TABLE II

DATA OBTAINED WITH THE SARGENT–HEYROVSKY POLAROGRAPH

All measurements made at −0.75 v. *vs.* the saturated calomel electrode at 25.00°, with 2.000 millimolar lead ion in 1 N potassium chloride. Capillaries F, G and H were hand-drawn. See ref. 1 for complete details of the measurements.

Capillary	h, cm.	m, mg./sec.	t, sec.	$\frac{i_d}{Cm^{2/3}t^{1/6}}$	$\frac{i_d}{Cm^{0.64}t^{1/6}}$
F	40.0	1.072	4.49	4.045	4.053
	50.0	1.354	3.60	3.990	4.022
	60.0	1.642	2.92	3.918	3.970
	70.0	1.922	2.56	3.880	3.948
G	30.0	2.988	2.50	3.864	3.973
	40.0	4.050	1.82	3.823	3.968
	50.0	5.113	1.41	3.807	3.976
	60.0	6.174	1.18	3.821	4.011
H	30.0	4.146	1.79	3.868	4.018
	40.0	5.617	1.31	3.834	4.015
				Av.	3.995
				Av. dev.	±0.028

with an average deviation from the mean of ±0.4%. As expected from the relatively short scale on the instrument (15 cm.) the data obtained with the Sargent–Heyrovsky Polarograph are least precise (average deviation from the mean ±0.7%), but the average value of $i_d/Cm^{0.64}t^{1/6}$ with the Polarograph agrees almost exactly with the mean of the other two methods.

These data constitute conclusive proof that these three commonest methods of measuring the diffusion current yield practically identical results. They also show that the diffusion current observed with the dropping electrode is reproducible to a few parts per thousand, and that under optimum conditions the polarographic method is inherently capable of greater accuracy than is usually assumed.

In view of the fact that the foregoing results were obtained with only one reducible substance they should not be construed as proof of the general validity of Eq. 3. However, the polarographic behavior of lead ion is normal in all respects, which leads us to expect that a value of α equal to 0.64 probably will be generally applicable. We plan to obtain data with several reducible and oxidizable substances to test the general validity of Eq. 3.

Summary

The diffusion current constant $i_d/Cm^{\alpha}t^{1/6}$ of lead ion in 1 N potassium chloride decreases by about 6% as m increases from 0.9 to 6.2 mg./sec., and t decreases from 8.9 to 1.3 sec., if the theoretical value of $\alpha = {}^2/_3$ is used. When the empirical value $\alpha = 0.64$ is employed the diffusion current constant of lead ion is truly constant to a few tenths of a per cent. over the same wide range of capillary characteristics. The value $\alpha = 0.64$ probably is generally applicable, but it should not be so assumed until confirmatory data are available.

CAMBRIDGE, MASS. RECEIVED NOVEMBER 26, 1945

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA]

Polymeric Compounds Formed by the Decomposition of 2,4,6-Tribromo-3-fluorophenol Bromide and the Sodium Salt of 2,4,6-Tribromo-3-fluorophenol[1,2]

BY L. CHAS. RAIFORD[3] AND ARTHUR L. LEROSEN[4]

In a previous paper[5] we have mentioned the formation of 2,4,6-tribromo-3-fluorophenol bromide (or hypobromite) in the bromination of *m*-fluorophenol. We report below some interesting reactions in which both this compound and the sodium salt of 2,4,6-tribromo-3-fluorophenol take part to yield a series of polymers of the composition $(C_6HOBr_2F)_n$. For comparison tribromophenol bromide, 2,4,6-tribromo-3-chlorophenol bromide, and the sodium salt of tribromophenol have also been studied.

The formation of amorphous compounds from tribromophenol bromide by the loss of bromine was reported by Benedikt.[6] These substances have been studied by Olivier,[7] Kastle and coworkers,[8] and by Hunter and his students. Hunter and his associates[9–14] have noted that the same type of polymer may be obtained from various salts of trihalogenated phenols by the effect of heat in benzene, or the catalytic effects of ethyl

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[1] From a Thesis submitted by Arthur L. LeRosen in partial fulfillment of the requirements for the degree of Doctor of Philosophy to the Graduate College of the State University of Iowa, June, 1940.

[2] Presented before the Regional Meeting of the American Chemical Society at Baton Rouge, Louisiana, October, 1945.

[3] Deceased January 8, 1944.

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[5] L. C. Raiford and A. L. LeRosen, THIS JOURNAL, 2080 (1944).

[6] R. Benedikt, *Ann.*, **199**, 127 (1879).

[7] S. C. J. Olivier, *Rec. trav. chim.*, **28**, 359 (1909).

[8] J. H. Kastle, A. S. Loevenhart, R. Speyrer and J. W. Bilbert, *Am. Chem. J.*, **27**, 31 (1902).

[9] H. A. Torrey and W. H. Hunter, *Ber.*, **40**, 4333 (1907); THIS JOURNAL, **33**, 200 (1911).

[10] W. H. Hunter, E. A. Daniells, A. O. Olson and L. Karatz, Orig. Comm. 8th Intern. Congr. Appl. Chem. (Appendix), **25**, 393; *cf. C. A.* **7**, 2189 (1913).

[11] W. H. Hunter and F. E. Joyce, THIS JOURNAL, **39**, 2640 (1917).

[12] W. H. Hunter and G. H. Woollett, *ibid.*, **43**, 131, 135 (1921).

[13] W. H. Hunter and R. B. Whitney, *ibid.*, **54**, 1167 (1932).

[14] W. H. Hunter and Miles A. Dahlen, *ibid.*, **54**, 2456 (1932).

iodide, bromine or iodine. Their work shows that halogen may be lost from salts of trihalogenated phenols either in the *o*- or the *p*-position resulting in colorless or colored polymers of the type $(C_6H_2OX_2)_n$. The latter seem to be mixtures of both the colored and colorless types. The presence of some quinoid oxygen in the colored polymers was demonstrated.

We have observed the same sort of behavior in the case of 2,4,6-tribromophenol bromide and the sodium salt of 2,4,6-tribromo-3-fluorophenol as summarized in Table I.

TABLE I

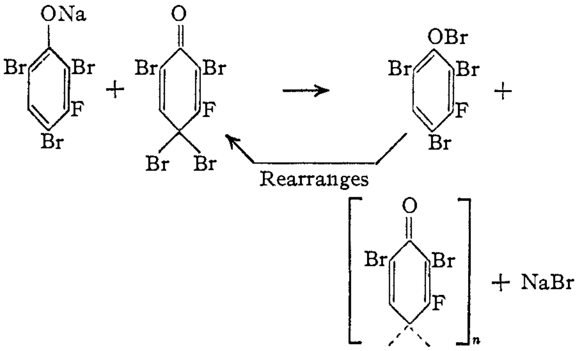
REACTIONS OF DERIVATIVES OF 2,4,6-TRIBROMO-3-FLUOROPHENOL

Compound	Reactant	Solvent	Product
Phenol bromide	NaOH, Na_2CO_3, $NaHCO_3$,	Acetone	Blue polymer, mol. wt. 1880
Sodium salt	Trace bromine or phenol bromide	Acetone	Blue polymer
Sodium salt	Bromine	Chloroform, dioxane	Orange dimer, mol. wt. 584
Sodium salt	Bromine	Carbon tetrachloride	Phenol bromide
Sodium salt	Satd. Na_2CO_3	Water suspension	Reddish polymer
Sodium salt	Standing only	None	Reddish polymer, mol. wt. 2185
Blue polymer	Sunlight	Ether	White polymer, mol. wt. 2050

The blue polymer was fractionated by methyl alcohol precipitation and found to consist of a dark blue component, molecular weight about 1740, and an almost white component, molecular weight about 2700 to 2350. Possibly the white material was formed from the unstable blue polymer by the action of light.

The blue substance is formed only in certain solvents. Hydrocarbons and indifferent compounds did not show color formation. In general, solvents containing a non-acidic, not easily oxidizable carbonyl group gave the blue color. Certain other compounds were effective, *viz.*, nitromethane and aliphatic nitriles. Color formation was observed in benzaldehyde, its *o*- and *m*-nitro derivatives and in *o*-chloro- and bromoacetophenone, but not in the closely related halogenated derivatives of benzaldehyde.

The effect of the solvent might be due to the facilitating of a tautomeric shift as indicated below. Presumably the polymers would be only formed when the quinoid form of the bromide reacts with the sodium salt of the phenol. This would explain the inhibiting effect of substances like phenol and aniline, noted by Hunter,[13] in that they react with the hypobromite form before it can rearrange. In solvents in which no tautomeric shift is possible there would be no polymer observed, and the reaction should stop with the production of the phenol bromide. This was the behavior observed when the sodium salt was treated with bromine in carbon tetrachloride. If the phenol bromide reacts in its *p*-quinoid form, the conversion might be represented as shown below.



Acknowledgment.—The author wishes to express his appreciation to Professor L. Zechmeister for valuable advice in the preparation of this and several preceding papers.

Experimental[15]

The Sodium Salt of 2,4,6-Tribromo-3-fluorophenol.—Tribromo-3-fluorophenol[5,16] dissolved in warm 6 *N* sodium hydroxide and filtered through asbestos. On cooling the salt separated out. It was filtered off, dried, dissolved in ether, and on careful addition of petroleum ether it was precipitated as colorless needles that did not melt up to 200°. Analysis for bromine showed this to be a hydrated salt.

Anal. Calcd. for $C_6HOBr_3FNa + 2.5\ H_2O$: Br, 57.53; H_2O, 10.9. Found: Br, 57.61; H_2O, 9.8 (loss at 100°).

The equivalent weight was determined by treating a sample with excess silver nitrate, filtering the precipitated silver salt, and titrating the excess silver ion.

Equivalent weight. Calcd. for $C_6HOBr_3FNa \cdot 2.5\ H_2O$: 416.2. Found: 416.7. A sample of the dehydrated salt was analyzed. *Anal.* Calcd. for C_6HOBr_3FNa: Br, 64.67. Found: Br, 63.89, 63.51.

The Sodium Salt of 2,4,6-Tribromophenol.—This compound, when prepared from tribromophenol in the way described above, formed colorless needles (from ether–petroleum ether).

Anal. Calcd. for $C_6H_2OBr_3Na$: Br, 67.97. Found: Br, 67.97.

Tribromophenol Bromide.—The preparation of this substance has been described elsewhere.[4,6]

2,4,6-Tribromo-3-fluorophenol Bromide.—Two ways of preparing this compound have been used.[1] A third method is described. A small quantity of the sodium salt of 2,4,6-tribromo-3-fluorophenol was treated with an excess of bromine in carbon tetrachloride. Most of the bromine and solvent were distilled off *in vacuo* and the precipitate formed was filtered. Upon extraction with hot chloroform it yielded crystals of 2,4,6-tribromo-3-fluorophenol bromide, m. p. 152–153° (with decomposition and evolution of bromine).

2,4,6-Tribromo-3-chlorophenol Bromide.—A small amount of *m*-chlorophenol dissolved in water was poured into excess bromine in potassium bromide solution. The precipitate was filtered off and dried. The yield was almost quantitative. Recrystallization from a carbon tetrachloride–petroleum ether mixture gave yellow platelets that decomposed at 138–139° with evolution of bromine.

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(15) Melting points are uncorrected. Analyses for the halogens were made by the Parr bomb method: bromine and chlorine were determined volumetrically by the Volhard method and fluorine was precipitated as lead chlorofluoride. Molecular weights were determined by freezing point depression in benzene.

(16) H. H. Hodgson and J. Nixon, *J. Chem. Soc.*, 1085 (1930); 272 (1932).

Anal. Calcd. for $C_6HOClBr_4$: Br + Cl, 77.46. Found: Br + Cl, 77.23.

Preparation of the Blue Decomposition Product of 2,4,6-Tribromo-3-fluorophenol Bromide.—Several grams of this bromide were dissolved in acetone and sodium carbonate solution was added (sodium bicarbonate was also effective). A blue color developed immediately. The mixture was stirred as long as the intensity of the color appeared to increase, then it was diluted with water; the solid was allowed to settle, and the supernatant liquid was decanted. The product was washed with water by decantation. After drying it was dissolved in ether and filtered to remove any inorganic material present. The filtrate was evaporated to yield an amorphous blue solid that on heating became yellowish at 110° and decomposed at a higher temperature without showing a definite melting point. Upon exposure to direct sunlight, in ether solution the blue color faded rapidly. The analysis of the blue substance indicated that two atoms of bromine, per molecule, had been lost.

Anal. Calcd. for C_6HOBr_2F: Br, 59.65. Found: Br, 61.20.

A second preparation, omitting the dissolution in ether, showed the following composition.

Anal. Calcd. for $(C_6HOBr_2F)_7$: Br, 59.65; F, 7.09; mol. wt., 1876. Found: Br, 58.87; F, 7.29; mol. wt., 1880.

In a third preparation 21.4 g. of the phenol bromide in acetone was treated with 84 g. of sodium bicarbonate (excess) to give 7.9 g. of the blue product on dilution with water. Further dilution caused the precipitation of an additional 2.4 g. of a pale blue substance. The total yield was 10.3 g. or 77%. The dark blue fraction was analyzed.

Anal. Calcd. for C_6HOBr_2F: Br, 59.65. Found: Br, 59.30.

Decomposition of Tribromophenol Bromide in Acetone by Sodium Hydroxide.—An acetone solution of this compound was shaken with a little 6 *N* sodium hydroxide. A pale greenish precipitate appeared but no intense blue color developed as in the case of 3-fluoro-tribromophenol bromide.

Decomposition of 3-Chloro-tribromophenol Bromide in Acetone by Sodium Hydroxide.—This reaction was carried out as in the preceding section. A green color developed in the acetone layer, followed by precipitation of the light blue product.

The Formation of the Blue Polymeric Decomposition Product from the Sodium Salt of 2,4,6-Tribromo-3-fluorophenol.—When a very small amount of either bromine vapor or 3-fluoro-tribromophenol bromide was added to an acetone solution of the sodium salt of 2,4,6-tribromo-3-fluorophenol an intense blue color developed. When small quantities of the sodium salt were added to the acetone solution of the phenol bromide the amount of the blue substance produced was negligible.

One millimole (0.367 g.) of the sodium salt of 2,4,6-tribromo-3-fluorophenol and 0.025 millimole (0.011 g.) of 2,4,6-tribromo-3-fluorophenol bromide were dissolved in 10 ml. of dioxane and 10 ml. of acetone was added. A blue color developed slowly. The mixture was then set aside for twelve hours during which period an inorganic precipitate formed. The mother liquor was decanted and the precipitate was washed by decantation with ether, dissolved in water, acidified with two drops of concentrated nitric acid and the bromide was determined by titration. The value found corresponded to 0.915 millimole of sodium bromide or 93% if all the sodium salt was decomposed to yield one mole of sodium bromide per mole of the salt.

The experiment was repeated with 15.0 millimoles of the sodium salt and 0.1 millimole of the phenol bromide to give 93% of the theoretical amount of sodium bromide and 92% of the organic polymer. On standing overnight the color of this solution faded and the product became almost white.

Anal. Calcd. for C_6HOBr_2F: Br, 59.65. Found: Br, 56.70; mol. wt., 2050 (7.6 times the unit).

The Effect of Solvent on the Formation of the Blue Polymer.—Only certain solvents allowed the characteristic blue color to develop when a solution of a small quantity of 2,4,6-tribromo-3-fluorophenol bromide in the solvent was treated with a few drops of 6 *N* sodium hydroxide. Low melting solids were melted for the test. Solutions of solvents giving the reaction, in other solvents, did not show color formation unless the mixture contained a large amount of the effective solvent.

The solvents in which color formation was observed were the following: acetone, diethyl ketone, methyl ethyl ketone, methyl *p*-toluyl ketone, methyl α-naphthyl ketone, acetophenone, *o*-chloro-acetophenone, *p*-chloroacetophenone, *o*-bromoacetophenone, benzophenone, benzal acetone, benzaldehyde, piperonal, furfural, *o*-nitrobenzaldehyde, *m*-nitrobenzaldehyde, *o*-nitro- and *p*-chlorobenzaldehyde (mixed), acetic anhydride, propionic anhydride, benzoic anhydride, ethyl acetate, ethyl benzoate, ethyl *n*-valerate, ethyl chloroacetate, ethyl malonate, ethyl dibromomalonate, *o*-toluyl isocyanate, benzyl cyanide, nitromethane and *n*-valeronitrile.

Some solvents which did not show the reaction were: acetaldehyde, butyraldehyde, heptaldehyde, *o*-chlorobenzaldehyde, *p*-chlorobenzaldehyde, *m*-chlorobenzaldehyde, *o*-bromobenzaldehyde, acetoacetic ester, *o*-chlorophenyl acetate, resorcinol diacetate, *p*-cresyl acetate, ethyl *n*-caprylate, ethyl *n*-propionate, benzoyl chloride, benzonitrile, diethyl ether, dibutyl ether, resorcinol dimethyl ether, *n*-propyl phenyl ether, ethyl alcohol, allyl alcohol, benzyl alcohol, cyclohexanol, *t*-butanol, pentanol-2, *m*-nitrotoluene, nitrobenzene, ethylene dibromide caproic acid, butylamine, aniline, phenyl isothiocyanate phenyl isocyanate, diethylene glycol, carbon disulfide, thiophene, and cyclohexane.

The solvents used were not specially purified, so that some of the negative reactions may have been due to impurities, *i. e.*, alcohols in the "negative" esters. This definitely was not the case with the chlorobenzaldehydes, since the mixture of *o*-nitro and *p*-chlorobenzaldehyde showed color formation.

Fractionation of the Blue Polymer.—This polymer contained some lighter colored material, possibly derived by the action of light, as shown by the following experiment.

A sample of the blue polymer, 4.26 g., obtained from the sodium salt of 2,4,6-tribromo-3-fluorophenol, was dissolved in ether and dioxane and methyl alcohol was added until a precipitate formed. This fraction was 1.22 g. of a dark blue powder, mol. wt. 1740. The mother liquor was diluted with more methyl alcohol to give 1.70 g. of a pale blue substance, mol. wt. 2760. The filtrate from this fraction was treated with water and a small amount of dilute sulfuric acid to coagulate the precipitate. This final fraction was almost white, yield 0.77 g., mol. wt., 2350.

The Decomposition of the Sodium Salt of Tribromophenol by Bromine.—Either bromine or tribromophenol bromide caused this reaction to occur. The sodium salt, 35.2 g., in acetone solution was treated with one drop of bromine. The solution became green and a greenish precipitate formed (22.4 g.). It was completely soluble in dioxane and partially soluble in nitromethane, carbon disulfide or benzene.

Anal. Calcd. for C_6H_2OBr: Br, 63.94. Found: Br, 63.28, 63.59.

Dimer from the Sodium Salt of 2,4,6-Tribromo-3-fluorophenol.—Twenty-five grams of this salt was treated with a slight excess of bromine in chloroform. The solvent and practically all of the bromine were removed *in vacuo* and dioxane was added to extract the reaction product; however, the dioxane initiated a reaction. The solution at first became dark green and after twelve hours was orange-red. The sodium bromide was filtered off and the filtrate was diluted with water to precipitate a red oil. This was worked up by dissolution in ether, drying over sodium sulfate and removing the solvent *in vacuo*. The viscous residue became a glassy orange-red solid after several days. It softened between 60 and 85° and began to flow at 100°. At about 150° bubbles appeared.

Anal. Calcd. for $(C_6HOBr_2F)_2$: Br, 59.65, mol. wt., 536. Found: Br, 58.48, mol. wt., 584.

Spontaneous Decomposition of the Sodium Salt of 2,4,6-Tribromo-3-fluorophenol.—The first sample prepared was kept for several months without decomposition, but almost all subsequent preparations decomposed in from several days to several hours as indicated by a change from colorless to brownish red. The decomposed salt showed no change in composition.

Anal. Calcd. for C_6HOBr_3FNa: Br, 64.67, Found: Br, 64.87.

The decomposed salt, 3.28 g., was extracted with 30 ml. of dioxane and the insoluble residue was centrifuged and washed twice with dioxane. After drying the yield was 0.86 g. of an almost white solid, corresponding to 94.5% of the sodium bromide expected on the basis of the formation of one molecule of sodium bromide per molecule of the sodium salt. Analysis for bromine indicated that the sodium bromide was 98.5% pure.

The dioxane soluble material was precipitated by the addition of water. After drying it was a brownish-red amorphous powder that did not melt up to 215°.

Anal. Calcd. for C_6HOBr_2F: Br, 59.65. Found: Br, 56.32; mol. wt., 2185 (8.2 times the smallest unit).

When the sodium salt of this phenol was heated with sodium carbonate solution it decomposed to give the same kind of brown, amorphous polymer described above.

Spontaneous Decomposition of the Sodium Salt of Tribromophenol.—This salt decomposed on standing in the same way as that of its 3-fluoro derivative. The decomposition in sodium carbonate solution was also observed. A sample of tribromophenol was treated with hot saturated sodium carbonate solution to give the same kind of polymer, a reddish-brown amorphous powder. This substance was washed free of inorganic salts and dried.

Anal. Calcd. for $C_6H_2OBr_2$: Br, 63.94. Found: Br, 61.73.

This product was purified by solution in dioxane and precipitation by alcohol. After two such treatments the analysis was better.

Anal. Calcd. for $C_6H_2OBr_2$: Br, 63.94. Found: Br, 63.68.

The molecular weight determination (mol. wt., 8300) was not reliable since the solution showed a Tyndall effect.

Summary

Several types of polymers of the composition $(C_6HOBr_2F)_n$ have been obtained, either from 2,4,6-tribromo-3-fluorophenol bromide by loss of two bromine atoms or from the sodium salt of 2,4,6-tribromo-3-fluorophenol by the elimination of one molecule of sodium bromide. Tribromophenol bromide, 2,4,6-tribromo-3-chlorophenol bromide and the sodium salt of tribromophenol undergo the same kind of reaction.

Baton Rouge, La. Received November 5, 1945

[Contribution from the Department of Chemistry of The Polytechnic Institute of Brooklyn]

Syntheses in the Pyrazine Series. The Preparation and Properties of the Pyrazyl Halides

By A. E. Erickson and Paul E. Spoerri

In comparison with benzene, pyridine, pyrimidine and other six-membered conjugated ring systems, the chemistry of pyrazine compounds has received little attention. On the basis of the available literature, it appears that the lack of information on simple functional derivatives and transformations is due mainly to the fact that pyrazine does not undergo with practical facility the orthodox substitution reactions of direct halogenation, nitration, sulfonation, etc., which serve quite well in the other cyclic series. The major portion of the work published thus far has dealt with the chemistry of the pyrazine carboxylic acids, their derivatives and degradation products. In order to prepare some of the synthetically more versatile derivatives, a new approach seemed necessary. The present investigation has been concerned mainly with the preparation of the simple halogen derivatives which have hitherto been so noticeably lacking in pyrazine syntheses.

In regard to the halogenation of pyrazine, it is reported[1] that pyrazine reacts with bromine to give an addition product which is too unstable for isolation and characterization. To effect substitution of bromine would probably require, as it does in the case of pyridine[2] a vapor-phase reaction at elevated temperatures. However, it is unlikely that the pyrazine ring would survive such conditions. As an alternative method of preparation, it was thought that the well defined amino-pyrazine[3] might serve as a source of the desired pyrazyl halides via diazotization and application of the Sandmeyer reactions. Preliminary efforts to diazotize amino-pyrazine by the usual procedure in dilute aqueous media were unsuccessful. As in the case of other weakly basic amines, it was found that the diazotization can be satisfactorily accomplished by the use of nitrosylsulfuric acid in concentrated sulfuric acid solution.

By diazotization in this way followed by hydrolysis of the diazo compound, amino-pyrazine was converted in a yield of 65% to hydroxy-pyrazine.[4] This transformation might be applied as well to other substituted amino-pyrazines. For example, 2-amino-3-carboxypyrazine was converted in a yield of 85% to 2-hydroxy-3-carboxypyrazine.[4]

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[1] Stoehr, *J. prakt. Chem.*, **51**, 456 (1895).

[2] Den Hertog and Wibaut, *Rec. trav. chim.*, **51**, 381 (1932).

[3] Gabriel and Sonn, *Ber.*, **40**, 4851 (1907).

[4] Weijlard, Tishler and Erickson, This Journal, **67**, 805 (1945), recently reported the preparation of these compounds by an alternative method.