and melted at 135–136°. Azoxybenzene (Eimer and Amend) was recrystallized from methanol and melted at 36°, lit.[14] m.p. 36°. Spectro Grade cyclohexane and absolute alcohol were used as solvents in the kinetic measurements.

aci-Nitro–Nitro Tautomerism.—Rate studies at low temperatures in the range −106.4 to −64.8° were carried out in a 2.5-cm. cell maintained at the required temperature in a specially constructed cryostat.[15] Ethanol solutions (10^{-3} M) cooled in the cryostat were exposed for 30 sec. to the unfiltered radiation from a General Electric H3FE 85-watt mercury lamp with a Pyrex glass envelope. Uniform coloring of the solutions was observed. The cryostat was quickly transferred to the sample cell compartment of a Cary Model 14 spectrophotometer, and the decrease in absorbance of the visible absorption band at 610 mμ was followed with respect to time. A matched cell containing pure solvent was in the reference beam.[15] In all cases, the absorbance of the system ultimately fell to zero. In order to obtain all the kinetic data reported in this paper, at least three runs were made at each temperature.

Room temperature measurements were carried out by flash photolysis techniques previously described.[4]

Geometrical Isomerization.—Rate measurements in the temperature range 11 to 50° were carried out in a 2.5-cm. cell on solutions ($\sim 10^{-5}$ M) in ethanol and cyclohexane. Required temperatures were maintained by circulating water from a Haake temperature-regulating bath through a thermostatable cell jacket.[16] Solutions were exposed for 30 sec. to the radiation from the lamp described above, and the cell was quickly transferred to the sample compartment of the spectrophotometer. For both compound I and azoxybenzene, the increase in absorbance of the ultraviolet absorption band at 330 mμ was followed with respect to time. A matched cell containing pure solvent was in the reference beam. In all cases, the absorbance at 330 mμ ultimately returned to its value before irradiation.

Temperature Measurement.—Measurements of temperatures were made by a glass encased copper-constantan thermocouple which dipped into the solutions at the cell neck.

Calculations.—Values of the first-order specific rate constant, k, were calculated from the slope of the straight line obtained in plots of log $D_t - D_\infty$ *vs.* time, where D_t is the optical density at a given time interval and D_∞ is the optical density after complete isomerization. In the case of the *aci*-nitro–nitro isomerization, D_∞ was equal to zero. The reactions were followed for at least three half-lives. Illustrative plots are given in Fig. 3. The Arrhenius activation energy, E_{exp}, the entropy of activation, ΔS^*, and the frequency factor, A, were calculated by procedures given previously.[4,6]

Ultraviolet and Visible Absorption Measurements.—A Cary Model 14 spectrophotometer was used. Solutions were measured in a 2.5-cm. cell against a reference of pure solvent in a matched cell.

Acknowledgment.—We wish to thank Dr. G. Wettermark for the flash photolysis experiments.

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[14] G. M. Badger, R. G. Buttery, and G. E. Lewis, *J. Chem. Soc.*, 2143 (1953).

[15] J. A. Sousa and J. Weinstein, *Rev. Sci. Instr.*, **34**, 150 (1963).

[16] W. R. Brode, J. H. Gould, and G. M. Wyman, *J. Am. Chem. Soc.*, **75**, 1856 (1953).

Thermal Reactions of Trifluoroiodomethane with Halobenzenes

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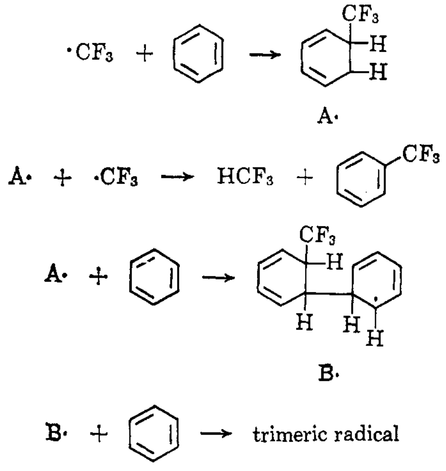
Received November 26, 1963

Trifluoroiodomethane reacts with chloro-, bromo-, and iodobenzene at 198° yielding the *o*-, *m*-, and *p*-halobenzotrifluorides, fluoroform, and molecular iodine. A mechanism involving addition of trifluoroiodomethane to the aromatic ring in a free-radical chain reaction followed by elimination of hydrogen iodide which reacts with trifluoroiodomethane to form fluoroform and iodine is proposed for these reactions.

Previous work by others has shown that trifluoromethyl radicals add readily to various aromatic systems. The gas phase reactions of benzene with trifluoromethyl radicals produced by the photolysis of hexafluoroacetone are reported to yield fluoroform, benzotrifluoride, and polymeric oils.[2] The formation of fluoroform and benzotrifluoride was observed to occur at low benzene pressures (less than 10 mm.), but no fluoroform was noted at higher benzene pressures (greater than 40 mm.). The following mechanism which is consistent with these observations is proposed (eq. 1–5).

$$CF_3COCF_3 \xrightarrow{h\nu} 2{\cdot}CF_3 + CO \qquad (1)$$



(2)

(3)

(4)

(5)

The cyclohexadienyl radical A· apparently is formed readily as shown in reaction 2, and at higher benzene pressures essentially all of the trifluoromethyl radicals formed by the photolysis react with benzene in this manner. Apparently, only at lower pressures is the concentration of trifluoromethyl radicals great enough for reaction 3, which produces the fluoroform, to occur. Szwarc and his co-workers point out that, in the liquid phase, where the concentration of the aromatic compound is about 3000 times that at 40-mm. pressure, no fluoroform would be expected from a reaction of an adduct radical such as A· with trifluoromethyl radicals.[3] This assumption formed the basis of the method used by Szwarc and his co-workers for determining the relative reactivities of various unsaturates and aromatics toward reaction with trifluoro-

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[1] Taken from the thesis submitted by E. Bedard in partial fulfillment of the requirements for the M.S. degree from the University of Kansas, 1963.

[2] S. W. Charles and E. Whittle, *Trans. Faraday Soc.*, **56**, 794 (1960); S. W. Charles, J. T. Pearson, and E. Whittle, *ibid.*, **57**, 1356 (1961); J. L. Holmes and K. O. Kutsche, *ibid.*, **58**, 333 (1962).

[3] I. M. Whittemore, A. P. Stefani, and M. Szwarc, *J. Am. Chem. Soc.*, **84**, 3799 (1962).

TABLE I

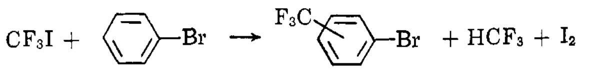
REACTIONS OF TRIFLUOROIODOMETHANE WITH HALOBENZENES AT 198°

Halobenzene (mmoles)	CF_3I, mmoles	Halobenzotrifluoride, mmole[a] *ortho*	*meta*	*para*	Isomer ratio *ortho–meta–para*	Yield, %[b]
Bromobenzene (94.4)	11.4	1.21	0.65	0.78	1.86:1.00:1.20	23
Bromobenzene (94.4)	10.7	1.31	0.63	0.82	2.1:1.00:1.30	26
Chlorobenzene (97.8)	3.84	0.96	0.44	0.53	2.17:1.00:1.20	50
Iodobenzene (88.1)	7.55	1.55	1.34	1.38	1.16:1.00:1.02	56

[a] Determined by infrared spectrometric analysis of the reaction mixtures. Experimental certainty of the values shown is of the order of about ±5% for each isomer. [b] Based on trifluoroiodomethane originally present.

methyl radicals generated in the liquid phase by the photolysis of hexafluoroazomethane.[3,4] Somewhat earlier, Haszeldine and Emeleus reported that a photochemical reaction occurred between benzene and trifluoroiodomethane, presumably in the liquid phase, in which fluoroform was a reaction product.[5] Dimeric and polymeric products were reported to be formed in these reactions as well.

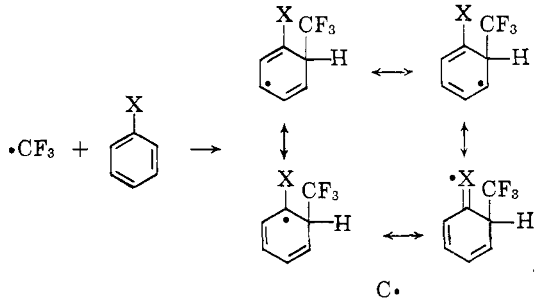
The present study is concerned with the reaction of the halobenzenes with trifluoroiodomethane. Attempts to induce a reaction between trifluoroiodomethane and bromobenzene at 40° by the use of light failed to yield any reaction products involving the aromatic halide (see Experimental). Similarly, benzoyl peroxide failed to induce any reaction between trifluoroiodomethane and bromobenzene. However, at 198°, a reaction between trifluoroiodomethane and bromobenzene did occur which produced a mixture of the *o*-, *m*-, and *p*-bromobenzotrifluorides, and molecular iodine and fluoroform. The halobenzotrifluorides were identified both by gas chromatography and infrared analysis of the reaction mixtures. Similar reactions occurred with chlorobenzene and iodobenzene. The quantitative determinations of the relative amounts of the isomeric halobenzotrifluorides formed in the thermal reactions of trifluoroiodomethane with bromo-, chloro- and iodobenzene shown in Table I were accomplished by infrared analysis.


(6)

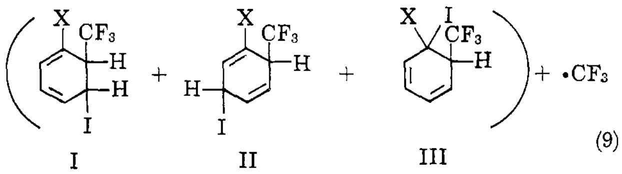
Fluoroform was identified as a reaction product by infrared analysis of the gaseous materials remaining at the end of the reactions. Although unchanged trifluoroiodomethane could be detected in the gaseous products, no hexafluoroethane was found. Distillation of the reaction mixtures left no higher boiling residues indicating the absence of polymeric material, and gas chromatographic analysis indicated the absence of any benzotrifluoride in the reaction mixtures.

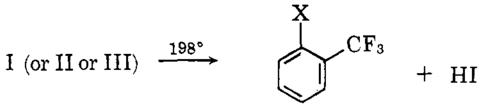
Any mechanism that might be suggested for these thermal reactions of trifluoroiodomethane with the halobenzenes in the liquid phase must account for the fact that no polymeric materials are formed and that fluoroform, a product not expected in a liquid phase reaction, is produced. The following mechanism (shown for formation of the *ortho* isomer) involving the thermally induced free-radical addition of trifluoroiodomethane to the aromatic compound satisfactorily accounts for these observations.

$$CF_3I \xrightarrow{198°} \cdot CF_3 + I\cdot \qquad (7)$$


(8)

C• + CF_3I →


(9)


(10)

$$HI + CF_3I \longrightarrow HCF_3 + I_2 \qquad (11)$$

The thermal decomposition of trifluoroiodomethane at elevated temperatures is evident from the observation that radical chain reactions involving this material can be induced thermally.[6] Reactions 8 and 9 comprise a radical chain sequence involving addition of trifluoroiodomethane to the halobenzene. The high reactivity of the trifluoroiodomethane toward radical attack could account for the fact that the cyclohexadienyl radical C· reacts exclusively with this reagent producing the addition product (or possibly products) rather than with another molecule of the aromatic compound leading to polymeric materials as in the case with the other sources of the trifluoromethyl radical cited previously. The loss of hydrogen iodide from the addition product (or products) as shown in eq. 10 at these elevated temperatures producing the aromatic nucleus and hydrogen iodide is not unexpected. If the addition product III is produced in the case of chloro- and bromobenzene, the elimination of hydrogen iodide is still more probable than the elimination of either of the other hydrogen halides. The reaction of the hydrogen iodide with trifluoroiodomethane then could produce the observed molecular iodine and fluoroform. This is not an unexpected

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(4) A. P. Stefani and M. Szwarc, *J. Am. Chem. Soc.*, **84**, 3661 (1962); A. P. Stefani, L. Herk, and M. Szwarc, *ibid.*, **83**, 4732 (1961).

(5) T. N. Haszeldine and H. J. Emeleus, *Research* (London), **1**, 715 (1948).

(6) R. N. Haszeldine, *J. Chem. Soc.*, 2856 (1949); 3037 (1950); 3761 (1953); J. Banus, H. J. Emeleus, and R. N. Haszeldine, *ibid.*, 3041 (1950); T. N. Bell, *ibid.*, 4973 (1961).

$$\overset{\delta-}{F_3C}\text{—}\overset{\delta+}{I}$$

reaction[7] in view of the positive character of the iodine in the highly polarizable trifluoroiodomethane.[8]

The orientation of the entering trifluoromethyl group is consistent with a mechanism involving the formation of a cyclohexadienyl-adduct radical in the same manner proposed for other free-radical aromatic substitution reactions.[9] Resonance contributions from the aromatically bonded halogen atom become important if the entering radical bonds at the positions *ortho* and *para* to the halogen atom. The reason more of the *ortho* isomer than the *para* isomer is formed is probably the statistical factor, namely that there are two *ortho* positions and only one *para* position. The apparent decrease in the reactivity of the *ortho* position in the case of iodobenzene may possibly be due to steric effects. Phenylation studies of the halobenzenes by Hey and his co-workers show a similar, although not so marked, decrease in the relative amount to the *ortho* isomer in the iodobenzene reactions compared to that of the other halobenzenes.[10]

Experimental

Materials.—The halobenzenes were obtained from Matheson Coleman and Bell and were redistilled before using. Trifluoroiodomethane (Research Chemicals Co.) was used without further purification. Authentic samples of the *o*-, *m*-, and *p*-bromo-, chloro-, and iodobenzotrifluorides used as standards for the infrared and gas chromatographic analyses were obtained from Pierce Chemical Co.

Attempted Photoinduced Reaction of Trifluoroiodomethane with Bromobenzene.—A reaction mixture consisting of 14.95 g. (0.095 mole) of bromobenzene and 4.45 g. (0.023 mole) of trifluoroiodomethane was illuminated in a sealed Pyrex tube at 40° for 2.5 hr. with a 275-watt sunlamp. The formation of molecular iodine was noted immediately. The gaseous materials were allowed to escape from the reaction mixture, the iodine was removed with a 10% sodium hydroxide solution, and the remaining material was distilled. Essentially all of the material distilled at 153° and proved to be unreacted bromobenzene. A qualitative test for fluoride ion in the sodium fusion mixture of the distillate performed by addition of cerous nitrate in acetic acid to the fusion mixture previously neutralized with acetic acid was negative.[11]

Attempted Benzoyl Peroxide-Induced Reactions of Bromobenzene with Trifluoroiodomethane.—A mixture of bromobenzene (18.7 g., 0.12 mole), trifluoroiodomethane (4.45 g., 0.011 mole), and benzoyl peroxide (0.10 g., 0.0004 mole) was heated in a sealed Pyrex tube at 80° for 19 hr. The reaction mixture was distilled and yielded a single fraction (17.9 g., b.p. 152–154°) which gave a negative test for fluorine.

Reaction of the Halobenzenes with Trifluoroiodomethane.—The halobenzenes and trifluoroiodomethane in the amounts shown in Table I were sealed in Pyrex tubes. The tubes were heated for a period of 72 hr. in a refluxing ethylene glycol vapor bath (198–200°). At the end of this period the reaction mixture assumed a deep purple color due to the free iodine produced. After cooling, the tubes were opened and any unchanged CF_3I and the fluoroform produced were allowed to escape (see below for identification of fluoroform). A weighed aliquot of the reaction mixture was diluted with carbon disulfide for infrared analysis. Infrared absorptions in the region 1400–1000 cm.$^{-1}$, absorptions not present in the parent halobenzene, were present and due to carbon–fluorine stretching.[12] Absorptions at 760.5, 790.5, and 833 cm.$^{-1}$ were assigned to the *ortho*, *meta*, and *para* halo-substituted benzotrifluorides, respectively. Quantitative determination of the isomers was made by comparison of the absorbance at these frequencies with those of several standard mixtures composed of authentic materials.

Gas chromatographic analysis of the bromobenzene reaction mixtures on a 16 ft. × 1/8 in. column packed with 10% dimenthyl sebacate (column temperature, 150°) showed four distinct peaks. These peaks corresponded exactly in retention time to the peaks of authentic samples of bromobenzene and the *o*-, *m*-, and *p*-bromotrifluorides. No peak corresponding in retention time with that of an authentic sample of benzotrifluoride was observed. Gas chromatographic analyses of the chlorobenzene reaction mixture gave only one broad peak on this column. No attempt was made to chromatograph the iodobenzene reaction mixture.

Attempts to separate the reaction mixture into its components by distillation were unsuccessful, largely because of the similarity of the boiling points of both the products and the starting material and to the small amounts of material involved.

Identification of Fluoroform.—The gaseous products from a reaction of chlorobenzene with trifluoroiodomethane at 198° were obtained by opening the tube after solidifying the reaction mixture in a liquid nitrogen bath and fitting the opened tube with a gas delivery tube leading to an evacuated trap immersed in liquid nitrogen. The contents of the reaction mixture tube were warmed to room temperature and the evolved gases were condensed in the liquid nitrogen trap. These gases were allowed to vaporize into an evacuated, 10-cm. infrared gas cell. The infrared spectrum of the gas showed absorptions at 3031, 1372, 1150, and 700 cm.$^{-1}$, the reported fundamental frequencies for fluoroform.[13] Absorption at 1183, 1076, and 746 cm.$^{-1}$, the fundamental frequencies reported for trifluoroiodomethane,[14] were also present. No absorptions at 1250, 1117, and 714 cm.$^{-1}$, fundamental frequencies reported for hexafluoroethane,[15] were observed.

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[7] Preliminary studies indicate that hydrogen iodide and trifluoroiodomethane react at room temperature to yield molecular iodine. No attempt was made to detect fluoroform. Hydrogen bromide and bromotrichloromethane, however, do react to produce molecular bromine and chloroform.

$$CCl_3Br + HBr \longrightarrow HCCl_3 + Br_2$$

[8] J. Banus, H. J. Emeleus, and R. N. Haszeldine, *J. Chem. Soc.*, 60 (1951).

[9] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 482–485.

[10] D. H. Hey and G. W. Williams, *Discussions Faraday Soc.*, **14**, 216 (1953).

[11] In a positive test for fluoride ion, cerous fluoride, a white precipitate which is insoluble in acetic acid, is formed [J. H. Simons and E. O. Ramler, *J. Am. Chem. Soc.*, **65**, 389 (1943)]. A positive test was obtained in the case of the thermal reactions of the halobenzenes with trifluoroiodomethane.

[12] R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p. 70.

[13] H. D. Rix, *J. Chem. Phys.*, **21**, 1077 (1953); E. K. Phyler and W. S. Benedict, *J. Res. Natl. Bur. Std.*, **47**, 202 (1951).

[14] S. R. Polo and M. K. Wilson, *J. Chem. Phys.*, **20**, 1183 (1952); P. R. McGee, F. F. Cleveland, A. G. Meister, C. E. Decher, and S. I. Miller, *ibid.*, **21**, 242 (1953).

[15] J. R. Neilson, C. M. Richards, and H. L. McMurry, *ibid.*, **16**, 67 (1948); D. G. Williams, W. B. Person, and B. Crawford, Jr., *ibid.*, **23**, 179 (1955).