THE PHOTOLYSIS OF TRIFLUOROMETHYL IODIDE

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Trifluoromethyl iodide is decomposed by light of wavelength 2537 Å to yield iodine and C_2F_6. At pressures above 1 cm small amounts of other products are formed. The quantum yield of the overall process varies from 0·02 to 0·13 depending on the pressure, the higher yields being at lower pressures. Both nitric oxide and silver increase the quantum yield. It is probable that the primary process is the division of the molecule into a trifluoromethyl radical and an iodine atom with an efficiency of unity. The reverse reaction or the reaction of CF_3 with I_2 causes the low quantum yield.

In an earlier publication [1] Dacey and Hodgins reported that carbon tetrafluoride is decomposed by xenon photosensitization using the xenon resonance line 1469 Å. The products of its decomposition are fluorine and tetrafluoroethylene. It was not possible to determine whether the primary step in this reaction was the splitting of carbon tetrafluoride into a fluorine molecule and a CF_2 radical or its division into a fluorine atom and a CF_3 radical. If the latter process occurred, the CF_3 radicals would have to react with one another ultimately to yield C_2F_4. One possibility is the disproportionation reaction which would give the starting material as one of its products and therefore could not be detected in this system. It is therefore of interest to produce CF_3 radicals from a different source and to determine the products produced from them. Trifluoromethyl iodide was chosen as a source of CF_3 radicals because of its availability and because it was thought that it should readily divide into CF_3 and I. The present paper gives a preliminary report on the photolysis of this compound.

EXPERIMENTAL

PREPARATION OF MATERIALS.—*Trifluoromethyl iodide* was prepared from the silver salt of trifluoroacetic acid and iodine by the method described by Hauptschein and Grosse.[2] The gas was purified by passage through aqueous sodium hydroxide followed by concentrated sulphuric acid. It was allowed to stand over dry sodium hydroxide and phosphorus pentoxide and finally stored over dry mercuric oxide which removed any traces of free iodine. Its purity was determined by gas density measurements which gave a molecular weight of 196·2.

Tetrafluoroethylene was prepared by thermally decomposing its polymer, Teflon. The gas was purified by distillation ; its molecular weight by gas density measurement was 100·08.

Hexafluoroethane was obtained from the Minnesota Mining and Manufacturing Company.

Nitric oxide was prepared by the method described by Blanchard.[3]

DESCRIPTION OF APPARATUS.—The photolysis was carried out in a silica cell, 10 cm deep and 5 cm diam., which was illuminated with light of 2537 Å wavelength. The light source was a mercury resonance lamp, the output of which was passed through a Corning, no. 9063, filter. The intensity of light entering the cell was determined by uranyl oxalate actinometry. Various intensities were used but most runs were done with $1{\cdot}42 \times 10^{-8}$ quanta entering the cell per second.

The reaction cell was part of a closed circuit which contained a total volume of 3119 ml. The reacting gas was continually circulated around this circuit by means of a magnetically operated all-glass pump. Two U-tube traps were included in the circuit so that the gas passed through each trap in succession on leaving the cell. The closed circuit was connected by a capillary tube through a mercury cut-off to a vacuum manifold. The cut-off contained two ground-glass valves which closed on raising the mercury level. Beyond the cut-off and connected to the manifold by a stop-cock was a multiple range McLeod gauge. A Ward type low pressure still was connected to the manifold so that the contents of the reaction space could be transferred directly to it.

PROCEDURE.—In making a run the reaction space was first evacuated then filled to the desired pressure through the mercury cut-off. The cut-off was then closed, the circulating pump started, and the shutter opened between the reaction cell and the lamp. During a run, the first of the traps through which the gas circulated was maintained at − 78° C with solid carbon dioxide in acetone. The iodine produced by the photolysis condensed in this trap. After the run was terminated, which was usually after about 5 % of the reacting gas had decomposed, liquid air was placed around the second trap. With all of the condensable gases frozen in this trap, the pressure of the non-condensable gases was then measured by opening the mercury cut-off to the McLeod gauge. In cases where the quantum yield was being determined the trap containing the iodine was removed for analysis ; when the gaseous products of the reaction were to be determined the contents of the second trap were transferred through the mercury cut-off to the Ward still.

ANALYSIS OF PRODUCTS.—Iodine was determined by washing out the trap with aqueous potassium iodide and titrating the solution with sodium thiosulphate using a starch indicator. In those runs where nitric oxide was added to the reaction mixture, the iodine was dissolved in chloroform and determined colorimetrically with a photoelectric colorimeter. In some cases, metallic silver ribbon was introduced into the reaction zone. When this was done very little iodine condensed in the trap while the silver became coated with silver iodide. The iodine on the silver was determined by weighing the silver ribbon before and after the run.

The gaseous products were separated from the starting material by distillation at 1 mm pressure in a modified Ward type still similar to that described by LeRoy.[4] The lower boiling fraction contain C_2F_6 and C_2F_4 whose vapour pressures are 1 mm at approximately − 150° C. CF_3I has a vapour pressure of 0·008 mm at this temperature. Of other possible products, CF_4 and F_2 are not condensible with liquid air in the pressure range covered by these experiments. $C_2F_4I_2$, CF_2I_2, together with possible products resulting from reactions between CF_3I and C_2F_4, ondense in the trap cooled to − 78° C.

The amount of the lower boiling fraction from the Ward still was determined by pressure and temperature measurement on the gas in a calibrated volume. The composition of the sample was then determined by either of two methods. For the first method the gas was removed by a Toepler pump, collected in a micro gas holder and analyzed with a Blacet-Leighton apparatus.[5] C_2F_4 may be separated from C_2F_6 in this apparatus by the action of sodium hydroxide + copper oxide mixture.[6] For the second method the gas was transferred to a quartz adsorption cell and its ultra-violet absorption determined in the region 2000 Å to 3000 Å. The latter method proved to be the more satisfactory except that the product of several runs had to be combined to give a sufficient pressure in the absorption cell. The higher boiling fraction which was wholly unreacted CF_3I was identified by its ultra-violet absorption and by vapour density determination.

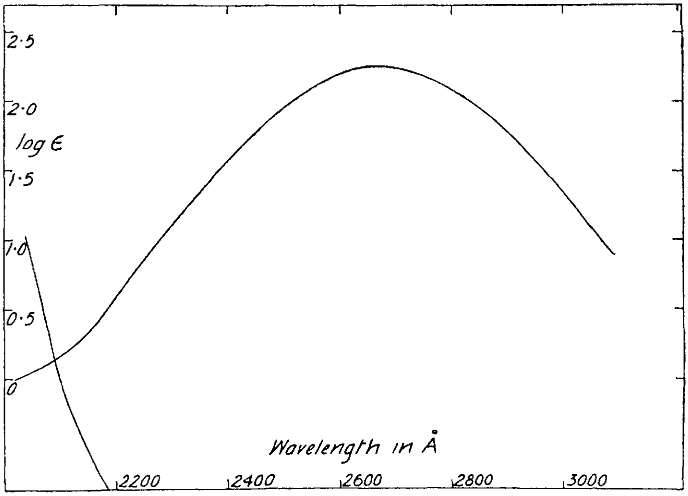

FIG. 1.

For the purpose of analysis, as mentioned above, the ultra-violet absorption of several gases was determined in the region 2000 Å to 3000 Å. The data for CF_3I and C_2F_4 appear in fig. 1 where the logarithm of the extinction coefficient, defined by the equation $\epsilon = \frac{1}{Cd} \log \frac{I_0}{I}$ is plotted against wavelength. C is measured in moles/l. and d in cm. 2065·5 Å was the lowest wavelength attainable with the Beckmann spectrophotometer used. At this wavelength C_2F_4 has an extinction coefficient of 3·84 while for CF_3I the value is 1·23. At 2700 Å, CF_3I absorbs strongly, the coefficient being equal to 173, while for C_2F_4 it is zero. C_2F_6 is perfectly transparent throughout the whole range. It is therefore possible by measuring the absorption at 2065·5 Å and at 2700 Å to analyze mixtures of C_2F_4 and C_2F_6 in the presence of small amounts of CF_3I.

RESULTS

THE PRODUCTS OF THE REACTION.—At low pressures the overall reaction is given by the equation $2CF_3I \rightarrow I_2 + C_2F_6$. However, at pressures above 10 mm, the boiling fraction removed from the Ward still contained appreciable amounts of a component which was adsorbed by the action of NaOH + CuO. This was thought to be C_2F_4 although it was not identified. The low boiling fraction had a vapour pressure of 1 mm at − 148·5° C which checked with the vapour pressure of C_2F_6 as determined in known samples tested in the still and agrees with that reported by Pace and Aston.[7]

The amount of iodine formed generally agreed with the volume of low boiling products recovered. At high pressures the agreement was poorer than at low pressures. No fluorine or carbon tetrafluoride was found except in two runs carried out at 50 and 42 mm where small pressure of gas not condensible in liquid air remained after cooling the products.

After a number of runs, a small amount of white deposit was observed on the glass wall of the pump where, due to the operation of the pump, the temperature was about 80° C. This material was not identified and was thought to be polymerized C_2F_4 or some solid product resulting from the action of C_2F_4 on CF_3I. The second trap in the reaction circuit was on one occasion warmed to 100° C during a run in an attempt to induce this deposit to form in the trap. After several hours' circulation, the faintest suggestion of a white deposit was observed on one side of the trap.

During most runs a pale yellow solid deposited in the dry ice trap together with the iodine. This material was present in very small amounts. It remained solid at room temperature, was insoluble in water but dissolved in aqueous potassium iodide. It was concluded that this material was mercury iodide formed from traces of mercury introduced into the system with the starting material.

Although, especially at higher pressures, this reaction is more complicated than the simple equation given above, it is concluded that at pressures below 1 cm this equation does represent the principal reaction that takes place. Table 1 gives some typical data for several reactions at different pressures.

TABLE 1

initial pressure (mm)	1·80	3·60	7·74	13·7
pressure (mm) of non-condensable gases in 3·12 l.	0·0005	0·0	0·004	0·0045
iodine recovered (g)	0·00172	0·00159	0·00254	0·00377
low boiling gaseous products	1 cm^3 at	1 cm^3 at	1 cm^3 at	1 cm^3 at
(volume at 24° C)	12·7 cm	11·0 cm	17·1 cm	20·3 cm.
ratio iodine recovered gaseous products	0·99	0·95	1·09	1·12
quantum yield	0·117	0·085	0·079	0·042

THE QUANTUM YIELD.—The quantum yield was determined from the iodine analysis, the intensity of the lamp, and the absorption of the CF_3I at the pressure of the reaction. At pressures above 1 cm the quantum yield is very low. It increases as the pressure is lower, the highest value of 0·13 occurring at a pressure of 0·195 mm. Fig. 2 gives the data obtained, plotted as quantum yield against pressure.

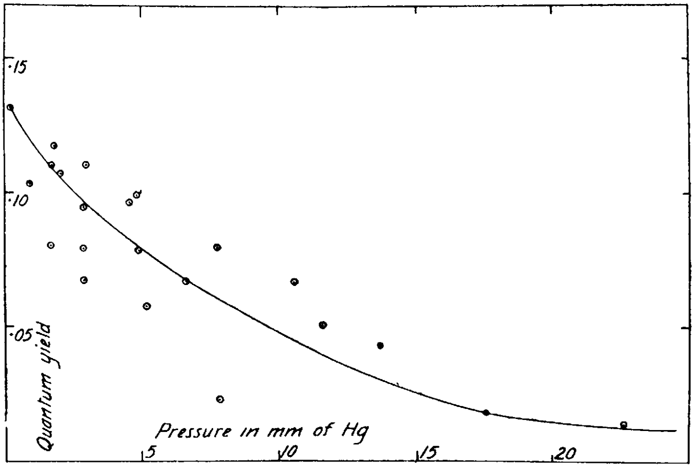

FIG. 2.

THE REACTION WITH NO PRESENT.—A number of runs were done with nitric oxide mixed with CF_3I. The data of these runs appear in table 2. The quantum yields are greatly increased by the action of NO. The gaseous products were not analyzed. CF_3NO was probably present since a deep blue solid was observed on cooling with liquid air.

THE REACTION WITH SILVER PRESENT.—Several runs were carried out with approximately ½ g fine silver ribbon inside the quartz reaction cell. When this was done, virtually no iodine appeared in the dry ice trap while the quantum yield, based on iodine found as silver iodide, increased. The gaseous products of these runs were not analyzed. The data for these runs also appear in table 2.

TABLE 2

initial pressure (mm)	additional agent	quantum yield
4·42	silver ribbon	0·36
7·65	silver ribbon	0·28
3·81	silver ribbon	0·33
1·97	silver ribbon	0·41
3·95	0·76 mm of NO	0·75
3·30	2·90 „ of NO	0·72
7·04	3·37 „ of NO	0·69
1·14	0·80 „ of NO	0·77

DISCUSSION

Trifluoromethyl iodide absorbs continuously at 2537 Å. The primary process is undoubtedly

$$CF_3I + h\nu \rightarrow CF_3 + I$$

and its efficiency is probably unity. In this respect CF_3I behaves like CH_3I.[8, 9] The low quantum yield must be due to either of the following processes:

$$CF_3 + I \rightarrow CF_3I$$

or

$$CF_3 + I_2 \rightarrow CF_3I + I.$$

The action of NO and of silver in increasing the yield is apparently by preventing these reverse reactions, the former removing the CF_3 radicals and the latter the iodine atoms.

Since the CF_3 radicals which do not recombine with iodine form C_2F_6 they would probably also do so if formed in the primary process of the decomposition of CF_4. It is therefore concluded that

$$CF_4 + \overset{*}{Xe} \rightarrow CF_2 + F_2 + Xe$$

is probably the initial step in the photosensitized decomposition of carbon tetrafluoride. Work is continuing on this problem and further discussion is reserved until more data are obtained.

[1] Dacey and Hodgins, *Can. J. Res. B*, 1950, **28**, 90.
[2] Hauptschein and Grosse, *J. Amer. Chem. Soc.*, 1951, **73**, 2461.
[3] Blanchard, *Inorganic Syntheses*, vol. 2 (McGraw-Hill, New York, 1946).
[4] LeRoy, *Can. J. Res. B*, 1950, **28**, 492.
[5] Blacet and Leighton, *Ind. Eng. Chem.* (*Anal.*), 1931, **3**, 266.
[6] Hodgins and Haines, *Can. J. Chem.* (in press).
[7] Pace and Aston, *J. Amer. Chem. Soc.*, 1947, **70**, 566.
[8] Steacie, *Atomic and Free Radical Reactions* (Reinhold, New York, 1946).
[9] Noyes and Leighton, *The Photochemistry of Gases* (Reinhold, New York, 1941).