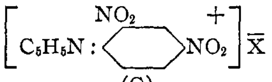
sentation explains very well the properties of the pyridine compounds with 2,4-dinitrochloro- and 2,4-dinitrobromobenzenes. They are white or almost so, are soluble in water, have a high melting point and in aqueous solution they precipitate their halide atoms quantitatively with silver nitrate. In other words they are salts and therefore polar compounds.



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Summary

1. New molecular organic compounds of 2,4-dinitrochlorobenzene and 2,4-dinitrobromobenzene have been isolated; no similar compounds with 2,4-dinitro-aniline could be isolated.

2. It has been shown in some cases that substitution products resulted through the intermediate formation of molecular compounds.

3. The influence of the substituent in the dinitrobenzenes upon molecular compound formation is discussed.

4. An electronic formula is proposed for the amine molecular compounds.

Knoxville, Tennessee

[The Results Presented in this Paper Were Obtained Privately in the Organic Laboratory, Bureau of Science, Manila, Philippine Islands]

PHENOLIC DECOMPOSITION OF CERTAIN MIXED ETHERS. THE VELOCITY CONSTANT

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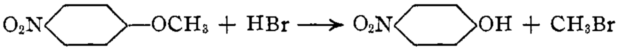
Introduction

It is well known that mixed ethers, *e. g.*, *p*-nitrophenyl methyl ether will give the corresponding phenol as one of the products of reaction according to the scheme



when they are acted upon by hydrogen bromide. Graebe and Martz[2] and also Raiford and Colbert[3] digested certain mixed ethers with 48% hydrobromic acid alone on the steam-bath for two hours and obtained varying degrees of decomposition depending upon the kind and number of substituents actually present in the phenyl residue. Stoermer[4] carried out

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[2] Graebe and Martz, *Ann.*, **340**, 220 (1905).

[3] Raiford and Colbert, This Journal, **48**, 1776 (1926).

[4] Stoermer, *Ber.*, **41**, 321 (1908).

the decomposition with acetic acid as reaction medium and reported varying extents of decomposition depending upon whether the substituent occupied the ortho or para position in the benzene nucleus. The kinetics of this reaction does not seem to have been investigated and it seemed interesting to study the factors influencing the phenolic decomposition of mixed ethers.

Experimental Part

A. Preparation of Materials

2,4-Dibromophenyl Methyl Ether.—Twenty grams of unsubstituted anisole dissolved in 20 cc. of chloroform was treated according to the procedure of Raiford and Birosel,[5] with 59.14 g. of bromine dissolved in 20 cc. of the same solvent. The mixture was allowed to stand at room temperature for four days, after which it was freed from the unused bromine by washing with a dilute solution of sodium hydroxide, then with distilled water, and dehydrated with anhydrous sodium sulfate. The solvent was evaporated and the residue consisted of solid and liquid derivatives. The solid was separated and crystallized from alcohol, giving shiny scale crystals melting sharply at 63°.[6]

***p*-Bromophenyl Methyl Ether.**—The liquid obtained above was found to distil mostly at 223°. It was redistilled and the portion going over at 223°[7] was reserved.

***o*-Bromophenyl Methyl Ether.**—Ten grams of unsubstituted anisole was treated as above with the required amount of bromine for a monomolecular proportion. A liquid was obtained which distilled at 210–213°. It was redistilled and the fraction going over at 210°[8] was reserved for use.

2,4,6-Tribromophenyl Methyl Ether.—This compound was prepared as above by treating 10 g. of 2,4-dibromophenyl methyl ether with the required amount of bromine for a monomolecular proportion. After four days the solvent and unused bromine were removed. Two distinct crystal forms were obtained when the residue was crystallized from alcohol. The needle crystal material was separated from the shiny scale crystals of dibromo-anisole and recrystallized from alcohol, giving a product which melted sharply at 87°.[9]

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[5] Raiford and Birosel, THIS JOURNAL, **51**, 1652 (1929).

[6] Cahours, *Ann.*, **52**, 331 (1884), obtained a liquid monobromo derivative of which he did not mention any characteristic and 2,4-dibromo-anisole, which gave shiny scale crystals, m. p. 54°, from alcohol, when he brominated anisole. Körner, *ibid.*, **137**, 206 (1866), prepared 2,4-dibromophenyl methyl ether from 2,4-dibromophenol, sodium methoxide and methyl iodide and obtained shiny scale crystals, m. p. 59°. Kohn and Pfeifer, *Monatsh.*, **48**, 211 (1927), prepared 2,4-dibromophenyl methyl ether from 2,4-dibromophenol obtained by the reduction of *sym.*-tribromophenol, with potassium hydroxide and dimethyl sulfate. Crystallizing from alcohol they obtained shiny scale crystals which they reported as melting from 62 to 64°.

[7] Henry, *Ber.*, **2**, 711 (1869), prepared *p*-bromo-anisole by treating anisole with one molecular proportion of phosphorus pentabromide. He obtained a liquid whch distilled at 220° (uncorrected). Autenrieth and Mullinghaus, *Ber.*, **39**, 4098 (1906), prepared this compound in the same way as Henry and obtained a liquid boiling between 213 and 216°.

[8] Michaelis and Geisler, *ibid.*, **27**, 256 (1894), prepared *o*-bromo-anisole according to the directions of Mulhauser, *Ann.*, **207**, 239 (1881), from *o*-anisidine, $CH_3OC_6H_4NH_2$. They obtained a liquid boiling at 210°.

[9] Kohn and Fink, *Monatsh.*, **44**, 18 (1923), prepared *sym.*-tribromo-anisole from 2,4,6-tribromophenol (1 mole), potassium hydroxide (10% solution) and dimethyl sulfate

B. Procedure of Decomposition

The velocity and extent of the phenolic decomposition of mixed ethers were determined at the temperature of the steam-bath. A weighed amount of the ether was digested with 30 cc. of constant boiling hydrobromic acid in glacial acetic acid solution made by adding 150 cc. of 48% hydrobromic acid to 300 cc. of acetic acid, for the desired period of time. The mixture was cooled and sodium hydroxide solution (1:4) was gradually added until the solution became slightly alkaline. The undecomposed ether was recovered by three ether extractions, washing each extraction with distilled water and adding the washings to the alkaline solution. Dilute sulfuric acid was added to the alkaline solution until slightly acidic and the phenol was extracted three times with ether. The solvent was evaporated, the residue heated on the steam-bath until the odor of acetic acid was no longer noticeable and then dehydrated in a desiccator.

The results obtained from experiments are given in the tables.

TABLE I

EXTENT OF DECOMPOSITION OF CERTAIN MIXED ETHERS

Compound	Time, hours	Ether used, g.	HBr used, cc.	AcH used, cc.	Acid soln. used, cc.	Phenol obtained, g.	Decomposition, %
o-Bromo-anisole	2	1.6835	10	20	30	0.4135	26.57[a]
	4	1.0840	10	15	25	.8755	87.28
p-Bromo-anisole	2	2.1500	15	25	40	1.5437	77.60[a]
2,4-Dibromo-anisole	2	1.0000	10	10	20	0.2035	21.48
	2	1.0000	10	20	30	.1710	18.05
2,4,6-Tribromo-anisole	2	0.5000	10	20	30	.1885	39.40

[a] Stoermer, Ref. 4, obtained 67.8% decomposition of *o*-bromo-anisole for four hours of digestion and 75% decomposition of *p*-bromo-anisole for two hours of digestion. He did not give data from which his figures can be recalculated.

TABLE II

THE RATE OF DECOMPOSITION OF 2,4-DIBROMOPHENYL METHYL ETHER IN GLACIAL ACETIC ACID AS MENSTRUM

Expt.	Time, minutes	Ether used, g.	Acid soln. used, cc.	Dibromo-phenol obtained, g.	Calcd. decomposed ether, g.	Decomposition, %	k
1	60	1	30	0.0965	0.1025	10.19	0.00180
2	90	1	30	.1375	.1458	14.79	.00178
3	120	1	30	.1705	.1807	17.19	.00166
4	150	1	30	.2508	.2658	18.05	.00206
5	240	1	30	.3270	.3466	34.51	.00177
6	360	1	30	.4460	.4728	46.55	.00178
7	480	1	30	.5080	.5385	55.04	.00161
8	600	1	30	.5650	.5989	59.64	.00152

($1^1/_4$ mole). Crystallizing from alcohol, they obtained needle crystals melting at 87°. Reinecke, *Z. Chem.*, 366 (1866), reported that by using three molecular proportions of bromine on anisic acid (*p*-carboxyanisole), 2,4,6-tribromophenyl methyl ether melting at 87° was obtained.

Table III

The Rate of Decomposition of 2,4-Dibromophenyl Methyl Ether as Influenced by Varying the Amount of Halogen Acid in Glacial Acetic Acid as Menstrum

Expt.	Time, minutes	Ether used, g.	HBr used, cc.	AcH used, cc.	Acid soln. used cc.	Dibromo-phenol[a] obtained, g.	Calcd. decomposed ether, g.	Decomposition, %	k
1	60	1	10	10	20	0.2035	0.2157	21.48	0.00202
2	60	1	10	20	30	.1705	.1807	17.19	.00166
3	60	1	10	30	40	.1130	.1198	12.04	.00106
4	60	1	10	40	50	.0880	.0933	9.27	.00082
5	60	1	20	10	30	.2179	.2310	23.00	.00219
6	60	1	30	10	40	.2250	.2385	23.75	.00227
7	60	1	40	10	50	.2300	.2438	24.28	.00233

[a] A nitro derivative, 2,4-dibromo-6-nitrophenol was prepared according to the directions of Kohn and Pfeifer, Ref. 6; crystallization from alcohol gave small yellow plate crystals melting at 118°.

Table IV

The Rate of Decomposition of 2,4-Dibromophenyl Methyl Ether in Formic Acid as Menstrum

Expt.	Time, minutes	Ether used, g.	Acid soln. used, cc.	Dibromo-phenol obtained, g.	Calcd. decomposed ether, g.	Decomposition, %	k
1	120	1	30	0.0140	0.0148	1.48	0.00012
2	180	1	30	.0220	.0233	2.32	.00013
3	240	1	30	.0240	.0254	2.53	.00011

Table V

The Rate of Decomposition of 2,4,6-Tribromophenyl Methyl Ether in Glacial Acetic Acid as Menstrum

Expt.	Time, minutes	Ether used, g.	Acid soln. used, cc.	Tribromo-phenol[a] obtained, g.	Calcd. decomposed ether, g.	Decomposition, %	k
1	60	0.5000	30	0.1085	0.1128	22.68	0.00426
2	120	.5000	30	.1885	.1960	39.60	.00415
3	240	.5000	30	.3005	.3125	62.83	.00409
4	360	.5000	30	.3780	.3931	79.04	.00392
5	360	.3700	15	.2602	.2720	79.59	.00369

[a] Crystallization from alcohol gave fine needle crystals, m. p. 92°; the melting point recorded in the literature for *sym.*-tribromophenol is 92–95°.

C. Discussion

In Table I are given the detailed results of the extent of decomposition of four bromo derivatives of anisole. Comparison of the decomposition for an interval of two hours shows that 2,4-dibromophenyl methyl ether is the least decomposed, that 2,4,6-tribromophenyl methyl ether appears to give higher phenolic decomposition than the dibromo derivative, and that *o*-bromo-anisole is more resistant to phenolic decomposition than the *p*-bromo derivative.

In Table II are shown the results of a typical experiment on the velocity of the phenolic decomposition of mixed ethers at the temperature of the steam-bath. The rate constants, *k*, are those calculated from the integrated form of the differential equation for first-order reactions, using logarithms to the base *e*. It will be noted that the constancy of *k* is quite satisfactory. The calculated amount of decomposed ether was obtained by multiplying the amount of dibromophenol obtained directly from experiment by the factor 1.06.

Table III shows the effect of changing the amount of hydrobromic acid in glacial acetic acid solution upon the phenolic decomposition of 2,4-dibromophenyl methyl ether. The greater the amount of halogen acid used, the greater the degree of decomposition and the higher the rate constant becomes. This does not mean that decomposition is greater when the halogen acid is used alone. Digesting a weighed amount of the ether for several hours on the steam-bath with hydrobromic acid alone did not give appreciable decomposition, which experience led to the employment of glacial acetic acid as menstrum. The solvent, though not entering into the reaction, seems to play an important role. In Table IV are expressed the results obtained from experiments when formic acid was used in place of glacial acetic acid. The extent of decomposition and the rate constant calculated in the same manner as the velocity constant in Table III are very much lower.

In Table V are given the detailed results of the experiments on the decomposition of 2,4,6-tribromophenyl methyl ether. The rate constants are those calculated from the integrated forms of the differential equation for first-order reactions, using logarithms to the base *e*. It will be noted that the constancy of *k* is quite satisfactory. The calculated amount of decomposed ether was obtained by multiplying the amount of tribromophenol obtained directly from experiments by the factor 1.04.

Summary

1. The kinetics of the phenolic decomposition of mixed ethers has been studied in the case of 2,4-dibromophenyl methyl ether and with 2,4,6-tribromophenyl methyl ether. Experiments were made in glacial acetic acid and formic acid as menstrums.

2. The velocity constants of the decomposition of 2,4-dibromophenyl methyl ether and 2,4,6-tribromophenyl methyl ether were calculated from the experimental results and their constancy is quite satisfactory. The phenolic decomposition of mixed ethers appears to be a first-order reaction.

3. The extent of decomposition is proportional to the amount of halogen acid used and seems to be influenced by the reaction medium. Decomposition is greater in glacial acetic acid than in formic acid as menstrum.

4. The degree of decomposition is also influenced by the number of substituents actually present and the position occupied in the phenyl residue.

The kinetics of the decomposition of other mixed ethers is being studied.

PASAY, RIZAL, PHILIPPINE ISLANDS