Pyrolysis of Fluorinated Organic Compounds. I. The Pyrolysis of 1, 2-Dibromo-1-chloro-1, 2, 2-trifluoroethane and Some Related Halogenated Ethane Derivatives

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It is known that chemical bonds may be broken homolytically by heat to produce free radicals which may further react to produce other compounds. This study involves the homolytic scission of the least thermally stable bonds in CF_2Br–CFClBr and related compounds. A temperature was selected for the pyrolysis which probably caused primarily carbon bromine bonds to be broken in the initiation steps of the reaction. The products were isolated and used as evidence to postulate reaction paths involving intermediate free radicals.

Results and Discussion

It was shown that pyrolysis of CF_2Br–CFClBr (I) produced two major products, CF_2Cl–CFClBr (II) and CF_2Br–$CFBr_2$ (III) in addition to starting material. The following reactions can be used to explain the products.

$$\mathrm{I} \xrightarrow{\text{heat}} \begin{cases} \to \dot{C}F_2\text{-}CFClBr + \dot{B}r \\ \to CF_2Br\text{-}\dot{C}FCl + \dot{B}r \end{cases} \quad \text{(initiation)} \quad (1)$$

$$\left.\begin{aligned} &\dot{C}F_2\text{-}CFClBr + \mathrm{I} \to CF_2Br\text{-}\dot{C}FBr + \mathrm{II} && (2) \\ &CFBr\text{-}\dot{C}FCl + \mathrm{I} \to CF_2Br\text{-}CFCl_2\ (\mathrm{IV}) && \\ &\qquad\qquad\qquad + CF_2Br\text{-}\dot{C}FBr && (3) \\ &CF_2Br\text{-}\dot{C}FBr + \mathrm{I} \to CF_2Br\text{-}\dot{C}FCl && \\ &\qquad\qquad\qquad \text{or } \dot{C}F_2\text{-}CFClBr + \mathrm{III} && (4) \end{aligned}\right\} \text{(propagation)}$$

The bond dissociation energies (kcal./mol.) were calculated for the starting material I, according to the equation developed by Errede.2)

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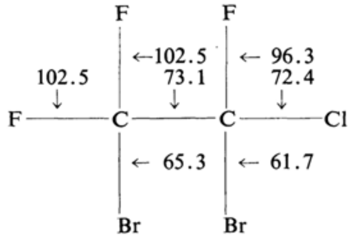
1) Frank J. Seiler Research Laboratory, Office of Aerospace Research, United States Air Force Academy, Colorado. This paper represesnts part of a thesis submitted by R. W. Lamb to the Graduate School, University of Colorado, in partial fulfillment of the requirements of the Ph. D. degree, June, 1961.

2) L. A. Errede, *J. Phys. Chem.*, **64**, 1031 (1960).



Assuming that the ease of breaking a bond in the initiation step is a function of the bond dissociation energy, it is postulated that the initiation step in the pyrolysis of I involves primarily the rupture of carbon-bromine bonds as is shown in reaction 1.

A small amount of $CF_2Cl\text{-}CFBr_2$ (VI) was also shown to be present in the product which indicates the presence of the free radical, $\dot{C}F_2\text{-}CFBr_2$ or $CF_2Cl\text{-}\dot{C}FBr$, during the course of the reaction. Both of these free radicals could originate from the further reaction of the products obtained in reactions 2 and 3.

There was no IV isolated in the product, therefore, the rate of reaction 3 must be slow compared to 2 and 4.

When a mixture of I and bromine was pyrolyzed, the same products were obtained in the same proportions as was obtained when elemental bromine was not used in the reaction. However, the yield was drastically reduced when I was pyrolyzed in the presence of nitric oxide as would be expected for a reaction involving free radicals.

When II was pyrolyzed, $CF_2Cl\text{-}CFCl_2$ (V), I and VI were the only products isolated. These products can be accounted for using the following reactions.

$$\text{II heat} \rightarrow CF_2Cl\text{-}\dot{C}FCl + \dot{B}r \quad \text{(initiation)} \qquad (5)$$

$$\left.\begin{aligned} &\text{II} + CF_2Cl\text{-}\dot{C}FCl \rightarrow \text{V} + \dot{C}F_2\text{-}CFClBr \\ &\qquad\qquad\qquad\qquad \text{or } CF_2Cl\text{-}\dot{C}FBr \quad (6) \\ &\text{II} + \dot{C}F_2\text{-}CFClBr \rightarrow \text{I} + CF_2Cl\text{-}\dot{C}FCl \quad (7) \\ &\text{II} + CF_2Cl\text{-}\dot{C}FBr \rightarrow \text{VI} + CF_2Cl\text{-}\dot{C}FCl \quad (8) \end{aligned}\right\} \text{(propagation)}$$

Pyrolysis of an equimolar mixture of III and V produced I, II and VI as the major products. Four different free radical intermediates are possible from the pyrolysis of III and V. The combination of these intermediates with a bromine or chlorine atom should lead to the formation of the products as follows :

$$\dot{C}F_2\text{-}CFCl_2 \xrightarrow{\text{Abstract Br}} \text{IV} \qquad (9)$$

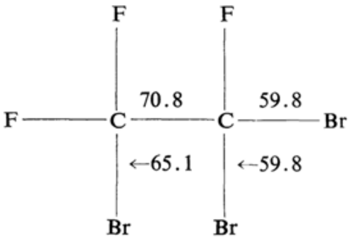
$$CF_2Cl\text{-}\dot{C}FCl \xrightarrow{\text{Abstract Br}} \text{II} \qquad (10)$$

$$\dot{C}F_2\text{-}CFBr_2 \xrightarrow{\text{Abstract Cl}} \text{VI} \qquad (11)$$

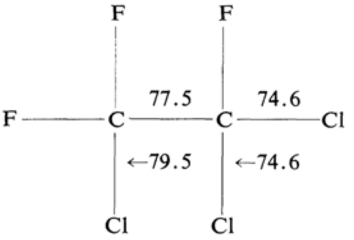
$$CF_2Br\text{-}\dot{C}FBr \xrightarrow{\text{Abstract Cl}} \text{I} \qquad (12)$$

The products which were isolated furnish evidence for reactions 10, 11 and 12. Since IV could not be isolated from the pyrolysis, it appears that either appreciable amounts of $\dot{C}F_2\text{-}CFCl_2$ are not present during the reaction or reaction 9 is slow compared to 10, 11, and 12. It is presumed that the carbon-chlorine bond in the chlorodifluoromethyl moiety of V is not appreciably broken under the conditions of the reaction. This particular bond is known to be relatively strong because of the strong negative inductive effect of the two fluorine substituents.³⁾

Using the equation developed by Errede,²⁾ a quantitative comparison of the strengths of the bonds in III and V can be made. The following model illustrates some calculated bond dissociation energies in kcal./mol.



III



V

It is presumed from the above calculated bond dissociation energies that the initiation step involves primarily the breaking of carbon-bromine bonds in III. Furthermore, the rate of production of $CF_2Br\text{-}\dot{C}FBr$ should exceed that of $\dot{C}F_2\text{-}CFBr_2$ because of the difference in the bond dissociation energies of the carbon-bromine bonds in III. Production of free radicals from V probably occurs during the propagation steps by the reaction of V with either $\dot{C}F_2\text{-}CFBr_2$ or $CF_2Br\text{-}\dot{C}FBr$. The high boiling liquid obtained from the pyrolysis of $CF_2Br\text{-}CFBr_2$ in the presence of nitric oxide was probably formed from the coupling of

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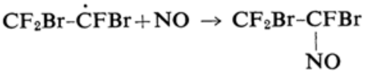
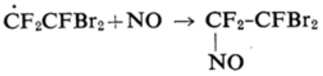
3) R. K. Steunenberg and G. H. Cady, *J. Am. Chem. Soc.*, **74**, 4165 (1952).

free radicals, such as $CF_2Br\text{-}\dot{C}FBr$ or $\dot{C}F_2\text{-}CFBr_2$.

An infrared spectrum of the slightly blue product showed no absorption peak at 6.25 μ, where the nitroso should absorb. The nitroso blue color is very intense; therefore, the presence of a small amount of nitroso compound could be enough to give a slight coloration to the product, but not enough to show up on a gas chromatogram, or in an infrared spectrum. This small amount of nitroso compound is to be expected. Nitric oxide is a known free radical scavenger; therefore, it would be expected to react with the free radicals formed in the following manner:



$$CF_2Br\text{-}\dot{C}FBr + NO \rightarrow CF_2Br\text{-}\underset{\displaystyle NO}{\underset{|}{C}}FBr \qquad (1)$$



$$\dot{C}F_2CFBr_2 + NO \rightarrow \underset{\displaystyle NO}{\underset{|}{C}}F_2\text{-}CFBr_2 \qquad (2)$$

These reactions represent termination steps; therefore, the products should be present only in small amounts. No attempt was made to isolate and identify the high boiling compound, which was a minor product, when $CF_2Br\text{-}CFBr_2$ was pyrolyzed in the presence of nitric oxide.

Experimental

General Procedures.—All pyrolysis runs were made using the same general procedures. When the reactants were liquids, as was the case in all but one reaction, they were added from a 50 ml. burette into a pyrolysis tube enclosed in an electric furnace. In the one reaction involving a gaseous reactant and a liquid reactant, the same apparatus was used except that the gas was introduced into the line leading to the pyrolysis tube via a T-connection just below the burette.

The tube used for pyrolysis was a platinum-lined nickel tube with an outside inconel jacket about 24 inches long and 3/4 inches in diameter. A section of the tube about 12 inches long was enclosed in the furnace. In order to make a distinct boundary for the region of pyrolysis, tap water was circulated through copper coils wrapped around the tube at the ends of the furnace. The volume of the section of tube used for pyrolysis was required in order to calculate the contact time. The temperature of the reaction was measured with a chromel-alumel thermocouple, which was inserted into the furnace along with the pyrolysis tube. The contact time was calculated by dividing the volume of the pyrolysis tube by the rate of flow of the reactants through the tube.

Gas chromatography was used to determine the composition of mixtures of liquids. All percentages are given in weight percents.

1, 2-Dibromo-1-chloro-1, 2, 2-trifluoroethane.—1,2-Dibromo-1-chloro-1, 2, 2-trifluoroethane was prepared by bubbling chlorotrifluoroethylene through liquid bromine in the presence of actinic light. In a typical reaction, 290 g. (2.50 mol.) of olefin was added to 375 g. (2.34 mol.) of bromine over a four hour period. The distilled product obtained was 637 g. (92% conversion), b. p. 86.5°C/630 mmHg (lit.[4] 92~92.5°C/760 mmHg). Gas chromatography showed this material to be pure.

Pyrolysis of 1, 2-Dibromo-1-chloro-1,2,2-trifluoroethane.—*A*) *at 500°C.*—Exactly 155 g. (0.56 mol.) of $CF_2Br\text{-}CFClBr$ was pyrolyzed at 500°C at a contact time of about 26~27 sec. The reactant was added at a uniform rate over a total time of four hours. All of the products (150 g.) were collected in a trap maintained at room temperature. Fractionation through a Todd column yielded the following three main fractions: a) $CF_2Br\text{-}CFClBr$ (I), b. p. 86~87°C/630 mmHg (84%); b) $CF_2Cl\text{-}CFClBr$ (II), b. p. 63°C/630 mmHg (5.5%) and c) $CF_2Br\text{-}CFBr_2$ (III), b. p. 108°C/630 mmHg (7.9%).

II was shown to be $CF_2Cl\text{-}CFClBr$ by comparison of its infrared spectrum with that of an authentic sample obtained from the addition of chlorine to trifluorobromoethylene. Similarly, compound III was compared with an authentic sample obtained form the bromination of trifluorobromoethylene.

B) *At 600°C.*—Although a trap maintained at −80°C was in the exit line, nearly all the products were collected in the trap kept at room temperature. In a typical reaction, 382 g. of $CF_2Br\text{-}CFClBr$ was pyrolyzed over a 3.5 hr. period to yield 367 g. of product. The product was washed with 5% sodium bisulfite solution to remove some bromine, washed with water, and dried over magnesium sulfate. The product was filtered and fractionated through a 50 cm. Todd column. The following materials were isolated and identified: a) mixture A consisting of $CF_2Br\text{-}CFClBr$ and $CF_2Cl\text{-}CFBr_2$, b. p. 86~87°C/630 mmHg: n_D^{25} 1.4254 (33%); b) $CF_2Cl\text{-}CFClBr$ (14%) and c) $CF_2Br\text{-}CFBr_2$ (19%).

The yields of the various components were calculated from a chromatogram of the mixture of undistilled products. The isomers, $CF_2Br\text{-}CFClBr$ and $CF_2Cl\text{-}CFBr_2$ gave only one peak on the chromatogram; therefore, they were treated as one compound in calculating yields.

The infrared spectrum of the mixture was compared with the spectrum of $CF_2Br\text{-}CFClBr$ prepared by adding bromine to chlorotrifluoroethylene. The spectrum of the mixture contained all of the absorption peaks of $CF_2Br\text{-}CFClBr$ plus two additional peaks at 9.75 μ and 13.27 μ. This evidence indicated that mixture A consisted of the two positional isomers, $CF_2Br\text{-}CFClBr$ and $CF_2Cl\text{-}CFBr_2$. In order to verify this supposition, and to determine the relative amounts of each isomer, A was treated with zinc and the resulting gaseous olefins brominated. The two isomers reacted by the following paths giving two products, which were easily separated by fractionation:

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[4] R. N. Haszeldine, *J. Chem. Soc.*, **1952**, 3423.

$$\left.\begin{array}{l}CF_2Br\text{-}CFClBr\\ \\ CF_2Cl\text{-}CFBr_2\end{array}\right] \xrightarrow[\text{ethanol}]{\text{Zn in}} \left\{\begin{array}{c}CF_2{=}CFCl\\ +\\ CF_2{=}CFBr\end{array}\right\}$$

$$\xrightarrow[\text{light}]{Br_2}\left\{\begin{array}{l}CF_2Br\text{-}CFClBr\ \text{ b. p. } 86^\circ C/630\ \text{mmHg}\\ \qquad + \\ CF_2Br\text{-}CFBr_2\ \text{ b. p. } 107^\circ C/630\ \text{mmHg}\end{array}\right.$$

The amount of each component was determined from a vapor phase chromatogram of the product. The product was found to be 73 mol. percent $CF_2Br\text{-}CFClBr$ and 27 mol. percent $CF_2Br\text{-}CFBr_2$.

Pyrolysis of a Mixture of 1, 2-Dibromo-1-chloro-1, 2, 2-trifluoroethane and Bromine at 600°C.—A mixture consisting of 535 g. (1.93 mol.) of $CF_2Br\text{-}CFClBr$ and 309 g. (1.93 mol.) of bromine was pyrolyzed at 600°C at a contact time of about 10 sec. The pyrolysis reaction was run over a period of fourteen hours and fifty minutes. The product was collected in a trap maintained at room temperature. It was then washed with a solution of 5% sodium bisulfide to remove the excess bromine, washed with water and dried over magnesium sulfate. The composition of the product was calculated from a gas chromatogram of the undistilled material. The individual peaks corresponding to each component of the products were identified by their retention times. The following products were obtained: a) mixture A consisting of $CF_2Br\text{-}CFClBr$ and $CF_2Cl\text{-}CFBr_2$ (32%); b) $CF_2Cl\text{-}CFClBr$ (13.6%) and c) $CF_2Br\text{-}CFBr_2$ (24%).

The reaction was repeated with a mixture consisting of 200 g. (0.72 mol.) of $CF_2Br\text{-}CFClBr$ and 109 g. (0.69 mol.) of bromine using a longer contact time (21.1 sec.). Apparently, there was very little change in the distribution of the pyrolyzates from that obtained above. The distribution was 27%, 13.6% and 19% for mixture A, $CF_2Cl\text{-}CFClBr$ and $CF_2Br\text{-}CFBr_2$, respectively.

Pyrolysis of a Mixture of 1, 1, 2-Tribromo-1, 2, 2-trifluoroethane and Nitric Oxide at 600°C.—Approximately 40 g. of $CF_2Br\text{-}CFBr_2$ was pyrolyzed in the presence of nitric oxide at 600°C over a 1.5 hr. period. The apparatus described under "General Procedures" was used, except that the nitric oxide was added at the rate of approximately 100 ml. per second. The product was all collected in the trap maintained at room temperature. It was washed with water, dried over magnesium sulfate, and filtered. The product was slightly blue, indicating a possible trace of a nitroso compound; however, the infrared spectrum of the product showed no absorption at the wavelengths, where the nitroso group should absorb. Calculations based on a gas chromatogram of the product indicate that it is approximately 92% starting material and 8.0% high boiling compound. The high boiling compound is probably a product of coupling of free radicals produced in the pyrolysis.

Pyrolysis of 1-Bromo-1, 2-dichloro-1, 2, 2-trifluoroethane at 600°C.—About 110 g. of $CF_2Cl\text{-}CFClBr$ was pyrolyzed at 600°C at a contact time of about 11 sec. over a period of one hour and thirty-five minutes. All of the product (102 g.) were collected in the trap, maintained at room temperature. It was washed with a solution of 5% sodium bisulfite to remove some bromine, washed with water and dried over magnesium sulfate. The product was fractionated through a Todd column. The pure products were obtained for identification from the distillation, but the yields were calculated from a chromatogram of the original mixture of products. The following products were identified. The yields given were based on the amount of starting material: a) $CF_2Cl\text{-}CFCl_2$ (10%); b) $CF_2Cl\text{-}CFClBr$ (43%), and c) mixture A consisting of $CF_2Cl\text{-}CFBr_2$ and $CF_2Br\text{-}CFClBr$ (9.5%).

Pyrolysis of a Mixture of 1, 1, 2-Tribromo-1, 2, 2-trifluoroethane and 1, 1, 2-Trichloro-1, 2, 2-trifluoroethane at 600°C.—A mixture consisting of 56 g. (0.17 mol.) of $CF_2Br\text{-}CFBr_2$ and 32 g. (0.17 mol.) of $CF_2Cl\text{-}CFCl_2$ was pyrolyzed at 600°C at a contact time of about 14 sec. The pyrolysis was run over a 1.5 hr. period. All of the product (49 g.) were collected in the trap kept at room temperature. It was washed with a solution of 5% sodium bisulfite to remove some bromine, washed with water, and dried over magnesium sulfate. The product was fractionated through a Todd column. The pure products were obtained for identification from the distillation; however, the yields were calculated from a chromatogram of the original mixture of products. The following products were isolated and identified from the reaction. The calculated yields were based on the total amount of material obtained from the pyrolysis: a) $CF_2Cl\text{-}CFCl_2$ (37.4%); b) $CF_2Cl\text{-}CFClBr$ (7.6%); c) mixture A consisting of $CF_2Br\text{-}CFClBr$ and $CF_2Cl\text{-}CFBr_2$ (14.5%) and d) $CF_2Br\text{-}CFBr_2$ (40.5%).

Dehalogenation of a Mixture of 1, 2-Dibromo-1-chloro-1, 2, 2-trifluoroethane and 1, 1-Dibromo-2-chloro-1, 2, 2-trifluoroethane.—About 166 g. (0.6 mol.) of a mixture of $CF_2Cl\text{-}CFBr_2$ and $CF_2Br\text{-}CFClBr$ was treated with zinc in ethanol to yield a mixture of $CF_2{=}CFBr$ and $CF_2{=}CFCl$. The reaction was carried out in a three-neck flask equipped with a stirrer, addition funnel, and a condenser. The halocarbons were added dropwise to a stirred suspension of powdered zinc in ethanol via an addition funnel. The exit line from the top of the condenser was collected to a dry-ice acetone trap, in which the olefins were collected. The olefins were used as a mixture in the next reaction, in which they were brominated.

Bromination of a Mixture of 1-Bromo-1, 2, 2-trifluoroethylene and 1-Chloro-1, 2, 2-trifluoroethylene.—Approximately 30 g. of a mixture, consisting of a mixture of $CF_2{=}CFCl$ and $CF_2{=}CFBr$, was passed from a trap through a glass frit into a glass flask approximately 6 cm. × 50 cm. The glass flask, which contained the bromine, was irradiated with light from a tungsten lamp to catalyze the reaction. The glass flask was equipped with a water-cooled condenser. The exit line was connected to a bubbler, which was connected to a dry-ice acetone-cooled trap to recover some unreacted olefin. The crude product was washed with a 10% sodium bisulfite solution to remove the excess bromine, washed with water, and dried over magnesium sulfate. Gas chromatography showed that the product (72 g.) consisted of a mixture of 78%

$CF_2Br-CFClBr$ and 22% $CF_2Br-CFBr_2$.

Pyrolysis of $CF_2Br-CFBr_2$ in the Presence of Nitric Oxide.—A sample of $CF_2Br-CFBr_2$ was pyrolyzed at 350°C in the presence of nitric oxide. At this temperature, 93% of the starting material was recovered and the absence of blue color was noted. This indicated no nitroso compounds, such as $CF_2NO-CFBr_2$ and $CF_2Br-CFBrNO$, were formed.

When the pyrolysis was run at 600°C a great deal of decomposition took place. After washing the product with water and drying, it retained a blue color, indicating that some nitroso compounds could be in the product. However, a gas chromatogram of the product showed it to consist of 92% of $CF_2Br-CFBr_2$ and 8% of an unidentified high boiling liquid.

Summary

The synthesis of various halogenated ethane derivatives was performed by the pyrolysis of $CF_2Br-CFClBr$ and other similar compound. The reactions were carried out in a platinum-lined tube at temperatures ranging from 350°C to 600°C alone and in the presence of nitric oxide or bromine. Various products were isolated and identified. A mechanism is postulated for the reaction.

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