Hach and Rundle[10] stated that it had not been determined experimentally whether polyiodine consists of chains with two different I–I distances, or whether all distances have become equal to 3.1 Å. From the V_0 value determined above, 1.9 e.v., it seems likely that polyiodine consists of chains with two I–I distances, due to unequal contributions of two limiting forms A and B.

$$\cdots \mathrm{I—I} \cdots\cdots \mathrm{I—I} \cdots\cdots \mathrm{I—I} \cdots \qquad (A)$$

$$\mathrm{—I} \cdots\cdots \mathrm{I—I} \cdots\cdots \mathrm{I—I} \cdots\cdots \mathrm{I—} \qquad (B)$$

TABLE I

No.	Concn. of KI, *M*	Concn. of EtOH, *M*	λ_{max}	*n* (chain length)
1	....	....	628	160
2	1.2×10^{-4}	....	625	134
3	6.1×10^{-4}	....	621	108
4	5.0×10^{-3}	....	613	77
5	3.0×10^{-2}	....	600	52
6	2.1×10^{-1}	....	572	30
7	5.0×10^{-1}	....	557	22
8	....	8.2×10^{-1}	594	45
9	....	1.6	588	40

Table I shows the values of λ_{max} observed and the corresponding chain lengths (n) which have been calculated with equation (1) and the V_0 value. Both the λ_{max} and the estimated chain length change in a regular fashion with the iodide concentration. Also, it appears that ethanol causes an effect similar to that of iodide.

Our data may not describe exactly the quantitative relation between the chain length and the λ_{max}, because the length of the polyiodine chain at zero iodide concentration is estimated. Nevertheless, our results indicated that Kuhn's theory is applicable to the polyiodine chain. They also account for the behavior of iodine in shifting the absorption spectrum of the complex.

Gilbert and Marriott[11] suggested that the amylose complex is composed mostly of groups of the type ($3I_2 \cdot 2I^-$), each probably a linear resonating group which develops the pure blue color in the complex. According to our model, it may be that iodide is chain terminating, even if it is in the resonating chain.

It is well known that the color of the complex disappears at higher temperature. The authors intend to investigate this phenomenon spectrophotometrically.

We are indebted to Mr. Tamotsu Fukuda of the Osaka Industrial Research Institute for the measurement of absorption spectra.

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[10] R. J. Hach and R. E. Rundle, THIS JOURNAL, **73**, 4321 (1951).

[11] G. A. Gilbert and J. V. Marriott, *Trans. Faraday Soc.*, **44**, 84 (1948).

LABORATORY OF BIO-PHYSICAL CHEMISTRY
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Removal of Halogen from Aromatic Nitrohalo Compounds

BY WALTER T. SMITH, JR., AND LOUIS CAMPANARO

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Earlier work has shown that the replacement of chlorine by hydrogen in aromatic compounds having a nitro group ortho to the chlorine can be accomplished by heating the compound with copper and benzoic acid.[1]

We wish to report a study of the application of this reaction to nitro compounds containing fluorine, bromine or iodine, and also the use of the reaction for the preparation of 3,5-dinitrotoluene.

In the earlier work it was found that a chlorine meta or para to a nitro group was not removed by the treatment with copper and benzoic acid. It has now been shown that a chlorine or bromine ortho to a nitro group can be removed without removal of a chlorine or bromine located meta to the same nitro group. Thus, the dehalogenation of 2,5-dichloro- and 2,5-dibromonitrobenzene leads to *m*-chloro- and *m*-bromonitrobenzene. The yields in these cases are 37–38%.

The monofluoronitrobenzenes did not dehalogenate under the conditions used. The *o*-, *m*- and *p*-isomers were all recovered without any formation of nitrobenzene.

The results observed with the monobromonitrobenzenes were comparable to those obtained with the chloronitrobenzenes. Only in the case of *o*-bromonitrobenzene did dehalogenation take place. While it might be expected that *p*-bromonitrobenzene might be sufficiently more reactive than the corresponding chlorine compound to permit dehalogenation, such was not the case. *p*-Bromonitrobenzene was recovered in 78% yield and there was no evidence that any nitrobenzene was formed.

The results with the iodonitrobenzenes are quite different than those obtained with the other halonitrobenzenes. As would be expected, the ortho isomer dehalogenated readily to give a 53% yield of nitrobenzene. It was not surprising to find that the presence of a nitro group para to the iodine was sufficient to activate the iodine, so that it was easily replaced by hydrogen upon treatment with copper and benzoic acid. The experiment with *m*-iodonitrobenzene indicates, however, that the location of the nitro group, and probably even its presence, is not an important factor in determining if iodine is replaced. The yield of nitrobenzene was 32% when *m*-iodonitrobenzene was used.

The dehalogenation of 2-chloro-3,5-dinitrotoluene provides a new synthesis of 3,5-dinitrotoluene. The presence of nitro groups located both ortho and para to the chlorine appears to enhance the ease of dehalogenation and 3,5-dinitrotoluene is obtained in 83% yield. This method of synthesis suffers from the low yield obtained in the preparation of the 2-chloro-3,5-dinitrotoluene. The usual "mixed acid" nitration of *o*-chlorotoluene was not successful, even at elevated temperatures. The use of concentrated sulfuric acid and sodium nitrate was also unsuccessful. By using a mixture of nitric, sulfuric and fuming nitric acids, *o*-chlorotoluene may be dinitrated to give a 9% yield of 2-chloro-3,5-dinitrotoluene.

Experimental

Dehalogenations.—The dehalogenations and attempted dehalogenations were carried out as illustrated below for *o*-fluoronitrobenzene. The results are summarized in Table I.

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[1] W. T. Smith, Jr., THIS JOURNAL, **71**, 2855 (1949).

TABLE I

DEHALOGENATION OF SOME HALONITROBENZENES

Halonitro-benzene	Starting material recovered, %	Dehalogenation product yield, %
o-Fluoro-	53	0
m-Fluoro-	65	0
p-Fluoro-	59	0
o-Bromo-	0	52[a]
m-Bromo-	70	0
p-Bromo-	78	0
o-Iodo-	0	53[a]
m-Iodo-	10	32[a]
p-Iodo-	22	32[a]
2,5-Dichloro-	0	37[b]
2,5-Dibromo-	0	38[c]

[a] Product is nitrobenzene. [b] Product is *m*-chloronitrobenzene. [c] Product is *m*-bromonitrobenzene.

***o*-Fluoronitrobenzene.**—To a molten mixture of 14 g. (0.11 mole) of benzoic acid and 5 g. (0.035 mole) of *o*-fluoronitrobenzene at 150–200° was added 10 g. of copper powder in several portions over a period of five minutes. Heating was stopped and the solidified mixture was taken up in 50 ml. of 20% sodium carbonate solution. The alkaline mixture was steam distilled until the distillate was clear. The distillate was extracted with ether and dried over barium oxide. The ether solution was filtered and evaporated. There was recovered 2.6 g. (53% recovery) of *o*-fluoronitrobenzene, m.p. −7 to −6°.

2-Chloro-3,5-dinitrotoluene.—In a 600-ml. beaker was placed 60 g. of fuming nitric acid (sp. gr. 1.59–1.60), 60 g. of concentrated nitric acid (sp. gr. 1.42) and 360 g. of concentrated sulfuric acid. To this solution was added 40 g. (0.318 mole) of *o*-chlorotoluene and the mixture was heated on the steam-bath for 3 hours. The solution was cooled, poured over ice, and extracted with a total of 500 ml. of ether. Evaporation of the ether gave a heavy yellow oil, which partly crystallized on standing in the ice-box for several days. The light yellow crystalline material was separated by drying on a clay plate. The product thus obtained weighed 24 g. and melted at 55–60°. It was recrystallized from carbon tetrachloride to give 16 g., m.p. 58–60°. Recrystallization from alcohol gave 12 g. (8.8%) of 2-chloro-3,5-dinitrotoluene, m.p. 62–63° (lit. m.p. 62–63°[2]).

Synthesis of 3,5-Dinitrotoluene.—To a hand-stirred mixture of 14 g. (0.11 mole) of benzoic acid and 5 g. (0.023 mole) of 2-chloro-3,5-dinitrotoluene was added 10 g. of copper powder, in several portions over a period of 5 minutes (temperature at 150–200°). Heating was stopped and the solidified mixture was then taken up with 50 ml. of 20% sodium carbonate solution. The insoluble residue was removed by filtration, dried, and extracted with ether. Evaporation of the ether gave 3.8 g., m.p. 90–91°. Recrystallization from 50 ml. of alcohol gave 3.5 g. (83%) of 3,5-dinitrotoluene, m.p. 93°.

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(2) G. R. Yohe, *Trans. Ill. State Acad. Sci.*, **33**, No. 2, 125 (1940).

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Azeotropes of Bromine. III. Azeotropes of Bromine with 1,2,2-Trichloro-1,1-difluoroethane and 1,1-Dichloro-2,2-difluoroethane

BY WILLIAM M. SPICER AND HENRY D. R. PAGE

RECEIVED MARCH 23, 1953

As a continuation of an investigation to prepare binary azeotropes consisting of one colored and one colorless component,[1,2] it was decided to study further possibilities in systems of bromine with colorless bromine solvents. Azeotropes of this general type are valuable in the study of the methods employed to separate azeotropic mixtures, since separation can be observed visually.

It was decided to investigate CHCl$_2$CHF$_2$ and CHCl$_2$CF$_2$Cl as bromine solvents since these liquids possess boiling points near that of bromine, a condition favorable for azeotrope formation. Besides it was anticipated that these liquids would be miscible with and inert toward bromine.

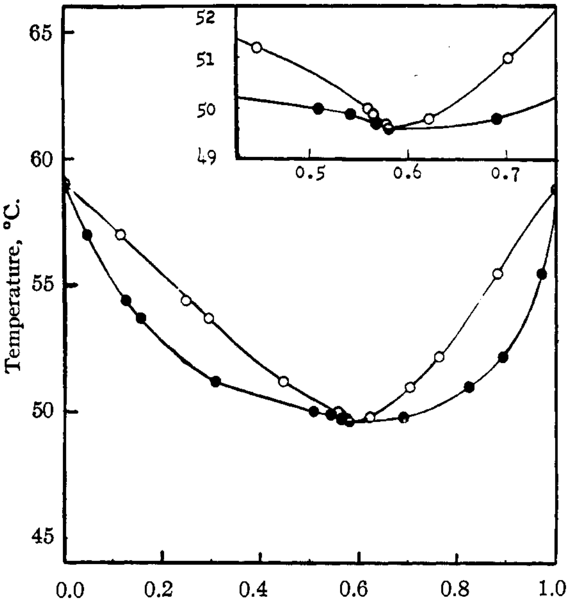

Fig. 1.—Temperature–composition diagram for the system Br$_2$–CHCl$_2$CHF$_2$ at 760 mm. pressure: ○, vapor; ●, liquid; ◒, vapor and liquid.

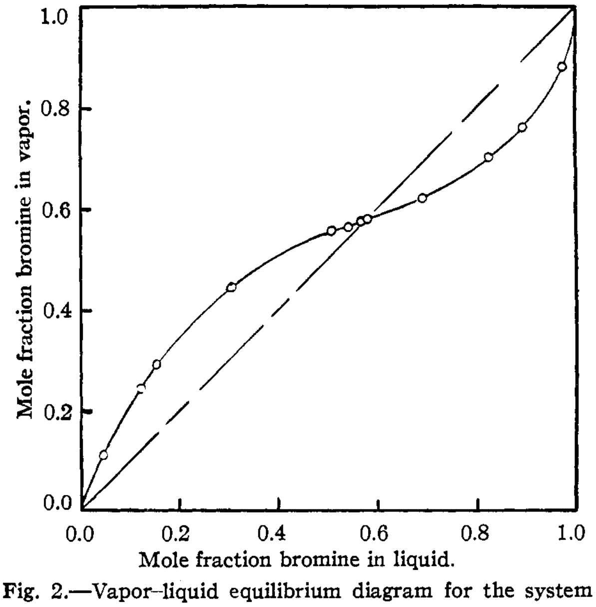

Fig. 2.—Vapor–liquid equilibrium diagram for the system Br$_2$–CHCl$_2$CHF$_2$ at 760 mm. pressure.

Experimental

Merck and Co., Inc., analyzed C.P. bromine was used without further purification. The CHCl$_2$CHF$_2$ and CHCl$_2$CF$_2$Cl were obtained from Halogen Chemicals, Inc., and were listed as being better than 95% pure. These were

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(1) W. M. Spicer and J. Kruger, THIS JOURNAL, **72**, 1855 (1950).

(2) W. M. Spicer and L. H. Myer, *ibid.*, **73**, 934 (1951).