

Reduction Reactions of Halonitrobenzenes by Copper(I) in Hydrochloric Acid Medium

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The copper(I) promoted reduction of the nitro group, which always competes to a small extent with the copper(I) catalysed halogen exchange reactions in substituted halonitrobenzenes, studied by the author, has been subject to a closer study in this paper. A common step is suggested for the reduction of the nitro group and for the reductive dehalogenation, which in a few cases also is observed as a by-product in the halogen exchange mixtures.

In the dichlorocuprate(I) ion catalysed iodine-chlorine exchange reactions of 3-halo-2-iodonitrobenzenes in an aqueous hydrochloric acid-acetic acid medium about 5 % of dehalogenation products ($\text{ArI} \rightarrow \text{ArH}$) were detected,¹ but in the bromine-chlorine exchange reactions only traces were obtained and, moreover, only from 2-bromo-3-fluoronitrobenzene.² These observations are in full accord with the experience of Bacon and Wright,³ Fanta,⁴ and Nilsson and Björklund⁵ in connection with reactions in non-aqueous media. In the copper(I) catalysed exchange reactions of halonitrobenzenes in aqueous media another side reaction is striking, *viz.* the reduction of the *ortho* nitro group, which always accompanies the iodine- and bromine exchanges to an extent of about 2–3 %.^{1,2} In the case of 3-bromo-2-fluoronitrobenzene this reduction of the nitro group was the only copper(I) promoted reaction.⁶ The question is whether these two side reactions have a common intermediate. To test if a free radical mechanism could be prevailing, the 2-bromo-3-methylnitrobenzene was tested with some added initiators and inhibitors and was submitted to UV irradiation at 350 nm.

The 3-bromo-2-iodonitrobenzene was also irradiated.

RESULTS

An ESR spectrum of the exchange reaction mixture of 2-bromo-3-methylnitrobenzene gave no radical signal, but this does not exclude the possibility that radicals may have been present in low concentration. The addition of 1,4-benzoquinone to 2-bromo-3-methylnitrobenzene in the molar ratio 2:1, with other conditions the same as in the exchange experiment, seemed to cause no change in the exchange or the reduction rates at 90 °C, nor did 1,4-dihydroxybenzene in the proportions 1:1 to the substrate. *trans*-Azobenzene in the ratio 1:1 apparently destroyed the catalysing copper(I) complex and the halogen exchange was quenched.

When the degassed reaction mixture with copper(I) chloride present was subjected to irradiation at 350 nm for 2 h at about 30 °C, the reduction of the nitro group dominated over the bromine-chlorine exchange, which did not increase its rate compared to an experiment with copper(I) chloride in the dark at 30 °C. Without copper(I) chloride present and in the dark neither exchange nor reduction occurred.

When 3-bromo-2-iodonitrobenzene, which gave 5 % together of 3-bromonitrobenzene and 3-bromoaniline as by-products in its copper(I) catalysed iodine-chlorine exchange reaction,¹ was irradiated for 2 h at 350 nm in the absence of copper(I) chloride, dehalogenation and

traces of halogen exchange also occurred, but without irradiation of this solution no dehalogenation and no exchange were observed.

DISCUSSION

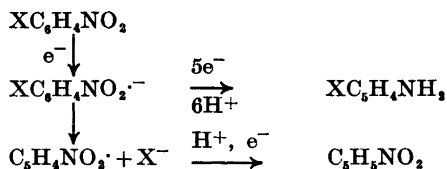
Judging from the results of the irradiation of 2-bromo-3-methylnitrobenzene at 350 nm (in this paper), and of 3-bromo-2-fluoronitrobenzene in a previous paper,⁶ some Cu(I) species seems to act as the electron donor in the observed reduction of the nitro group, which is accelerated by the irradiation. The aqueous hydrochloric acid – acetic acid medium can serve as the proton donor. The copper(I) catalysed dehalogenation observed in 2-iodonitrobenzenes¹ took also place with irradiation at 350 nm.

These observations suggest a free radical mechanism, but the possibility that the nitrobenzenes in their excited states resulting from absorption of radiation might react *via* an ionic mechanism cannot be excluded.

The photochemical reduction of nitrobenzene to aniline in 2-propanol-hydrochloric acid solution has been described by Hashimoto *et al.*⁷ It is proposed that the excited $n \rightarrow \pi^*$ triplet state abstracts a hydrogen from 2-propanol. Ayscough *et al.*⁸ have published ESR spectra of radical anions formed by the addition of an electron to the nitro compounds during chemical and photochemical reduction of a number of substituted nitrobenzenes in aqueous alcohols. Lagercrantz and Yhland⁹ reported that solutions of electron acceptors such as *m*-dinitrobenzene in donor solvents such as THF exhibit a photoinduced ESR signal. The spectrum is consistent with the formation of negative radical ions. Ito *et al.*¹⁰ reported electron transfer from a copper(I) isonitrile complex to nitrobenzenes, producing radical anions as seen from the ESR spectra. Danen *et al.*¹¹ used ESR to establish that the lifetime of electrochemically generated anion radicals of halogenated nitrobenzenes sharply decreases with increasing halogen atomic number. The 2-iodonitrobenzene anion radical loses iodide ion very rapidly and is converted into a nitrophenyl radical.

The over-all reduction of nitrobenzene *via* the radical anion to aniline involves six electrons and six protons. A common step is suggested for the copper(I) promoted reduction

of the nitro group and of the dehalogenation in 2-halonitrobenzenes in aqueous hydrochloric acid-acetic acid medium.



In this reaction scheme X = I or Br.

EXPERIMENTAL

Mass spectra were obtained with an AEI MS 20 instrument. The irradiation was carried out in a photochemical reactor Rayonet RPR-100 and the GLC with a Perkin Elmer F 11 Hot Wire Gas Chromatograph with a SE 30 column.

2-Bromo-3-methylnitrobenzene was prepared from 2-methyl-6-nitroaniline as described in Ref. 2. M.p. 40.0–41.5 °C.

3-Bromo-2-iodonitrobenzene was synthesized from 2-bromo-6-nitroaniline. See Ref. 1. M.p. 120.5–121.5 °C.

The reaction of the halonitrobenzenes with copper(I) chloride was performed in the medium and with the method described in Ref. 12.

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