

THE FORMATION OF CHLOROANILINE DURING REDUCTION OF NITROBENZENE

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Received August 17, 1939

It has long been known that the substitution of metallic zinc for the tin commonly used with hydrochloric acid in reducing an aromatic nitro compound to amine may introduce difficulties. Kock (1) found with nitrobenzene that nearly 25% of the quantity taken was diverted into monochloroanilines when zinc was used. With iron, no chloroaniline appeared. Apparently no explanation has been offered for the contrast in behavior of metals in such a reaction, and it is to this point that the present report is directed.

Bamberger (2) has shown that β -phenylhydroxylamine is rearranged in the presence of hydrochloric acid (through the possible intermediate *N*-chloroaniline) to give not *p*-aminophenol, but *p*-chloroaniline, which incidentally is the principal chlorinated by-product from the zinc process cited above. Accepting the assumption of Haber (3) that nitrobenzene is transformed into the hydroxylamine before the ultimate reduction to aniline, one finds no difficulty after all in accounting for the strange reaction in which a strong reducing agent seems to be able to replace hydrogen with chlorine. The proportions of aniline and chloroaniline obtained from the zinc process therefore depend largely upon the relative efficiencies of the two reactions, reduction and rearrangement, which compete for the transient supply of phenylhydroxylamine.

This plausible mechanism still offers no direct explanation of the fact that different metals yield greatly different fractions of chloroaniline. Accordingly, a long series of simple reduction experiments was carried out with numerous variations in choice of metallic reagent and conditions to suit various hypotheses.

EXPERIMENTAL

In each experiment a small sample of nitrobenzene was treated with concentrated hydrochloric acid and a quantity of metal somewhat more than the theoretical requirement to reduce the nitro compound completely to aniline. Reaction mixtures were usually cooled by hand in tap water. If the reduction was not complete, the excess of nitrobenzene was expelled from the acid solution by steam distillation. The aniline was isolated in the usual manner described in elementary manuals, save

that no final distillation was made, since it was desirable to preserve and sample the entire amine product for analysis.

Weighed samples of the aniline mixtures were heated in alcoholic sodium ethoxide, and chloride ion estimated in the resulting solutions by the Volhard method. The table shows the percentages of chloroaniline in the amine products in a group of significant experiments.

TABLE
CHLORINATED COMPOUNDS IN THE ANILINE PRODUCTS

METAL	PER CENT CHLOROANILINE	METAL	PER CENT CHLOROANILINE
Iron.....	0	Cu-Zn alloy (1.2% Cu) ..	3.9, 4.35
Tin.....	2.75, 3.47	Cadmium.....	23.1, 24.3
Tin, rod, rotated.....	7.5	Aluminum.....	No reduction
Zinc.....	26.07, 27.08	Calcium.....	No reduction
Zinc, rod, rotated.....	9.46, 11.46	Magnesium.....	No reduction
Zinc, rod, rot., temp. 25°.	2.6, 3.5	Magnesium, below 0°, (solid CO ₂).....	62.0, 66.4
Zinc-tin alloy (90% Zn) ..	23.06		
Zinc-tin alloy (10% Zn) ..	6.7		

Note.—Metals were in the form of mossy fragments, or turnings, except in three experiments, in which cylindrical rods of the metals were rotated rapidly in the acid solution by mechanical stirrer during the reactions.

These analytical values, like those of Kock, are at best only approximate. There were so many variables, such as purity, size and form of metallic fragments, temperature, concentration, methods of stirring and cooling, etc., that it was scarcely possible to line up the experiments by rigorous standards. Results with different metals were so widely variant, however, that general trends are evident.

The suggestion that certain metals have peculiar valence-shell configurations responsible for a specific, perhaps catalytic, effect on chlorination was rejected as intangible and improbable. Too many metals cause entry of chlorine. It seemed preferable to seek a correlation of chlorination behavior with some definite and known gradation of properties.

Admitting the existence of competition between the reactions of reduction and rearrangement one would naturally expect metals of high reduction potential to accelerate the former reaction and thus cut down the yield of chloroaniline. A comparison of the above table, however, with the electromotive series reveals no correlation which supports this hypothesis.

In like manner the theory that metals of high hydrogen overvoltage might effect reduction more rapidly, and thus minimize chlorination, met no better success, as tables of overvoltage will show. After all, any of the base metals under consideration has ample potential to effect any of the steps of reduction involved with nitrobenzene, and an explanation depending on thermodynamics is not convincing.

The fact that tin and iron exist as reducing agents in the form of ions of lower valence, while zinc does not, suggested the possibility of the better reduction in the former cases by such ions. Unfortunately, however, the addition of ferrous or stannous ions to a zinc-nitrobenzene reacting mixture does not prevent the chloroaniline reaction. Ferrous ion in particular seems to have no significance here.

Numerous additional variations, more or less backed by hypotheses, were tested without significant results. These introduced such features as organic solvents, impressed external electric potentials, high temperatures, amalgamated metals and metal powders. Although almost any variation affected chlorine content, the actual changes did not seem to be related in any consistent and convincing way to the specific variable chosen.

There is one correlation, however, which seems to be valid, namely: the fraction of nitrobenzene diverted into chloroaniline varies directly with the velocity of the reaction producing hydrogen gas. The tabular data for tin, zinc and magnesium illustrate this assumption consistently. This relation naturally suggests two postulates, (a) that the chloroaniline rearrangement is favored by a high rate of elimination of hydrogen ion, or (b) by an excessive output of hydrogen gas.

The well known fact that reduction of nitrobenzene stops at the hydroxylamine stage in neutral solution throws light on option (a) above. In a mixture of hydrochloric acid and metallic fragments there is one location where the neutral state is attainable, namely just at the surface of the metal, where the content of acid has been largely eliminated by the metal itself. The more active the metal, the more thorough this neutralization of the interfacial layer of electrolyte. Substantial quantities of phenylhydroxylamine should then be formed from the droplets of nitrobenzene which reach this layer. Agitation now removes part of the hydroxylamine to regions which are out of reach of the additional metal needed to complete the reduction. Such outer regions, while devoid of metal, contain ample hydrochloric acid which promptly effects the Bamberger rearrangement to chloroaniline. Less active metals, like iron, are unable to maintain the neutral zone, and accordingly the complete reaction to aniline proceeds smoothly with iron and nitrobenzene as prime reagents in close contact. This agrees with the common industrial knowledge that iron will reduce nitrobenzene in the presence of much less than the equivalent amount of hydrochloric acid.

Confirmation of this hypothesis of reduced activity is seen not only in the relatively high chloroaniline yield from active metals, but also from the experiments with rotated metallic rods. With zinc the sharply reduced yields of 9 to 11% suggest that the neutral zone of electrolyte tends to be forcibly stripped off, admitting more of the nitrobenzene globules to the active metal surface in the presence of strong acid. Continuation of the rotating rod technique, and reduction of temperature with consequent reduction in activity of the metal, virtually transforms zinc into a metal comparable with tin at a higher temperature, and the resulting figures of 2.6 to 3.5% show the added advantage.

Alloying of tin with zinc has no significance beyond an interpolative effect, but addition of a noble metal (copper) to the zinc is another matter. In the latter case the usual coating of copper mud promptly forms, and the undesirable reaction $2\text{H}_3\text{O}^+ \rightarrow \text{H}_2 \text{ gas} + 2\text{H}_2\text{O}$ occurs on the surface of copper instead of zinc, as in the voltaic cell. It is thus reasonable to expect less tendency for a neutral solution to form at the surface of the zinc. Zinc is free to react directly with nitrobenzene, and the amine product is almost all aniline, as shown in the table.

Postulate (b) is a question of reaction time. If a nitrobenzene molecule, in contact with a moderately active metal, does not have time to get beyond the phenylhydroxylamine stage before a lively outburst of hydrogen gas pushes it away, chloroaniline would naturally result. It would not matter whether a zone of neutral solution had been present. Zinc and cadmium are good illustrations.

If now an extremely active metal be chosen, such as magnesium, postulate (b) might predict so vigorous an evolution of hydrogen that nitrobenzene could not

even reach the metal surface. No reduction would occur, as indeed experiments indicate. As a test of this reasoning, the usual nitrobenzene-acid mixture was chilled with solid carbon dioxide until the reaction with magnesium was greatly retarded. A slow, inefficient and incomplete reduction of nitrobenzene was then attained. The high chloroaniline yield (62-66%) suggests that the magnesium was forced to play a rôle more like that of zinc, and that a large fraction of the nitrobenzene molecules was unable to maintain contact with the metal long enough to get past the phenylhydroxylamine stage.

Postulate (a) operates counter to (b) in the experiment of reduction with motor-driven rods. Since the motor action in the case of zinc actually causes a *lowering* of chloroaniline content, one is inclined here to credit postulate (a). With tin, however, rotation causes *greater* chloroaniline content. Tin is relatively inactive, and is scarcely able to maintain a neutral zone. Accordingly one may well expect the operation of the motor would enhance chlorination by the mechanism of postulate (b). It must be admitted at least that neither (a) nor (b) alone will explain experimental results in general.

We wish to thank Messrs. S. Tierney, L. S. Trimble, and V. Morgan for assistance in laboratory tests of various methods.

SUMMARY

The formation of chloroaniline as a by-product in the preparation of aniline from nitrobenzene in the usual manner apparently varies directly with the rate of the wasteful reaction of metal with acid to yield hydrogen. This correlation is explained by assuming either that a zone of neutral solution is maintained at the surface of a more active metal, hindering complete reduction of the nitro group, or that the excessive output of hydrogen drives the nitrobenzene away before it is completely reduced. Incompletely reduced molecules are then rearranged to *p*-chloroaniline. Experimental data are given showing the great differences in yields of chloroaniline.

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