

STUDY ON BAUDISCH REACTION

Kazuhiro Maruyama, Iwao Tanimoto and Ryozo Goto

Department of Chemistry, Faculty of Science,

Kyoto University, Kyoto,

and

Kyoto Women's University, Kyoto,

Japan

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The one-step synthesis of o-nitrosophenols from benzene or substituted benzenes using the reagent which consists of aqueous hydroxylamine hydrochloride, hydrogen peroxide and copper(II) ion was developed about 25 years ago by Baudisch (1).

Baudisch (2) and Cronheim (3) have proposed a reaction mechanism in which copper(I) nitrosyl ion radical,  $\text{CuNO}^+$ , was supposed to play an important role as the nitrosation agent at first stage and then the hydroxylation at the ortho position to the nitrosated site would follow. Recently, Konecny (4) postulated another reaction mechanism suggesting nitrous acid to be a nitrosation agent of the phenol produced by the preliminary reaction between benzene and hydrogen peroxide in the presence of copper(I). Except these presuming reaction mechanisms, there has been no systematic investigation of the mechanism of Baudisch reaction.

With much interest in this one-step ortho nitrosohydroxylation and with some doubt about the mechanisms suggested by

these investigators, especially on their views of the role of copper(II) ion, the present authors reinvestigated the reaction and have come to the conclusion that none of their mechanisms are appropriate to explain our experimental findings described below (i-vi).

(i) The aromatics examined were benzene, toluene, chlorobenzene, anisole, phenetole, methyl p-tolyl ether, phenol, 2,3-, 2,5-, 2,6- and 3,5-xylenols, o-, m- and p-cresols, m- and p-chlorophenols. The reactivities of various aromatics to ortho nitrosohydroxylation in nitrogen atmosphere changed strongly in accordance with their structures. All of the aromatics which have no hydroxyl group showed lower reactivities than phenols. The difference in reactivity should not be ascribed to difference in solubility in water, as was suggested by Cronheim (3), because the similar inclination of reactivity was observed also in alcohols in which aromatic hydrocarbons and phenols dissolved completely.

(ii) Phenols reacted smoothly to give ortho nitrosophenols, whereas their ethers did not produce any appreciable amount of ortho nitrosophenolic compounds under the same conditions.

(iii) Contrary to Konecny's postulation (4), the rate of ortho nitrosohydroxylation of benzene was faster than that of hydroxylation of benzene by hydrogen peroxide in the presence of copper(II) ion.

(iv) Copper(I) chloride accelerated ortho nitrosohydroxylation of benzene under Baudisch's conditions, whereas no similar accelerating action was observed in the case of ortho nitrosation of phenol.

(v) The methyl group at the meta position to phenolic hydroxyl group exerted steric hindrance to nitrosation at the position between these two groups. That is, 6-nitroso-m-cresol was the exclusive product in ortho nitrosation of m-cresol under Baudisch's conditions, though both 2- and 6-nitroso-m-cresols could be expected. Therefore, the effect of steric hindrance may be responsible to the difference of reactivity among the xylenols. (See Figure 1).

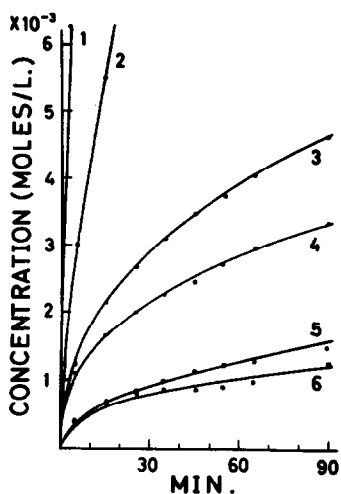


Figure 1. Rate of formation of o-nitrosophenolic compounds under Baudisch's conditions at 30°. (1) phenol, (2) 3,5-xylene, (3) benzene, (4) 2,3-xylene, (5) anisole, (6) 2,5-xylene.

reaction mechanisms involving the attack of cationic nitroso ion are hardly acceptable to Baudisch reaction.

(vi) The proportion of ortho nitrosophenol formed from phenol in Baudisch reaction was much higher than that of para isomer (o-/p- in ca. 20:1 ratio), while in usual nitrosation of phenol by nitrous acid para isomer predominated over ortho isomer (o-/p- in ca. 1:30), regardless of the existence of copper(II) ion. This unambiguous difference between the proportions of the two isomers in the above reactions clearly shows that the

From (i) to (vi), it may be concluded that the formation of phenolic compounds is essential in Baudisch reaction of aromatic hydrocarbons and that the hydroxylation of aromatic hydrocarbons proceeds through the decomposition of hydrogen peroxide catalyzed by copper(I) ion. The important role of hydroxyl group in Baudisch reaction and the steric effect of methyl group occupying the meta position to hydroxyl group suggest the intermediate formation of a bulky complex. Since the copper(II) ion tends to form the complexes with various amines, it might be assumed that the formation of a bulky complex between copper(II)-hydroxylamine complex and phenoxy ion is the essential requirement for the ortho nitrosohydroxylation. This assumption has another support from the fact that pentacyanoammine ferrate(II) complex ion, which is as effective as copper(II) ion for the exclusive ortho nitrosohydroxylation of benzene (5), can exchange its coordinating ammonia molecule for hydroxylamine.

Further investigation of the reaction mechanism is now in progress in our laboratories.

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