

염기성 용액에서 니트로벤젠의 환원 메카니즘에 대한 고찰¹

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Mechanism of the Reduction of Nitrobenzene in Basic Solution¹

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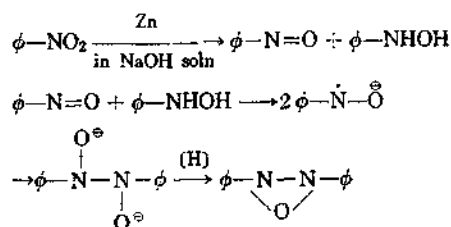
요 약. 염기성 용액에서 니트로벤젠의 환원에 대한 새로운 메카니즘을 제안하였다. 페닐히드록실아민이 중간체로서 관여하지 않고, 니트로소벤젠이 이합화(dimerization)하여 아록시벤젠으로 변환한다.

ABSTRACT. A new mechanism is proposed for the reduction of nitrobenzene in basic solution that does not involve hydroxylamine as an intermediate. This paper presents evidence that the azoxybenzene is not formed from the hydroxylamine, but formed instead from the dimerization of nitrosobenzene.

The partial reduction of nitrobenzenes to azoxy, azo, and hydrazo compounds is not only a valuable synthetic tool, but also one of long-known fundamental reactions. The currently accepted mechanism², however, does not fit into our observations. We wish to present some conclusions to account for the results.

The currently accepted mechanism² for the partial reduction of nitrobenzene is that one molecule of nitro compound is reduced to a nitroso compound and another to a hydroxylamine, and these two combines:

Scheme 1.



Evidences for the formation of nitrosobenzene and its radical anion have been demonstrated. The intermediate role of the hydroxylamine, however, is postulated based mainly on the results obtained with isotopically labeled compounds. When nitrosobenzene and phenylhydroxylamine are coupled, ¹⁸O, ¹⁵N labeling show that the two nitrogens and the two oxygens become equivalent.² These results were interpreted in terms of formation of nitrosobenzene and phenylhydroxylamine, followed by rapid condensation of these two intermediates as shown in Scheme 1.

The critical evidence against the involvement of phenylhydroxylamine is found in the reduction of nitrobenzene in the presence of phenylhydroxylamine. When the hydroxylamine is added at the early stage of the reduction of

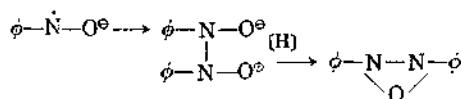
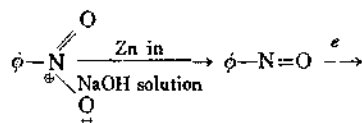
nitrobenzene, where nitrobenzene and azoxybenzene are two main spots on the TLC plate, the amounts of azoxybenzene are significantly reduced with concomitant increase of both nitrobenzene and hydrazobenzene on the TLC plate. These results are contrary to what may be predicted from the current mechanism (Scheme 1), and thus suggest that hydroxylamine is not a true intermediate in the reduction of nitrobenzene. The postulated role of phenylhydroxylamine as an obligatory intermediate may be not due to its reality, but to an experimental artifact in the formation of azoxybenzene from phenylhydroxylamine and nitrosobenzene.

It is well known³ that nitrosobenzene alone can give azoxybenzene under the same conditions.

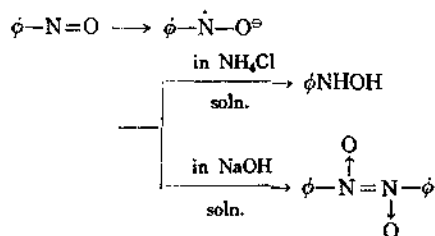
Based mainly on these two evidences, an alternative mechanism to the currently accepted reduction mechanism is proposed in Scheme 2.

The indirect evidence for the proposed mechanism may come from the findings⁴ that nitrosobenzene rapidly dimerizes to form azo-dioxy compound in aqueous sodium hydroxide solution. But, at lower pH such as in ammonium chloride solution, where dimerization is

Scheme 2.

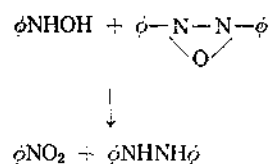


Scheme 3.



insignificant, instead protonation to the radical intervenes to form hydroxylamine (Scheme 3).

The reaction which is involved in the addition of phenylhydroxylamine during the course of reduction of nitrobenzene may be rationalized as follows.



EXPERIMENTAL

To a stirred solution of 8.4 g of sodium hydroxide in 18.5 ml of water and 50 ml of methanol was added 8.2 g of zinc powder. The solution was purged with nitrogen and heated at 80° for 2.5 hr. The solution showed mainly three spots corresponding to nitrobenzene, azoxybenzene, and azobenzene on the TLC using carbon tetrachloride. The spot corresponding to hydrazobenzene is barely visible on the TLC.

A small amount of phenylhydroxylamine⁵ was added at this stage under nitrogen atmosphere. The amounts of nitrobenzene and hydrazobenzene were instantly increased with concomitant decrease of azoxybenzene. After stirring for a further 2 hr, the solution indicated mainly azoxybenzene.

ACKNOWLEDGMENT

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