left([C_2F_4] + \frac{k_3}{k_1[C_2F_4]}\right)\right] \quad (21)$$

Q is the rate of reaction (12), here assumed equal to the rate of quenching excited mercury atoms by tetrafluoroethylene when the latter is expressed in quanta per second per c.c. of the reaction zone. Concentrations are in molecules per c.c., and reaction rates in molecules per c.c. per second.

At low intensities and pressures wall reactions predominate and both expressions reduce to

$$\eta_{C_3F_6} = \frac{[C_2F_4]}{[C_2F_4] + k_3/k_1[C_2F_4]} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (22)$$

giving a curve similar in shape to the graph of $\eta_{C_3F_6}$ for experiments in the F group. The values of $\eta_{C_3F_6}$ for experiments in this group give an average value of $0{\cdot}47 \times 10^{39}$ for k_3/k_1 in the small reaction tube. On the assumption that $k_3/k_1 = 0{\cdot}3 \times 10^{39}$ for the larger reaction tube and that the reaction takes place in the first 3 cm. of the tube, the more general equations can be fitted to the results of the K group of experiments by taking $k_1{}^2/k_2 = 1{\cdot}14 \times 10^{-6}$ or $k_1{}^2/k_2' = 2 \times 10^{-25}$. Plots of the two general expressions for $\eta_{C_3F_6}$ with the constants as given above and the intensities as in the K groups of experiments and of (21) with intensities as in the F group are given in Fig. 6. The experimental results above 3-cm. pressure are moderately well represented by either (20) or (21). At 1-cm. pressure the experimental value of $\gamma_{C_3F_6}$ is several times higher than the values obtained from the above functions. This point will be discussed below.

According to the above values for the ratios of rate constants, at 13-cm. pressure under the conditions of the K group of experiments over half the recombination of radicals takes place in the gas phase compared with one-fifth at 5-cm. pressure. Added hexafluoro*cyclo*propane will cause some reduction in the rate of excitation of tetrafluoroethylene. When wall reactions are important it should function also as an inert gas reducing the rate of diffusion of radicals to the walls and increasing the yield of hexafluoro*cyclo*propane. This should partly or completely counteract the reduction in the rate of excitation. This effect is observed at 3 and at 6 but not at 13-cm. pressure (see Table 5).

Variations in the size of the reaction tube should affect the efficiency when wall reactions are important. In accordance with this it was found that at 14-cm. pressure with the low-intensity beam the ratio, pressure decrease × volume/quanta absorbed, was increased by a factor of 1·4 when the long reaction tube was substituted for the short one. However, it must be remembered that the rate of wall reactions depends partly on the distribution of the light beam relatively to the tube walls.

The rate of formation of solid polymer varies with intensity and pressure in a complex manner. The general form of this variation is sufficiently similar to the variation in the rate of formation of hexafluoro*cyclo*propane to indicate a connection between the two parts of the reaction. This is in accord with the above mechanism, which provides a satisfactory explanation for the initiation of polymerisation in the system. The present results do not show whether or not this is the only mechanism by which polymerisation is initiated.

As it stands, the above mechanism does not explain the increase in the rate of polymerisation when polymer is allowed to accumulate in the reaction zone. Also it indicates a lower rate of polymerisation at low pressures than that observed. It appears that when the rate of diffusion of free radicals to surfaces is high, the polymerisation rate is abnormal. This is probably due to a reaction involving an adsorbed layer

$$CF_2 + \text{adsorbed layer} = \text{polymer} \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

The yield of hexafluoro*cyclo*propane at 1-cm. pressure, although low, is about 10 times that predicted by the equations given above. This introduces the possibility that

$$CF_2 + \text{adsorbed layer} = C_3F_6 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

should be added to the reaction scheme.

There is no obvious method of chain termination in the reaction system. The evidence obtained at present does not justify discussion of this problem here.

DISCUSSION

There is a very marked difference between the mechanism proposed above and that of the mercury-photosensitised reactions of ethylene. With ethylene, there is no dissociation of the carbon–carbon bond although the excited molecules have a sufficiently long average life for many to lose their energy by collision. Unless deactivated, the excited molecules dissociate into acetylene and hydrogen. Although the heat of reaction for

$$C_2F_4 = C_2F_2 + F_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

is not known it is clear that, owing to the high energy of the carbon–fluorine bonds and the low energy of the fluorine–fluorine bond, the value will exceed the 112 kcal. per g.-mol. available in the mercury-photosensitised reaction. However, it follows from the results given above and the work of LeRoy and Steacie with ethylene (*loc. cit.*) that this amount of energy is sufficient to cause the dissociation of the carbon–carbon bond in tetrafluoroethylene but not in ethylene.

It is uncertain which of two reasons accounts for the failure of ethylene to dissociate into methylene in the mercury-photosensitised reaction. The heat of reaction for

$$C_2H_4 = 2CH_2 \text{ (singlet)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

may be as low as 77 kcal. (Steacie, " Atomic and Free Radical Reactions," p. 149). From values for the energy of removal of hydrogen from methane given by Laidler and Casey in a theoretical discussion (*J. Chem. Phys.*, 1949, **17**, 1087), it may be deduced that the heat of reaction for (26) is less than 119 kcal., but may be greater than 112 kcal. According to the principle of conservation of spin angular momentum enunciated by Laidler (*J. Chem. Phys.*, 1942, **10**, 43), a reaction of the type

$$\mathrm{Hg}^3P_1 + C_2H_4 = 2CH_2 \text{ (singlet)} + \mathrm{Hg}^1S_0 \quad . \quad . \quad . \quad . \quad (27)$$

is one of low probability in the quenching of triplet mercury to a singlet state. A sequence of high probability would be of the type

$$\mathrm{Hg}^3P_1 + C_2H_4 = \mathrm{Hg}^1S_0 + C_2H_4 \text{ (triplet)} \quad . \quad . \quad . \quad . \quad (28)$$

$$C_2H_4 \text{ (triplet)} = 2CH_2 \text{ (triplet)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

and this cannot occur because the energy acquired in the first step is about 40 kcal. less than the energy needed for the second. Because of the uncertainty about the heat of reaction for (26) there is no proof of the validity of the spin theory as applied to this case. It is therefore necessary to be very cautious in discussing the reaction of tetrafluoroethylene.

Difluoromethylene radicals in both the singlet and the triplet state are stabilised by delocalisation of electrons in π orbitals. This effect in the singlet state has been discussed by Mulliken (Venkateswarlu, *Phys. Review*, 1950, **77**, 676). In the triplet state, if the free radical is linear, there will be two sets of three overlapping π orbitals with five electrons in each set. Thus the heat of reaction for both

$$C_2F_4 = 2CF_2 \text{ (singlet)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

and

$$C_2F_4 = 2CF_2 \text{ (triplet)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

will include a resonance contribution. This makes it practically certain that the heat of reaction for (30) will be below 112 kcal., and possible that the heat of reaction for (31) will also be below this figure.

The experimental results given in this paper show that one of the following reactions occurs :

$$\mathrm{Hg}^3P_1 + C_2F_4 = \mathrm{Hg}^1S_0 + 2CF_2 \text{ (singlet)} \quad . \quad . \quad . \quad . \quad (32)$$

or

$$\mathrm{Hg}^3P_1 + C_2F_4 = \mathrm{Hg}^1S_0 + 2CF_2 \text{ (triplet)} \quad . \quad . \quad . \quad . \quad (33)$$

or

$$\mathrm{Hg}^3P_1 + C_2F_4 = \mathrm{Hg}^1S_0 + C_2F_4 \text{ (triplet)} \quad . \quad . \quad . \quad . \quad (34)$$

followed by

$$C_2F_4 \text{ (triplet)} = 2CF_2 \text{ (singlet)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

or

$$= 2CF_2 \text{ (triplet)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

If the rules of conservation of spin angular momentum applicable to atoms and very simple molecules can be applied to tetrafluoroethylene, (32) and (35) can be ruled out and the heat of reaction for (31) must be below 112 kcal. As stated above, it has not been proved that these rules apply to ethylene, and therefore further evidence must be obtained before a definite conclusion can be reached.

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