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Abstract

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THE MECHANISM OF ADDITION OF IODINE CHLORIDE TO CHLOROTRIFLUOROETHYLENE

In 1951 Barr et al. (^{1}), and in 1952 Haszeldine (^{2}), reported that the addition of iodine chloride to trifluorochloroethylene gives a single addition product, namely 1,2-dichloroiodotrifluoroethane. The authors ascribe an ionic character to the reaction; the more negatively polarized chlorine atom of iodine chloride adds to the positively polarized carbon atom of trifluorochloroethylene

$$\overset{\delta+}{\mathrm{C}}\mathrm{F_2{=}CFCl} + \overset{\delta-}{\mathrm{J}}\mathrm{Cl} \rightarrow \mathrm{CF_2Cl{-}CFClJ}.$$

Such an interpretation was in agreement with the order of addition of nucleophilic agents to unsymmetrically substituted fluoro- and fluorochloro-olefins.

As a result of the reaction of trifluorochloroethylene with iodine chloride under the conditions described for this reaction by Haszeldine, an addition product is formed whose narrow boiling range (53°/150 mm) led Haszeldine to the erroneous conclusion that it was an individual substance. Earlier, Bigot (^{3}) observed the formation of two isomers in the addition of iodine chloride to allyl alcohol.

As we have established, the product of addition of iodine chloride to chlorotrifluoroethylene is also a mixture of two isomers—1,2-dichloroiodotrifluoroethane ($CF_2ClCFClJ$) and 1,1-dichloro-2-iodotrifluoroethane ($CFCl_2CF_2J$)—in an approximate ratio of $4:1$.

When oleum acts on this addition product, a mixture of the fluoroanhydrides of difluorochloroacetic acid (CF_2ClCOF) and dichlorofluoroacetic acid ($CFCl_2COF$), iodine, iodine chloride, sulfur dioxide, and 1,1,2-trichlorotrifluoroethane (Freon 113) is formed.

The reaction with SO_3 is radical in character

$$\mathrm{CF_2ClCFClJ} \rightarrow \mathrm{CF_2Cl\dot{C}FCl} + \mathrm{J}^\bullet$$

$$\mathrm{CFCl_2CF_2J} \rightarrow \mathrm{CFCl_2\dot{C}F_2} + \mathrm{J}^\bullet$$

$$2J^{\bullet} \rightarrow J_2$$

$$CF_2Cl\dot{C}FCl + SO_3 \rightarrow CF_2ClCFClOS\dot{O}_2 \rightarrow CF_2ClCFCl\dot{O} + SO_2$$

$$CF_2ClCFClO^{\bullet} \rightarrow CF_2ClCOF + Cl^{\bullet}$$

$$Cl^{\bullet} + CF_2ClCFClJ \rightarrow CF_2ClCFCl^{\bullet} + ClJ$$

$$CF_2Cl\dot{C}FCl \begin{array}{l} \nearrow \ CF_2ClCFClOS^{\bullet}O_2 \\ \searrow \ CF_2ClCFCl_2 \end{array}$$

Similarly, 1,1-dichloro-2-iodotrifluoroethane, under the action of oleum, is converted into the fluoroanhydride of dichlorofluoroacetic acid, while the radical $CFCl_2\dot{C}F_2$ formed in the reaction with the radical F gives 1,1-dichlorotetrafluoroethane. The formation of two fluoroanhydrides under the action of oleum can be explained only by the presence of two isomeric addition products, $CF_2ClCFClJ$ and $CFCl_2CF_2J$. The fluoroanhydrides formed, on interaction with alcohol, give a mixture of esters of difluorochloro- and dichlorofluoroacetic acids that is readily separable by distillation.

The product of addition of iodine chloride to trifluorochloroethylene was previously used by us in the telomerization reaction with tetrafluoroethylene ([4]); it has now been established that dichloroiodotrifluoroethane distilled off from the telomerization products proves to be enriched in 1,1-dichloro-2-iodotrifluoroethane. This follows from the fact that, under the action of oleum on dichloroiodotrifluoroethane recovered from the telomerization reaction, a mixture of the fluoroanhydrides of difluorochloroacetic and dichlorofluoroacetic acids is formed, containing considerably more fluoroanhydride of dichlorofluoroacetic acid than upon treatment with oleum of a mixture of isomeric dichloroiodotrifluoroethanes that had not been used in the telomerization reaction.

This fact of enrichment in one of the isomers cannot be explained by rearrangement of the radical $CF_2Cl\dot{C}FCl$ into the radical $CFCl_2\dot{C}F$ under the conditions of the telomerization reaction, since specially designed experiments show that the ratio of isomers does not change either upon heating the product of addition of iodine chloride to trifluorochloroethylene with benzoyl peroxide under the conditions of the telomerization reaction or upon its prolonged storage (3 months). Evidently, 1,2-dichloroiodotrifluoroethane is more readily radicalized and enters into the telomerization reaction, as a result of which the dichloroiodotrifluoroethane recovered from the telomerization reaction contains more of the second, more difficultly radicalized isomer, 1,1-dichloro-2-iodotrifluoroethane.

On the basis of these facts it is not excluded that the addition of iodine chloride, and possibly of many other electrophilic reagents, to chlorotrifluoroethylene proceeds by a radical mechanism rather than by an ionic one, as postulated by Haszeldine,

$$\mathrm{JCl} \rightarrow \dot{\mathrm{Cl}} + \mathrm{J}$$

$$\mathrm{CF_2{=}CFCl} + \dot{\mathrm{Cl}} \left\{ \begin{array}{l} \longrightarrow \mathrm{CF_2Cl\dot{C}FCl} \xrightarrow{\mathrm{JCl}} \mathrm{CF_2ClCFClJ} + \dot{\mathrm{Cl}} \\ \longrightarrow \mathrm{CFCl_2\dot{C}F_2} \xrightarrow{\mathrm{JCl}} \mathrm{CFCl_2CF_2J} + \dot{\mathrm{Cl}} \end{array} \right.$$

The formation of freons also confirms the radical mechanism of the reaction and is a consequence of the recombination of the radicals $\mathrm{CF_2Cl\dot{C}FCl}$ and $\mathrm{CFCl_2\dot{C}F_2}$ with a chlorine or fluorine radical

$$\begin{array}{l} \mathrm{CF_2Cl\dot{C}FCl} \\ \mathrm{CFCl_2\dot{C}F_2} \end{array} \xrightarrow{\mathrm{Cl}} \mathrm{CF_2Cl{-}CFCl_2}$$

Experimental Part

Addition of iodine chloride to chlorotrifluoroethylene. In a steel ampoule of 250 ml capacity were placed 136 g (0.84 mole) of iodine chloride; the ampoule was cooled, 81 g (0.7 mole) of chlorotrifluoroethylene was added, and the ampoule was shaken on a rocking apparatus at 40° for 4 hours. The reaction product was fractionated on a column, efficiency 17 theoretical plates. Obtained were 23 g of 1,1,2-trichlorotrifluoroethane, b.p. 47°, and 153 g of iododichlorotrifluoroethane, b.p. 53°/150 mm, n_D^{20} 1.4490, yield 81.5%.

Action of oleum on iododichlorotrifluoroethane. Into a three-necked flask equipped with a stirrer, dropping funnel, and ob-

a reflux condenser connected by a gas outlet tube to two Drechsel bottles connected in series, 230 ml of 15% oleum was placed. At a bath temperature of 100–102° and with stirring, 223 g (0.8 mole) of a freshly distilled mixture of isomers of iodine chlorotrifluoroethane (b.p. 53°/150 mm) was gradually added.

The gaseous reaction products were absorbed with absolute alcohol in Drechsel bottles cooled with ice.

After completion of the reaction, the dark liquid, which proved to be iodine chloride, was distilled off from the reaction flask. On cooling, iodine crystallized in the flask. The alcoholic solution containing the gaseous reaction products was distilled with a good fractionating column; sulfur dioxide condensed in the trap. The alcoholic distillate was poured into ice water; the separated layer was washed with water, sodium bicarbonate solution, and again with water, dried over magnesium sulfate, and distilled on a column of 30 theoretical plates. The following fractions were obtained: 1) b.p. 47-48°, n_D^{20} 1.3590, Freon 113; 2) b.p. 95-96°—ethyl difluorochloroacetate with an admixture of unreacted iodine chlorotrifluoroethane; 3) b.p. 131°, n_D^{20} 1.4040, d_4^{20} 1.321—ethyl dichlorofluoroacetate. *MR* found 32.40; calculated for $C_4H_5FCl_2O_2$, 31.89.

$$\begin{array}{lll} C_4H_5FCl_2O_2. & \text{Found \%:} & \text{C } 27.52;\ \text{H } 3.15 \\ & \text{Calculated \%:} & \text{C } 27.43;\ \text{H } 2.86 \end{array}$$

Fraction 2, in order to separate it from the admixture of unreacted dichloroiodotrifluoroethane, was heated for 6 hr with zinc dust at 60-70° and distilled on a column: b.p. 96°, n_D^{20} 1.3572, d_4^{20} 1.253, *MR* found 27.06, calculated for $C_4H_5F_2ClO_2$ 26.88.

$$\begin{array}{lll} C_4H_5F_2ClO_2. & \text{Found \%:} & \text{C } 30.42;\ \text{H } 3.37 \\ & \text{Calculated \%:} & \text{C } 30.28;\ \text{H } 3.16 \end{array}$$

The yields of the reaction products are given in Table 1, based on 223 g (0.8 mole) of iodine chlorotrifluoroethane.

Table 1

Iodine chlorotrifluoroethane, 223 g (0.8 mole)	$CFCl_2-CF_2Cl$, g	$CFCl_2-CF_2Cl$, %	$CF_2ClCOOC_2H_5$, g	$CF_2ClCOOC_2H_5$, %	$CFCl_2COOC_2H_5$, g	$CFCl_2COOC_2H_5$, %
Freshly prepared	5.5	4	66	52	18	13
Kept for 3 months at room temperature	16.2	11	65	51	20	14

Iodine chlorotrifluoroethane, 223 g (0.8 mole)	$CFCl_2{-}CF_2Cl$, g	$CFCl_2{-}CF_2Cl$, %	$CF_2ClCOOC_2H_5$, g	$CF_2ClCOOC_2H_5$, %	$CFCl_2COOC_2H_5$, g	$CFCl_2COOC_2H_5$, %
Heated for 4 hr at 110° in the presence of 1% benzoyl peroxide	10.2	7	64	50	16	11
Returned from the telomerization reaction with tetrafluoroethylene	12.5	8	39	30	44	31

The starting iodine chlorotrifluoroethane was distilled before the reaction on a column of 17 theoretical plates, b.p. 53°/150 mm, n_D^{20} 1.4492.

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CITED LITERATURE

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Note: Figure translations are in progress. See original paper for figures.