TABLE I

CHANGE OF E.M.F. OF DISCHARGING HYDROGEN WITH PRESSURE AT CONSTANT CURRENT DENSITY

	—E.m.f. against Hg,Hg_2SO_4 electrode— H_2 on platinized Pt				—H_2 on smooth lead—			
Pressure Cm. of Hg	10 ma. per sq. cm.	50	200	1000	Pressure Cm. of Hg	10	100	1000
76.5	0.7042	0.7197	0.7357	0.78	75.5	1.451	1.753	1.875
36.1	.7051	.7194	....	..	48.3	1.451	1.752	1.868
15.2	.7040	....	.7357	..	27.2	1.451	1.752	1.869
6.3	.7036	.7192	....	.81	12.6	1.450	...	1.875
2.4	.7029	.7183	.7360	..	6.6	1.450	...	...
2.2	.7033	.7186	.7360	.83	2.2	1.451	1.751	1.92

	—H_2 on smooth copper—			—H_2 on smooth nickel—		
	10 ma. per sq. cm.	100	1000	10	100	1000
75.5	1.304	1.322	1.800	1.163	1.392	1.605
48.1	1.302	1.320	1.800	1.164	1.392	1.589
27.4	1.301	1.318	1.798	...	...	...
12.6	1.299	1.316	1.802	1.160	1.386	1.605
6.6	...	1.317	1.809	...	1.390	1.63
2.2	1.299	1.314	1.82	1.155	1.392	1.77

The values at the lowest pressure are somewhat uncertain due presumably to the violent stirring.

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RECEIVED JUNE 18, 1924
PUBLISHED DECEMBER 13, 1924

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO AND FROM THE CHEMICAL LABORATORY OF MOUNT HOLYOKE COLLEGE]

THE REACTION OF BROMONITROMETHANE WITH AROMATIC COMPOUNDS IN THE PRESENCE OF ALUMINUM CHLORIDE[1]

BY MARY L. SHERRILL

RECEIVED JUNE 17, 1924 PUBLISHED DECEMBER 13, 1924

In the field of the nitro aliphatic compounds, a number of investigators, Victor Meyer, Nef, Hantzsch, Holleman and L. W. Jones, have studied the structure and instability of these compounds and have proposed various structural formulas. Jones[2] has given an electronic interpretation of the nitroparaffins and by intramolecular oxidation and reduction has explained the various decomposition products. Very little work has

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[1] This communication is an abstract of part of a dissertation submitted by Mary L. Sherrill in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Chicago. The experimental work was done in the Chemical Laboratory of Mount Holyoke College.

[2] Jones, *Am. Chem. J.*, **50**, 429 (1913).

been recorded with regard to the structure of the mono-halogen nitromethanes or the activity of their halogen atoms. Clarke[3] has studied the velocity of the reaction of bromonitromethane with pyridine. Macbeth[4] has shown that the halogen atoms in the mono halogen nitromethanes were not as labile as those in the di- and trinitromethanes. Through a study of the absorption spectra of these compounds he concludes that the reactivity of the halogen atom is not due to an oxygen-halogen linkage nor to the tendency of the halogen atom to acquire a tautomeric hydrogen,[5] but he interprets the lability of the halogen atom according to the alternate polarity principle of Lapworth and others. An interpretation of Macbeth's work from the point of view of the Lewis-Langmuir co-valence theory has been made by Fraser and Humphries.[6] The results of the present investigation suggest an electronic interpretation of this reactivity of the halogen in bromonitromethane on the basis of an equilibrium between a positively charged bromine atom and a negatively charged one.

Erich Schmidt[7] has brominated an aromatic nucleus by means of bromotrinitromethane and, also, formed a brominated ether of the formula —CH(OR).CHBr— by its action with an olefin in the presence of alcohol.

In view of the fact that bromonitromethane is the main product in the action of bromocyanogen on sodium nitromethane[8] and also that there is marked similarity between the activity of the halogen nitromethanes and the cyanogen halides,[9] it was thought that the behavior of bromonitromethane might be similar to that of bromocyanogen. The cyanogen halides react in a Friedel and Crafts synthesis;[10] thus, the chloro-compound gives chiefly nitriles, the bromocyanogen, however, gives both nitriles and brominated compounds, while the iodo derivative gives only iodides or free iodine. A similar behavior is found when these compounds are used in a Grignard synthesis.[11]

Other reactions of the cyanogen halides[12] seem to show that their behavior can best be explained by electronic formulas, the type of the reaction depending on the positive or negative charge on the halogen.

It is believed that a similar relationship may be found to exist between

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[3] Clarke, *J. Chem. Soc.*, 97, 416 (1910).

[4] Macbeth, *ibid.*, **119**, 1357 (1921); **121**, 892, 904, 1109, 1116, 2169, 2327 (1922).

[5] Burton and Kenner, *ibid.*, **121**, 489 (1922).

[6] Fraser and Humphries, *Chem. News*, **126**, 167 (1923).

[7] Schmidt, *Ber.*, **55B**, 2099 (1922).

[8] Scholl, *Ber.*, **29**, 2416 (1896).

[9] Hantzsch, *Ber.*, **32**, 628, 640 (1899).

[10] Friedel and Crafts, *Ann. chim. phys.*, [6] **1**, 528. Scholl, *Ber.*, **32**, 3492 (1899); **33**, 1052 (1900); **36**, 322 (1903). Karrer, *Helvetica chim. Acta*, **2**, 482 (1919); **3**, 261 (1920). Folin, *Am. Chem. J.*, **19**, 322 (1897).

[11] Grignard, *Ann. chim. phys.*, [9] **4**, 28 (1915); **12**, 364 (1920).

[12] Chattaway, *J. Chem. Soc.*, **81**, 196 (1902). Jones, THIS JOURNAL, **36**, 1283 (1914). Nef, *Ann.*, **308**, 320 (1899).

chloro-, bromo- and iodonitromethanes. The experimental work of this investigation which justifies this interpretation has been a study of the reaction of bromonitromethane in the presence of anhydrous aluminum chloride upon the following aromatic compounds: benzene, monobromobenzene, monochlorobenzene and anisole. In every case that has been studied two types of products have been isolated; the one is either the aromatic nitromethane, or the corresponding aromatic aldehyde or acid, the two latter compounds being formed by the decomposition of the aromatic nitromethane, the other is the brominated aromatic compound. The yields of the former have been from 10–45% of those calculated; of the latter 25–65%.

From these experimental results it seems that in order to account for the formation of the aromatic nitromethanes and their decomposition products, the corresponding aldehyde and acid, it is necessary to assume that part of the reaction proceeds as a normal Friedel and Crafts synthesis, thus: $C_6H_6 + Br.CH_2.NO_2 + (Al_2Cl_6) \longrightarrow C_6H_5.CH_2.NO_2 + HBr + (Al_2Cl_6)$. The evolution of hydrogen halide would also be accounted for by this. On the other hand, the bromination of the aromatic compound must have taken place according to the following equation: $C_6H_6 + Br.CH_2NO_2 + (Al_2Cl_6) \longrightarrow C_6H_5.Br + CH_3.NO_2 + (Al_2Cl_6)$. There has been no isolation of nitromethane, as such, but there has been qualitative evidence of various decomposition products such as hydroxylamine, nitrous acid, ammonia and in some case isonitriles. If nitromethane is formed, the reaction of this with nitrous acid would account for methylnitrolic acid, whose presence has been indicated.

These facts lead to the conclusion that bromonitromethane must consist of an equilibrium mixture of two electromers, the one with a positive bromine atom, and the other with a negative bromine atom, the equilibrium point tending perhaps toward the positively charged form: $\overset{+}{Br}.\overset{-}{CH_2.NO_2} \rightleftarrows \overset{-}{Br}.\overset{+}{CH_2.NO_2}$. This interpretation of positive bromine would explain the instability of bromo-isonitromethane which Hantzsch[13] regarded as an exception to his rule that a negative atom increased the stability of the isonitro compounds.

Since the pure bromonitromethane, in a non-hydrolyzing medium, reacts with potassium iodide to give iodine, an investigation of the extent of this is being made with the hope of obtaining some quantitative evidence with regard to the amount of positive bromine and possibly also some determinations of the velocity of the reaction. Further study of the reactions of bromonitromethane will be pursued. It is proposed also to investigate the reactions of chloronitro- and iodonitromethane in a similar way.

[13] Hantzsch, *Ber.*, **32**, 612 (1899).

Experimental Part

Nitromethane was prepared from monochloro-acetic acid and sodium nitrite according to the method of Steinkopf and Kirchhoff[14] and that of Roger Adams.[15] From 500 g. of monochloro-acetic acid, 125–140 g. of nitromethane was obtained. Adams gives yields of 240–250 g. from 1000 g. of the acid.

Bromonitromethane was prepared both by the method of Tscherniac[16] and that of Scholl.[17] The former seemed to offer advantages in that it avoided the isolation of the sodium salt but the product could not be obtained of sufficient purity nor in satisfactory yield by this method. A slight variation in the proportions of reagents as recorded by Scholl gave a 60–63% yield, which after vacuum distillation, was of high purity, boiling at 70–72° (40–50 mm.).

Anal. Calc. for $BrCH_2NO_2$: Br, 57.11. Found: 56.72.

Condensation of Bromonitromethane with Aromatic Compounds.—The condensation of bromonitromethane with benzene was carried out by adding a benzene solution of it to large amounts of benzene containing aluminum chloride. In the condensations with bromobenzene, chlorobenzene and anisole, aluminum chloride was added to solutions of these substances in carbon disulfide and then a solution of bromonitromethane in carbon disulfide added to the mixture. About 1 molecular equivalent of bromonitromethane and 0.5–0.7 equivalent of aluminum chloride were used for each molecular equivalent of aromatic compound (except in the case of benzene). In general, the method was to cool the reaction mixture in an ice-bath for the first six or eight hours and then allow the reaction to proceed at room temperature for two or three days, the mixture being vigorously agitated during the entire condensation. A mercury-seal stirrer and a reflux condenser were used and moisture was carefully excluded.

The treatment of the product has been, in general, to separate the solvent as much as possible from the complex addition product and from this, after treatment with ice and acid, to isolate the halogenated products by steam distillation and final distillation. Almost all of the halogen substitution product was found in the solvent, whereas the aromatic nitromethane derivatives were almost entirely obtained by decomposition of the complex addition product. Therefore this addition product has been treated with ether until the gum was transformed into an emulsion whereupon the ether was treated with ice and acid. From this ether the acids and aromatic nitromethane products were extracted with solutions of sodium carbonate and sodium hydroxide and the aldehyde and some halogenated products were obtained from the residual ether.

Benzene.—Fifty g. of bromonitromethane gave 15 g. of bromobenzene (155–

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[14] Steinkopf and Kirchoff, *Ber.*, **42**, 3439 (1909).

[15] Adams, *Univ. Illinois Bull.*, Oct. 9, 1921.

[16] Tscherniac, *Ber.*, **30**, 2588 (1897).

[17] Scholl, *Ber.*, **29**, 1824 (1896).

157°), or a yield of 26.75%; 9 g. of benzaldehyde (b. p., 176–179°), or 23.21%; 6 g. of benzoic acid (m. p., 121°), or 14.11%; and 4 g. of phenylnitromethane, or 8.11%.

Because of the ease of decomposition one condensation was carried out at diminished pressure and the products were fractionated under a pressure of 25 mm. Fifty g. of bromonitromethane gave 17 g. of bromobenzene (b. p., 50–70°; 25 mm.), or 30.35%; and 12 g. of phenylnitromethane (b. p., 135°; 25 mm.), or 23.9%.[18] An analysis of the latter gave 9.48% nitrogen instead of the calculated amount, 10.2%; this compares favorably with Holleman's[18] analysis of phenylnitromethane in which he obtained 9% of nitrogen.

A comparison of phenylnitromethane prepared in this way with that prepared from benzyl iodide and silver nitrite[19] and also from benzyl chloride and mercurous nitrite[20] showed that the purity of the product obtained by this new method is as satisfactory as that from either of the other methods and the yields were much better.

Bromobenzene.—Thirty-five g. of bromobenzene gave 29 g. of *p*-di-bromobenzene (m. p., 89°), or 52.64%; 2.6 g. of pure *p*-bromobenzaldehyde (m. p., 57°), or 6.2%; and 5 g. of pure *p*-bromobenzoic acid, or a 11.2% yield. The aldehyde was further identified by converting it into the oxime (m. p., 110–111°); *p*-bromobenzoic acid was found difficult to purify but recrystallizations from boiling benzene gave lustrous crystals (m. p., 255°).

Chlorobenzene.—Twenty-eight g. of chlorobenzene gave 36 g. of *p*-bromochlorobenzene (m. p., 68°), or 62.95%; 2 g. of *p*-chlorobenzaldehyde (m. p., 45°), or 5.71%; and 6 g. of *p*-chlorobenzoic acid (m. p., 238°), or 15.4%.

Anisole.—In the case of anisole the reaction seemed to be less complete than in the other cases and large quantities of anisole were recovered unchanged. *p*-Bromoanisole was obtained and small amounts of anisaldehyde and anisic acid. The *p*-bromoanisole was found difficult to separate from the anisole. The product boiling at 213–222° was nitrated[21] in order to identify it. A yellow crystalline compound (m. p., 85°) was formed. From the alkaline extracts an oil was obtained which seemed to have some of the properties of anisyl-nitromethane. An alkaline solution of this was treated with diazonium acetate in an excess of acetic acid and an orange-red precipitate formed which crystallized from alcohol in the form of brick-red crystals. These, when put into a bath at 100°, melted at 116°. This seemed to show that they were the anisyl-nitroformaldehydrazone crystals by which Bamberger[22] identified anisyl-nitromethane. This compound showed properties similar to those given by Bamberger.

The water extracts from all condensations have given qualitative tests for hydroxylamine and those from the runs in which carbon disulfide was used gave thiocyanate tests. The alkaline extracts, on acidification, have all had more or less of an oil present which was very unstable and somewhat irritating. The evidence, so far obtained, indicates that this is largely methylnitrolic acid containing traces of bromonitromethane.

Summary

1. The preparation of bromonitromethane by the Scholl method,[17] with slight modifications, was found to be more satisfactory than by other methods recorded in the literature.

2. Bromonitromethane reacts with benzene in the presence of aluminum chloride in two ways. In one, phenylnitromethane and its decomposition products, benzaldehyde and benzoic acid, are formed. In this forma-

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[18] Holleman, *Rec. trav. chim.*, **13**, 402 (1894).

[19] Hantzsch, *Ber.*, **29**, 699 (1896).

[20] Neogi, *Z. anorg. Chem.*, **69**, 270 (1910).

[21] Reverdin, *Ber.*, **29**, 2598 (1896).

[22] Bamberger, *Ber.*, **34**, 2027 (1901).

tion bromonitromethane reacts like an aliphatic halide, according to the Friedel and Crafts synthesis, the group $-CH_2.NO_2$ enters the nucleus and hydrogen bromide is freed. The ease of decomposition of phenylnitromethane, especially in the presence of strong acid, explains the formation of the aldehyde and acid. In various runs the total percentages of this type of compound are 19–45%. The second type of reaction is shown in the formation of bromobenzene. In this case the bromonitromethane acts as a brominating agent, the bromine atom entering the aromatic nucleus. Bromobenzene is formed in yields of 12–30%. The products formed in the two types of reaction account for from 40 to 80% of the total bromonitromethane used.

3. Bromonitromethane reacts with bromobenzene, chlorobenzene and anisole in the same way to give two types of compounds. The group enters in the *para* position in each case, the yields accounting for approximately 40–85% of the material used.

4. The two types of reaction are interpreted on the assumption that bromonitromethane in this reaction exists as an equilibrium mixture of two electromeric forms: $\overset{+}{Br}.\overset{-}{CH_2}.NO_2 \rightleftarrows \overset{-}{Br}.\overset{+}{CH_2}.NO_2$, one in which the bromine atom is negatively charged and therefore reacts as an alkyl halide in a Friedel and Crafts synthesis, and a second form in which the bromine atom is positively charged and therefore capable of brominating the aromatic nucleus.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE STRUCTURE OF DEHYDRO-ACETIC ACID

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RECEIVED JUNE 19, 1924 PUBLISHED DECEMBER 13, 1924

Dehydro-acetic acid is easily formed by the action of dehydrating agents on aceto-acetic ester or by acetic anhydride on acetone dicarboxylic acid and is readily converted by various reagents into a large variety of compounds such as diacetyl-acetone, pyridines, dimethylpyrone, etc. It has proved to be a most useful substance in organic chemistry.

Its structure has been a subject of controversy since its discovery in 1866.[2] Omitting a discussion of the earlier proposed formulas which have been readily disproved,[3] a brief review of the two alternative formulas which will explain all of the reactions of this substance may be

[1] This communication is an abstract of a portion of a thesis submitted by C. F. Rassweiler in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Geuther, *Chem. Zentr.*, **11**, 801 (1866); *Z. Chem.*, **2**, 8 (1866).

[3] (a) Feist, *Ann.*, **257**, 253 (1890). (b) Hale, THIS JOURNAL, **33**, 1119 (1911).