12. *The Heterolytic Fission of the Carbon–Iodine Bond in Trifluoroiodomethane.*

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Trifluoroiodomethane reacts with potassium hydroxide, alone or in solution in solvents of high dielectric constant, to give fluoroform, iodine being replaced by a positive iodine mechanism. Nucleophilic substitution of the iodine by OH, NH_2, CN, and NO_2 has so far proved impossible. The exchange reaction between iodide and trifluoroiodomethane in alcoholic solution at 20° has been studied by using radioactive iodide as a tracer. The reaction is of first order with respect to the trifluoroiodomethane and of zero order with respect to the iodide. The rate-determining step at low temperatures is believed to be the heterolysis of the carbon–iodine bond to give a trifluoromethyl anion and an iodine cation.

It is known that the carbon–iodine bond in trifluoroiodomethane can undergo homolytic fission to give the free perfluoroalkyl radical, CF_3, which can yield organometallic derivatives (Emeléus and Haszeldine, *J.*, 1949, 2948, 2953) and also initiate the polymerisation of olefins (Haszeldine, *J.*, 1949, 2856; *Nature*, 1950, **165**, 152). It has also been found that the iodine in trifluoroiodomethane acts in the presence of solvents of high dielectric constant and strong ionic reagents as if it were positive, and treatment with potassium hydroxide yields fluoroform:

$$\overset{\delta-}{CF_3}\text{–}\overset{\delta+}{I} + KOH \longrightarrow CHF_3 + KOI$$

The reaction of potassium hydroxide is slow in ethereal solution, but, as might be expected, increase in the dielectric constant of the solvent increases the rate. Thus, a rapid and complete destruction of the fluoroiodide is observed in alcohol or acetone at room temperature and fluoroform may be isolated in high yield. The reaction possibly proceeds by attack of a hydroxyl ion on the fluoroiodide, followed either by reaction of the CF_3^- ion with the solvent or with water, or by the decomposition by water of CF_3K formed as intermediate:

$$OH^- + I\text{–}CF_3 \longrightarrow CF_3^- + HOI \xrightarrow{KOH} KOI + H_2O$$

A polymolecular reaction is also possible. If the interpretation of the results of radio-chemical experiments (see below) is correct, however, then CF_3^- ions do not react with alcohol at moderate temperatures. The hypoiodite formed is largely destroyed by reaction with the solvent, and potassium iodide is the main inorganic reaction product. When, however, the fluoroiodide is treated with potassium hydroxide in the absence of a solvent and under conditions such that homolytic fission of the carbon–iodine bond does not occur, potassium iodate and iodide can be detected. Pentafluoroiodoethane (Emeléus and Haszeldine, *loc. cit.*) undergoes analogous reactions with potassium hydroxide and yields pentafluoroethane. Both the fluoroiodides are stable to dilute aqueous alkali at room temperature. Preliminary results have shown that fluoroform is also produced by the slow reaction of trifluoroiodomethane with sodamide in liquid ammonia.

The interaction of trifluoroiodomethane and several of the reagents which will effect nucleophilic substitution of normal alkyl halides—moist silver oxide, potassium phthalimide, metallic cyanides and nitrites—was examined. In no case was the product analogous to that given by methyl iodide in the same circumstances. The fluoroiodide was resistant to attack by the reagents at lower temperatures, whilst increase in temperature brought about decomposition to ionic fluorine and iodine.

Trifluoroiodomethane (b. p. $-22{\cdot}5°$) and pentafluoroidoethane (b. p. 13°) have a conductivity in the pure state of less than 4×10^{-9} ohm^{-1} at $-45°$ and 0°, respectively. Furthermore, on the macro-scale, there is no formation of free iodine when these fluoroiodides are treated with potassium iodide solution, as is the case with inorganic and organic positive iodine compounds. The liquid fluoroiodides are not appreciably ionised, but the existence of ions in alcoholic solution may be deduced from a study of the exchange reaction in this solvent between trifluoroiodomethane and sodium iodide containing radioactive iodine ($CF_3I + Na^{131}I \longrightarrow CF_3{}^{131}I + NaI$). This proves to be a slow reaction at 20°. The rate is independent of the sodium iodide concentration and proportional to the first power of the trifluoroiodomethane concentration, the first-order velocity coefficient being $2{\cdot}6 \times 10^{-8}$ sec.$^{-1}$. The reaction may proceed by the unimolecular ionic mechanism (1), followed by an electron transfer presumably involving I_2 or $I_3{}^-$ (2), and recombination (3).

$$CF_3I \rightleftharpoons CF_3{}^- + I^+ \qquad (1)$$

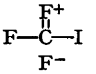
$$I^+ + (^{131}I)^- \rightleftharpoons I_2 \rightleftharpoons I^- + (^{131}I)^+ \qquad (2)$$

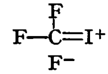
$$CF_3{}^- + (^{131}I)^+ \rightleftharpoons CF_3{}^{131}I \qquad (3)$$

When the reaction mixture is shaken with mercury at 20°, the rate of exchange is reduced by one-third, whilst the kinetic order is unaffected. This is probably due to the removal by mercury of the molecular iodine postulated as an intermediate in (2). A much faster first-order reaction occurs at temperatures above 80° and involves homolytic fission of the carbon–iodine bond. Preliminary studies on the variation of the rate constant with temperature ($-66°$ to 105°) have shown that below 60° the energy of activation is small, as for an ionic reaction, whilst the reaction above 80° has a much higher activation energy.

The work of Brockway (*J. Physical Chem.*, 1937, **41**, 185, 747) indicated a shortening of the carbon–fluorine and carbon–chlorine bond lengths to 1·36 (±0·02) and 1·73 (±0·02) A. in molecules such as CF_3Cl, CF_2Cl_2, and CHF_2Cl, where two or more fluorine atoms are attached to one carbon atom. This shortening implies a stronger bond between carbon and fluorine and carbon and chlorine, and this is in agreement with the chemical properties of these compounds. Apart from decomposition, they do not show reactions involving the homolytic or heterolytic fission of the carbon–chlorine bond.

It might be expected that the more polarisable the halogen attached to a trifluoromethyl group the more readily would double-bond formation be possible, so that the contribution of canonical forms involving $C{=}X^+$ to the resonance hybrid would decrease in the order $I > Br > Cl > F$. In the case of trifluoroiodomethane the canonical forms (*A*), and particularly (*B*), would therefore contribute appreciably to resonance and shortened and strengthened carbon–fluorine and carbon–iodine bonds would be found.


(*A*.)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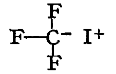
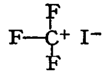

(*C*.)


(*D*.)

Coles and Hughes (*Physical Rev.*, 1949, **76**, 858) report carbon–fluorine and carbon–chlorine bond lengths of 1·32(3) and 1·76(5) A. in CF_3Cl, and these values suggest that it is only the carbon–fluorine bond which is shortened appreciably [cf. methyl fluoride, C–F 1·42 (Brockway, *loc. cit.*), C–F 1·38(4) (Gordy, Simmons, and Smith, *Physical Rev.*, 1948, **74**, 243); methyl chloride, C–Cl 1·77 (Schomaker, quoted by Allen and Sutton, *Acta Cryst.*, 1950, **3**, 46)]. A similar situation is revealed by recent microwave spectroscopic studies on CF_3Br which lead to carbon–fluorine and carbon–bromine bond lengths of 1·32(6) and 1·93(3) A. (Sheridan and Gordy, *Physical Rev.*, 1950, **77**, 292) and 1·32(1) and 1·93(6) A. (Sharbaugh, Pritchard, and Madison, *ibid.*, p. 302) [cf. C–Br in CH_3Br, 1·93(6) (Simmons, Gordy, and Smith, *ibid.*, 1948, **74**, 1246)], and by studies on CF_3I which give a carbon–iodine bond length of 2·16(2), a carbon–fluorine bond length of 1·32(6) being assumed (Sheridan and Gordy, *loc. cit.*) [cf. C–I in CH_3I 2·13(2) (Simmons, Gordy, and Smith, *loc. cit.*)]. It is, therefore, evident that the contribution of canonical forms involving $C{=}X^+$ decreased in the order $F > Cl > Br > I$ (cf. Pauling, " Nature of the Chemical Bond," p. 236).

This is in accord with the reactions of trifluoroiodomethane. The apparent absence of reactions which involve the nucleophilic replacement of iodine in trifluoroiodomethane does not necessarily mean that the carbon–iodine bond is shorter or stronger, since it can be accounted for by a reversed polarity (C^-I^+) of the carbon–iodine bond, with appreciable contribution to resonance of form (*C*) of a type unimportant in the alkyl halides, and only a slight contribution of form (*D*). The thermal stability of trifluoroiodomethane does not indicate a strong carbon–iodine bond, since the recombination of the trifluoromethyl radical and iodine atom takes place easily; trifluoroiodomethane is known to give a trifluoromethyl radical whereas chlorotrifluoromethane is not.

EXPERIMENTAL.

Conductivity of Liquid Trifluoroiodomethane and Pentafluoroiodoethane.—The conductivities of the fluoroiodides were measured in a cell of 6-ml. capacity with platinum electrodes 15 mm. in diameter and 1 mm. apart, a cathode-ray oscilloscope being used as null-point detector (Haszeldine and Woolf, *Chem. and Ind.*, 1950, **27**, 544). Trifluoroiodomethane at −45·2° and pentafluoroiodoethane at 0° had specific conductivities of $<4 \times 10^{-9}$ ohm^{-1}.

Reaction of Trifluoroiodomethane and Pentafluoroiodoethane with Alkali.—The reactions described below were carried out in the dark in sealed Pyrex tubes. Fluoroform and pentafluoroethane were identified by molecular-weight and vapour-pressure determinations. (i) No reaction was detected when trifluoroiodomethane was shaken with aqueous sodium hydroxide for 2—3 days. (ii) Trifluoroiodomethane (4·6 g.), potassium hydroxide (5·0 g.), and absolute ethyl alcohol (15 ml.) were shaken for 1 hour and gave an 80% yield of fluoroform. No unchanged fluoroiodide was detected: the alcoholic solution contained potassium iodide but no oxidising agent. With similar quantities, conversion into fluoroform was quantitative at 100°. (iii) Trifluoroiodomethane did not react with ethyl alcohol at room temperature, but when 1·5 g. were heated for 48 hours at 150° with 10 ml. of ethyl alcohol a 19% conversion into fluoroform was obtained. (iv) Pentafluoroiodoethane (1·5 g.), heated with potassium hydroxide (2·0 g.) in ethyl alcohol (25 ml.) for 12 hours at 140°, gave a 74% yield of pentafluoroethane.

Reaction with Potassium Hydroxide in Acetone and Ether.—Potassium hydroxide (3·5 g.) was shaken with trifluoroiodomethane (3·0 g.) and dry acetone (10 ml.) at room temperature. The solution turned brown within a few minutes, and after 0·5 hour all the fluoroiodide had been destroyed and 70% of the theoretical amount of fluoroform had been produced.

Trifluoroiodomethane (3·0 g.), potassium hydroxide (3·0 g.), and dry ether (20 ml.) reacted slowly at room temperature and after 5 days a 30% yield of fluoroform was obtained. When the contents of the reaction tube were acidified, iodine was liberated, and potassium iodate was identified in a repeat experiment.

Reaction with Potassium Hydroxide in the Absence of a Solvent.—Potassium hydroxide pellets (3·0 g.) were crushed and heated in vacuum to remove volatile matter. Trifluoroiodomethane (3·0 g.) was then added, and the reaction tube sealed. After being shaken in the dark at room temperature for 48 hours, the contents of several such tubes were examined: 96% of the fluoroiodide was unchanged and 1% of the theoretical yield of fluoroform was isolated; 60% of the theoretical amount of potassium iodate was present. Repeat experiments gave a 9% yield of fluoroform and an 88% recovery of the fluoroiodide after 15 days' shaking. Potassium iodate was detected qualitatively in the product. The rate of reaction was increased by raising the temperature; for instance, after 30 hours at 90° a mixture of potassium hydroxide (3·0 g.) and trifluoroiodomethane (3·0 g.) gave 7% of the theoretical amount of fluoroform and an 88% recovery of fluoroiodomethane. A radical reaction may be involved in the reactions of 90°. Pentafluoroiodoethane (1·5 g.), shaken with powdered potassium hydroxide in the dark at room temperature for 7 days, gave a 7% yield of pentafluoroethane and an 87% recovery of fluoroiodide.

Attempted Double-decomposition Reactions.—The reaction of trifluoroiodomethane (1·4 g.), potassium cyanide (3·0 g.), and ethyl alcohol (10 ml.) at 160° gave a 61% yield of fluoroform. No trifluoroacetonitrile was isolated. Similar results were obtained with silver cyanide, toluene being used as solvent, and the amount of fluoroform isolated increased as the temperature was raised. Cuprous and mercuric cyanides in absence of a solvent brought about the decomposition of trifluoroiodomethane at elevated temperatures.

With potassium phthalimide (4·5 g.), trifluoroiodomethane (1·5 g.), and toluene (8 ml.) there was little reaction in 12 hours at 180°, and at 220°, although extensive decomposition occurred, no *N*-trifluoromethylphthalimide or primary fluoroamine could be isolated. When trifluoroiodomethane, (2·0 g.) was heated with silver nitrite (3·0 g.) in ether (6 ml.) at 80° the fluoroiodide was unattacked. Reaction occurred at 150° and 200° and some fluoroform was formed by reaction with the ether, but fractionation of the volatile products gave no indication of a compound such as trifluoronitromethane, containing fluorine and nitrogen. In similar experiments, reaction with sodium and potassium methoxides failed fo give a fluoro-ether, and with moist silver oxide no trifluoromethano was obtained.

Exchange Studies, with Radioactive Iodide as a Tracer.—Trifluoroiodomethane is insoluble in water but dissolves readily in absolute ethyl alcohol, in which sodium iodide is also soluble. Radioactive sodium iodide, $Na^{131}I$ (activity 10 μc.), was added to 150 mg. of anhydrous sodium iodide dissolved in ethyl alcohol, and the solution made up to 25 ml. Activities, measured with standard β-counting apparatus, were corrected to zero time in all of the measurements recorded below. A quantity of the sodium iodide solution containing the tracer (referred to as $Na^{131}I$ solution), containing about 30 mg. of sodium iodide in 5 ml. of ethyl alcohol, was sealed with about 40 mg. of trifluoroiodomethane in an 8-ml. Carius tube. Roughly equimolecular proportions of sodium iodide (concentration *b* moles/l.) and trifluoroiodomethane (concentration *a* moles/l.) were then present. The gas-space was kept small so that the greater part of the fluoroiodide was in solution. The tubes were stored in the dark to prevent photolysis of the fluoroiodide, and, in the experiments in which mercury was added, were shaken vigorously in a vibro-shaker.

After reaction, the trifluoroiodomethane was removed, glass-wool plugs being used to filter the gas and prevent $Na^{131}I$ being carried into the vacuum system as spray. The fluoroiodide and ethyl alcohol (*ca.* 1 ml.), which was simultaneously transferred, were heated in a Carius tube at 100° for 12 hours with alcoholic sodium hydroxide to transform the iodine in the fluoroiodide into sodium iodide. The hydrolysate was neutralised with dilute nitric acid, made slightly alkaline with sodium hydrogen carbonate, and evaporated to dryness. The residue was taken up in 1 ml. of water, centrifuged to remove insoluble matter, and the solution made up to 5 ml. A 0·5-ml. aliquot was acidified with dilute nitric acid and treated with silver nitrate. After coagulation, the silver iodide was centrifuged, washed, and transferred as a slurry to a platinum tray. The water was evaporated and the activity measured. The precipitate was also weighed as a check and losses of 3—8% were found to occur. The β-count was corrected to the theoretical weight of material, based on the weight of trifluoroiodomethane taken. Loss of fluoroiodide as fluoroform was negligible. Standard counting corrections were used throughout.

The reaction may be represented by the equation :

$$\begin{array}{ccccccc} CF_3I & + & Na^{131}I & \rightleftharpoons & CF_3{}^{131}I & + & NaI \\ (a-x) & & (b-x) & & (x) & & (x) \end{array}$$

The sodium iodide is considered to be uniformly of a low activity, rather than a mixture of active salt and carrier, since its specific activity was constant throughout the series of measurements. In calculating x, allowance was made for the fact that there is a 50% probability that interaction between $^{131}I^-$ and I^+ will produce $^{131}I^+$ and I^-. In all experiments x at the end of the reaction was less than 1% of a and b, and could be neglected in comparison with them. In determining rate coefficients the active mass of NaI, b', was used instead of the concentration b. The activity coefficients of sodium iodide in ethyl-alcoholic solution, derived from the data of Partington and Simpson (*Trans. Faraday Soc.*, 1930, **26**, 625) for the concentrations used (b = 0·02, 0·04, 0·08 mole/l.) are 0·64, 0·57, 0·50, respectively. The results shown in Table I (in which a, b, b', and x are in moles/l.) were obtained at 20°. The rate coefficient k_1 is given by x/at.

TABLE I.

Expt.	CF_3I (counts/min.).	a.	b.	b'.	10^6x.	t (hours).	$10^6dx/dt$.	10^8k_1.
1	828	0·047	0·040	0·0228	281	65	4·33	2·56
2	342	0·047	0·040	0·0228	116	25	4·63	2·74
3	621	0·047	0·040	0·0228	210	50	4·20	2·48
4	1080	0·047	0·040	0·0228	366	85	4·30	2·54
5	178	0·047	0·020	0·0128	603	13	4·64	2·74
6	1287	0·047	0·080	0·0400	436	103	4·23	2·50
7	1030	0·069	0·040	0·0228	348	49	7·11	2·89
8	1262	0·094	0·040	0·0228	427	50	8·54	2·53

Mean $k_1 = 2·62 \times 10^{-8}$.

TABLE II.

Expt.	CF_3I (counts/min.).	a.	b.	b'.	10^6x.	t (hours).	$10^6dx/dt$.	10^8k_1.
9	469	0·047	0·040	0·0228	159	61	2·61	1·54
10	731	0·047	0·040	0·0228	247	85	2·91	1·72
11	835	0·047	0·040	0·0228	283	110	2·58	1·52
12	336	0·047	0·020	0·0128	114	40	2·85	1·69
13	823	0·047	0·081	0·0400	279	100	2·79	1·65
14	1160	0·075	0·040	0·0228	393	83	4·74	1·76
15	1130	0·094	0·040	0·0228	383	65	5·90	1·74
16	1435	0·141	0·040	0·0228	486	61	7·96	1·57

Mean $k_1 = 1·65 \times 10^{-8}$.

In Expts. 1—4, a and b' were constant and t was varied; the plot of x against t is linear (Fig. 1, *A*; the circles show $\pm 5\%$ experimental error). The amount of change x was small, and x/t therefore measured the intial rate and was constant. In Expts. 5—8 the concentrations of CF_3I and $Na^{131}I$ were varied, for, as McKay has pointed out (*Nature*, 1938, **142**, 997), it is impossible to determine the order of an isotopic reaction from a single concentration–time curve, since the concentration remains constant throughout the reaction which then appears to be of first order even if it is in fact bimolecular in mechanism. A plot of log x/t against log b', a being constant in Expts. 1—6, gives a line of nearly zero slope (Fig. 2, *A*). The plot of log x/t against log a, derived from the data of Expts. 1—8, is a line of unit slope, showing the reaction to be of first order with respect to trifluoroiodomethane and independent of the sodium iodide concentration.

The results shown in Table II are for experiments in which the reactants were shaken at 20° with 1 ml. of mercury.

Expts. 9, 10, and 11 have the same constant values of a and b' as in Expts. 1—4, and these values of x and t are plotted in Fig. 1, *B*. The quantity x/t is again constant, but lower than in Expts. 1—4. Expts. 12 and 13 (b' varied, with constant a) and Expts. 9, 10, and 11, which are plotted in Fig. 2, *B*, show the reaction to be of zero order with respect to sodium iodide. Expts. 14, 15, and 16 (a varied, with constant b') and Expts. 9—13 may be used to plot log x/t against log a and yield a line of unit slope, which shows the reaction in presence of mercury to be also of first order with respect to CF_3I. The values of the first-order velocity constant k_1 are included in Tables I and II. Variations in b' do not affect the initial rate. Expts. 5 and 6, and 12 and 13, where a is constant, are plotted on Figs. 1, *A* and 1, *B*.

FIG. 1.

Initial rates.

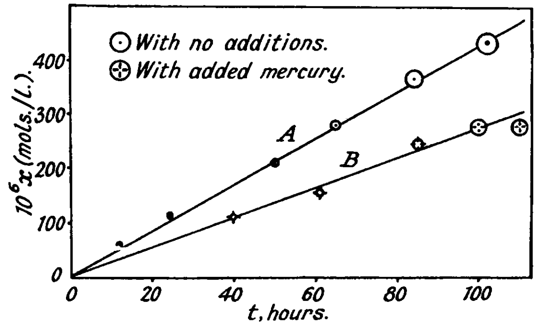
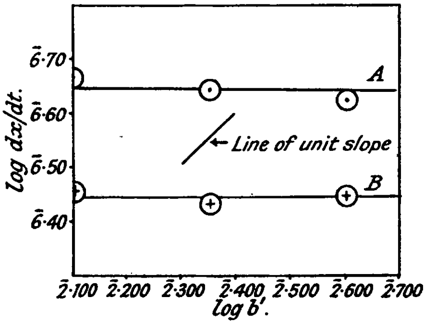


FIG. 2.



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