

The lactone of the hydroxytetrahydropimarinic acid was then saponified with a 10% solution of butyl alcoholic potassium hydroxide. After removal of the alcohol by steam distillation, the potassium salt of the hydroxy acid was dissolved in water and some unsaponified lactone removed by filtration. The alkali solution was made acid with dilute acetic acid and the product recrystallized from acetone, m. p. 143–144° (corr.). This product was insoluble in alkali and did not lower the melting point in the mixed melting point test with the original lactone, showing that the intermediately formed hydroxytetrahydropimarinic acid had been transformed into the original lactone.

This investigation is being continued.

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## A Modification of Bettendorff's Arsenic Test. II. Catalyzed by Mercury<sup>1</sup>

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In a previous paper<sup>2</sup> the authors reported that traces of mercuric chloride hastened markedly the reduction of arsenic compounds with stannous chloride. They also found that the time required for the appearance and development of the arsenic suspension was a function of the concentration of mercuric chloride in the solution. This behavior was utilized to determine the concentration of mercuric chloride in concentrations as low as  $2 \times 10^{-8}$  molar mercuric chloride. The authors, following the example of other investigators, used the terms "inductor" and "its inductive effect" without questioning the correctness of these terms. In the following report, data are presented which show that the modified Bettendorff test is catalytic and not induced.

### Reagents and Procedure

**The Preparation of Mercurous and Mercuric Chloride Solutions of Identical Concentrations.**—By means of a microbalance a few milligrams of mercurous chloride was weighed out, dissolved in concentrated hydrochloric acid and diluted with the same solvent until the solution was  $9 \times 10^{-7}$  molar. One hundred cubic centimeters of this solution was thoroughly saturated with chlorine gas which was passed through some of the same solvent before going into the sample. The chlorine was allowed to stand overnight in contact with the mercurous chloride solution, after which the excess was swept out completely by a cur-

rent of hydrogen chloride gas. It required about two hours for the greenish yellow color of the chlorine to disappear. Another sample of this  $9 \times 10^{-7}$  molar mercurous chloride solution was then saturated with hydrogen chloride gas in order to have both the oxidized and non-oxidized portions at the same concentration of hydrogen chloride. The mercuric chloride solution, *i. e.*, the oxidized portion, and the mercurous chloride solution, the non-oxidized portion, were then compared with regard to their catalytic effects.

The data reported were secured by the use of 50-cc. Nessler tubes. Two comparison tubes A and B were employed. The time at which a changing suspension becomes darker than an unchanging standard is more easily determined than the time at which reduction is complete. This required of course that the unchanging standard be less dense than the completely reduced experimental sample. The values obtained are shown in Table I. The times required to match the colors or densities of reference solutions A and B are expressed in minutes and seconds.

TABLE I

A COMPARISON BETWEEN THE CATALYTIC EFFECTS OF MERCUROUS AND MERCURIC CHLORIDE SOLUTIONS OF IDENTICAL CONCENTRATION

Tube	Cc.		Cc.		Cc.		Time for reduction	
	HgCl	HgCl <sub>2</sub>	HCl	SuCl <sub>2</sub>	As <sub>2</sub> O <sub>3</sub>	A	B	
1	10	0	35.5	2.5	2	3:40	6:55	
2	0	10	35.5	2.5	2	3:45	7:00	
3	10	0	35.5	2.5	2	3:36	6:58	
4	0	10	35.5	2.5	2	3:37	7:00	
5	10	0	35.5	2.5	2	3:30	6:56	
6	0	10	35.5	2.5	2	3:36	6:30	
7	0	0	45.5	2.5	2	11:00	19:40	

The concentration of the arsenious oxide solution was 0.001 *M*, of the stannous chloride approximately 8.0 *M*. Standard A consisted of completely reduced arsenious oxide in which the final concentration after dilution was 0.00001 *M*. Standard B had a final concentration which was double that of A.

The results show quite conclusively that mercuric and mercurous chloride solutions have equal catalytic power in the reduction of arsenic compounds with stannous chloride. They also suggest that the actual catalyst is the mercury atom formed by the reduction of the mercury salt.

Confirmation of the probability that free mercury was the catalytic agent, and not the mercury ions or its salts was established by a simple experiment. All that needed to be changed in the previous experiments was the order of adding the reagents. Instead of adding stannous chloride last, as had been the practice, it was added just after putting in the mercury salts, causing them to be reduced to free mercury. The arsenious oxide solution was added last. A glance at the values as shown in Table II shows that com-

(1) Original manuscript received May 9, 1938.

(2) King and Brown, *Ind. Eng. Chem., Anal. Ed.*, **5**, 168 (1933).

pletely reduced mercury is just as effective as the salt itself.

TABLE II  
A COMPARISON BETWEEN THE CATALYTIC EFFECTS OF MERCURIC CHLORIDE AND FREE MERCURY SOLUTIONS OF IDENTICAL CONCENTRATIONS

Tube	Cc. HgCl <sub>2</sub>	Cc. Fe-duced	Cc. As <sub>2</sub> O <sub>3</sub>	Cc. SnCl <sub>2</sub>	Cc. HCl	Time for reduction	
						A	B
1	15	0	2	2	31	4:30	8:55
2	0	15	2	2	31	4:14	8:50
3	10	0	2	2	36	5:34	10:22
4	0	10	2	2	36	5:12	10:28
5	5	0	2	2	41	6:58	12:55
6	0	5	2	2	41	6:44	12:30
7	1	0	2	2	45	10:10	18:30
8	0	1	2	2	45	10:08	18:40
0	0	0	2	2	46	12:20	19:40

Preliminary investigation of some other reactions which have been called induced reactions show that they are catalytic just as the modified Bettendorff test is catalytic. The investigation of these reactions will be continued.

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### The Preparation of *m*-Bromophenol

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The usual procedure involved in the replacement of an aromatic amino group by a hydroxyl group consists in warming an aqueous solution of the corresponding diazonium salt. This procedure, however, when applied to the preparation of *m*-bromophenol is quite unsatisfactory,<sup>1</sup> and the suggestion recently has been made<sup>2</sup> that this phenol is best obtained from *m*-bromoaniline through *m*-bromobenzenediazonium borofluoride and *m*-bromophenylacetate, the over-all yield in this series of three reactions being approximately 37.5%.

In the patent literature<sup>3</sup> it has been reported that *m*-bromophenol and the other *m*-halogenophenols can be prepared "in nearly quantitative yields" from *m*-halogenoanilines by the choice of the proper conditions for the hydrolysis of the corresponding diazonium sulfates. It has been found in this Laboratory that this patent claim is substantially true; by following the procedure described below one can obtain good yields (75-80%) of *m*-bromophenol rapidly and with a minimum expenditure of labor.

(1) Diels and Bunzl, *Ber.*, **38**, 1486 (1905).

(2) Smith and Haller, *THIS JOURNAL*, **61**, 143 (1939).

(3) English Patent 200,714 (1922); *Chem. Zentr.*, **96**, II, 2297 (1925).

### Experimental

*m*-Bromoaniline (50 g.) is dissolved by boiling in a mixture of water (400 ml.) and sulfuric acid (50 ml.). The solution is then cooled to 10° and diazotized by the addition of sodium nitrite (21 g.) dissolved in a small amount of water. The resulting diazonium salt solution is run in a thin stream during fifteen to thirty minutes into a boiling mixture of water (300 ml.) and sulfuric acid (100 ml.) contained in a flask fitted with a dropping funnel, a steam inlet tube reaching to the bottom of the flask, and an efficient condenser set for downward distillation. During the addition of the diazonium salt solution the acid solution is heated so that its volume remains constant, and steam is passed in at such a rate that at the end of the addition approximately 1 liter of distillate has been collected. Steam distillation is then continued until 2-liters of distillate has been collected. To this is added sodium chloride (150 g.), and the phenol is extracted with ether, using portions of 200, 100, and 100 ml. The ether is removed from the combined extracts and the product is distilled under reduced pressure.

Eight runs<sup>4</sup> of 50 g. each of *m*-bromoaniline gave 330 g. of crude *m*-bromophenol boiling at 100-140° (20-30 mm.). Redistillation gave 313 g. (77.8%) of *m*-bromophenol which boiled at 125-130° at 25 mm.

Treatment of this 313 g. of product with sodium hydroxide and methyl sulfate gave 285 g. of *m*-bromoanisole, b. p. 100° at 20 mm.

(4) The last five of the eight batches were steam distilled from the accumulating sulfuric acid and sodium sulfate solution whose volume was allowed to increase somewhat during the successive runs. No drop in yield resulted from this procedure.

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### The Melting Point of Barium Molybdate

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Barium molybdate, precipitated from an ammoniacal ammonium molybdate solution by adding aqueous barium chloride, washed until only a trace of chloride remained, charged into a platinum crucible that was placed in an electric furnace, then melted and cooled (7° per minute) in air, gave a cooling curve with a sharp break at 1480 ± 5° (platinum to platinum-10% rhodium thermocouple). This result confirms an earlier, less accurate, melting point determination, also made in air, in which an induction oil and an optical pyrometer were used. Attack of the platinum was absent or negligible, and there was no indication that the molybdate had been decomposed.

When melted in vacuum, the surface of the molybdate darkened, indicating partial decomposition, and some evaporation occurred; rough