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# The Cobalt-Catalysed Reduction of Aromatic Nitrogen Compounds by Sodium Borohydride*

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*The borohydride reduction of various aromatic nitrogen-containing compounds is catalysed by cobalt bromide and by bis(dimethylglyoximato) cobalt species. The products of reduction are investigated and the possible mechanisms for reduction discussed.*

## Introduction

Sodium borohydride is not a particularly strong reducing agent, and will not reduce, for example, aromatic nitro or azoxy groups[1] at all readily. However rapid reduction can be induced by various cobalt compounds. Vlček and Rusina[2] have observed that nitrobenzene and various derivatives are readily reduced in the presence of cobalt ion and bipyridyl, the active agent being tris(bipyridyl)cobalt(I). Hill and Williams[3] have observed that vitamin B12s will also catalyse the reduction of nitrobenzene, while Wagner[4] has reported that the nitro group in 10-nitrocobalamin is reduced by sodium borohydride. Sal'nikova and Khidekel'[5] have found that nitrobenzene is reduced by sodium borohydride in the presence of platinum and bis(dimethylglyoximato)cobalt(I). Green, Mawby and Swinden[6] have observed that 4-nitroso-N,N-dimethylaniline is readily converted to 4-amino-N,N-dimethylaniline by sodium borohydride in the presence of either cobalt bromide or *trans*-[aquobromobis(dimethylglyoximato)cobalt(III)]. The mechanisms of this last process are investigated here, a study having been made of the products formed on reducing nitrosobenzene, 4-nitroso-N,N-dimethylaniline, azoxybenzene, substituted azobenzenes, phenylhydroxylamine, hydrazobenzene and diphenylnitrosamine, of which only the first[7] is reduced at all readily by sodium borohydride in the absence of a catalyst.

## Results

The reactions studied are exothermic and go rapidly starting at room temperature, over a period of about five minutes, except in the cases of azobenzene and diphenylnitrosamine. The reduction products are listed in Table I. Reductions were carried out in either methanol or ethanol in the presence of either cobalt(II) bromide or *trans*-[aquobromobis(dimethylglyoximato)cobalt(III)] (hereafter referred to as the bromide and oxime systems).

In the bromide systems, sodium borohydride produced a black or grey precipitate, presumably either metallic cobalt or cobalt boride.[8] No similar precipitate was observed in the oxime systems probably because of the stability of bis(dimethylglyoximato)cobalt(I).[9]

The chief products of reduction of nitrosobenzene in the bromide case were azoxybenzene and azobenzene. The figures quoted refer to a 1:1 mole mixture of cobalt compound and nitrosobenzene, but variation of this ratio made only a small difference to the relative proportions of products. There was no indication of any complexing when nitrosobenzene and cobalt bromide were mixed prior to the addition of sodium borohydride. In contrast, 4-nitroso-N,N-dimethylaniline reacts quantitatively with cobalt bromide to give $(Me_2NC_6H_4NO)_2CoBr_2$.[6,10] Reduction of this complex or of mixtures of cobalt bromide and 4-nitroso-N,N-dimethylaniline (in ratios 1:1, 1:2 and 1:4) yielded 4-amino-N,N-dimethylaniline as sole product. No azo product could be detected when cobalt catalyst was present in only small quantity, or when only a little amount of borohydride was used on a 1:1 mixture. Only when a fifteen fold excess of the nitroso compound (relative to cobalt) was present, was there any evidence for the possible production of the azo compound.

Azoxybenzene and azobenzene were the chief products in the oxime catalysed reduction of nitrosobenzene. Though the figures quoted refer to a 1:1 mole mixture of cobalt compound to nitrosobenzene, the ratio of products is insensitive to this ratio. Again in contrast, reduction of 4-nitroso-N,N-dimethylaniline in the oxime system gave 4-amino-N,N-dimethylani-

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(*) Much of the work presented in this paper was reported at the Second Inorganica Chimica Acta Symposium held in Venice in August 1969.

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(4) F. Wagner, Chemical Society Symposium on Corrins (Nottingham), 1967.

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**Table I.** Products of reduction of aromatic nitrogen compounds using sodium borohydride and a cobalt complex as catalyst

| Starting material | Catalyst | Azoxybenzene $^{a}$ | Azobenzene $^{a}$ | Aniline $^{a}$ |
|---|---|---|---|---|
| Nitrosobenzene | br | 60% | 37% | 3% |
| | ox | 47% | 41% | 12% |
| 4-nitroso-N,N-dimethylaniline | br | | trace | $^{b}$ |
| | ox | | | $^{b}$ |
| 4-(N,N-dimethylamino)- and 4,4'-*bis*(N,N-dimethyl amino)-azobenzene | br | | | $^{b}$ |
| | ox | | | $^{b}$ |
| Azoxybenzene | br | | $^{b}$ | |
| | ox | | $^{b}$ | |
| Azobenzene | br | | no reduction | |
| | ox | | no reduction | |
| Hydrazobenzene | br | | | $^{b}$ |
| | ox | | | $^{b}$ |
| Phenylhydroxoxylamine | br | | | $^{b}$ |
| Diphenylnitrosamine | br | | diphenylamine (at 80°C) | |

$^{a}$ Or derivatives. $^{b}$ Principal product; br bromide system *i.e.* cobalt bromide; ox oxime system *i.e.* bis(dimethylglyoximato)-cobalt.

**Table II.** Substituted azo compounds reduced by sodium borohydride in the presence of cobalt bromide

| 3 | 4 | 2' | 4' | 5' |
|---|---|---|---|---|
| | $NMe_2$ | | | |
| | $NMe_2$ | | $NMe_2$ | |
| | OH | | | |
| | | OH | | Me |
| | Me | | OH | |
| | Me | OH | | Me |
| $CF_3$ | | | OH | |
| $CF_3$ | | OH | | Me |
| | Cl | | OH | |
| | Cl | OH | | Me |
| | $SO_3H$ | | $NMeCH_2Ph$ | |
| | OMe | | OH | |
| | OMe | OH | | Me |
| | OMe | Me | $NEt_2$ | |
| | $NO_2$ | | OH | |
| | $NO_2$ | OH | | Me |
| | $NO_2$ | $NMe_2$ | | Me |

line as the major product. A dark red crystalline compound is formed on mixing dimethylglyoxime, cobalt bromide and 4-nitroso-N,N-dimethylaniline, which could be an intermediate in the reduction process.[6] Indeed, the dark red compound undergoes comparable reduction.

In the reductions of azoxybenzene, azobenzene was the only identifiable product. The conversions were by no means complete, about 80% of the azoxybenzene remaining unchanged. The quantity converted did not appear to depend on the ratio of azoxybenzene to cobalt species. No reduction of azobenzene itself could be detected in either the bromide or the oxime system. However 4-(N,N-dimethylamino)azobenzene and 4,4'-bis(N,N-dimethylamino)azobenzene were reduced to anilines, although at least one mole of cobalt compound per mole of azo compound was needed in the first case to bring about complete reaction and rather more in the second. (Tests on the derivatives of azobenzene listed in Table II showed that they were all reduced by sodium borohydride in the bromide system. The products were thought to be anilines but this was not verified).

Reduction of hydrazobenzene gave aniline. (This observation is important as hydrazobenzene is easily oxidised to azobenzene particularly in the presence of a metal ion. It means that in cases where azobenzene is produced without any aniline, hydrazobenzene was not formed). The only product found in the bromide reduction of phenylhydroxylamine was aniline. Diphenylnitrosamine did not react in the bromide case at room temperature but on refluxing in ethanol, diphenylamine and ammonia were produced.

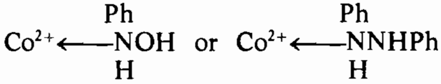
No reductions could be brought about using finely divided cobalt metal or, in contrast to some systems,[8] cobalt boride (formed by the action of sodium borohydride on cobalt bromide).[8]

## Discussion

The most surprising overall result is the speed of reduction. With the exception of nitrosobenzene,[7] reduction of aromatic nitrogen compounds with sodium borohydride is difficult or impossible. Of the reducing agents which do attack these compounds, many react slowly (as illustrated by several classical organic preparations). Two particular curiosities here are the absence of a reaction with hydrazobenzene and the reduction of azobenzene.

Hydrazobenzene is reduced to aniline, which is surprising in view of the fact that under alkaline conditions reduction of azobenzene by zinc or sodium stops at the hydrazobenzene stage.[11a] Moreover lithium aluminium hydride does not appear to reduce hydrazobenzene,[12] nor does sodium borohydride in the presence of palladium/charcoal.[13] These data suggest a necessity for both metal ion and hydride in order to achieve reduction (see later).

The failure of the cobalt systems to reduce azobenzene contrasts with the effect on hydrazobenzene, for other metallic systems, such as zinc and sodium in alkali, reduce the former but not the latter.[11a,b] The same is true of sodium borohydride but only in the presence of palladium/charcoal.[13] Titanium(III) reduces azobenzene in sodium acetate quantitatively in about three minutes.[14]

The catalysis by the cobalt compounds in the reactions considered here could occur in two ways: the nitrogen containing systems could be more easily reduced when complexed with cobalt, or the reducing entities could be cobalt(I) (or cobalt hydride) species. Support for the first suggestion is provided by the existence of the complexes of 4-nitroso-N,N-dimethylaniline, $(Me_2NC_6H_4NO)_2CoBr_2$ and $[(Me_2NHC_6H_4NO)CoBr(dmg)_2]Br$,[6] that can be isolated prior to reduction of the nitroso compound with sodium borohydride. Replacement of OH or NHPh by H in complexes such as  $Co^{2+}\longleftarrow \overset{Ph}{\underset{H}{N}}OH$ or $Co^{2+}\longleftarrow \overset{Ph}{\underset{H}{N}}NHPh$ involving an $S_N2$ attack by $H^-$ on the nitrogen atom, would be encouraged by the presence of $Co^{2+}$ acting as an acceptor:[15] phenylhydroxylamine appears to be reduced more readily here than in other systems,[11c] while a comment has already been made on the anomalous behaviour of hydrazobenzene.

Evidence for the second supposition comes from the various cobalt(I) species of moderate stability that have been prepared such as vitamin B12s, tris(bipyridyl)cobalt(I)[2] and bis(dimethylglyoximato)cobalt(I).[9] Vlček and Rusina[2,16] have suggested that the second of these reduces nitrobenzene by a one electron redox process, $Co^I \rightarrow Co^{II}$. An analogous process would be very reasonable for various reductions here such as $PhNO \rightarrow PhNO^{\cdot-}$. Though strictly one needs redox potentials in discussing thermodynamic reducing power, the polarographic reduction potentials[9b] around −0.95 volts (w.r.t. S.C.E.) for $Co^{II} \rightarrow Co^I$ for various bis(dimethylglyoximato)cobalt compounds point to a fairly strong reducing system. (However in the case of azobenzene there must be a kinetic barrier to reduction by the oxime system, as the substance is reduced by titanium(III), under conditions for which the $Ti^{IV} \rightarrow Ti^{III}$ half wave potential lies between −0.7 and −0.9 volts (w.r.t. S.C.E.)).[17a] A two electron transfer, $Co^I \rightarrow Co^{III}$, looks convenient for processes such as

$$PhN{:}N(O)Ph \longrightarrow PhN.N(O^{2-})Ph \xrightarrow[OH^-]{H^+} PhN{:}NPh$$

However cobalt(III) is very strongly oxidising in the bromide systems, while for the oxime case, half wave data[9b] point to a potential of about −0.55 volts (w.r.t. S.C.E ) for $Co^{III} \rightarrow Co^I$. Thus thermodynamically the one electron path is preferable to the two in both systems.

(Of the compounds discussed here, azobenzene, azoxybenzene and phenylhydroxylamine have half wave potentials between −0.6 and −0.8 volts; nitrosobenzene has a slightly value about −0.4 volts at the pH used here[17b]).

In sufficiently acid solutions, there is both potentiometric[9] and mechanistic[18] evidence that bis(dimethylglyoximato)cobalt(I) forms a hydride. (Hydrides will be represented CoH, without indication of oxidation state, to avoid polemics over the protonic character of the hydrogen). Involvement of a hydride would provide a convenient pathway for hydrogen transfer in reduction, *e.g.*

$$PhN{:}N(O)Ph + CoH \longrightarrow PhN{:}NPh + OH^- + Co^{III}$$

The low concentrations of cobalt hydride, as opposed to $Co^I$, that will exist in solutions as basic as those used, would account for the rather inefficient conversion of azoxybenzene to azobenzene. However a difficulty that arises in any hydrogen transfer process here is that although the oxime and bromide systems give similar products and product ratios (Table I), suggesting identical mechanisms of reduction, there is little evidence for a hydride species in the second case.

Although the discussion of mechanism is speculative more definite deductions can be made about routes of formation of compounds. Azobenzene could be formed by self-condensation of phenylhydroxylamine, condensation of nitrosobenzene and aniline, or the reduction of azozybenzene. Though the first reaction occurs in basic solution,[19] there is insufficient time for it to take place here to any significant extent. The second possibility can be excluded in both the bromide and oxime systems, as no methylated products (other than the starting material) could be found when the reductions were carried out in the presence of *p*-toluidine. Thus azobenzene must be formed by reduction of azoxybenzene.

Hydrazobenzene is readily reduced to aniline. It cannot, therefore be an intermediate in the reduction of nitrosobenzene or azoxybenzene as little or no aniline is formed in these processes.

Reduction of nitrosobenzene to azoxybenzene (and hence azobenzene) involves formation of an NN bond, which might occur either through the nitroso-

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(12) F Bohlmann, *Chem. Ber.*, *85*, 390 (1952).
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(16) See also A. Rusina, H. P. Schroer and A. A. Vlcek, *Z. anorg. allgem. Chem.*, *351*, 275 (1967).
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(18) G. N. Schrauzer and R. J. Windgassen, *J. Amer. Chem. Soc.*, *89*, 1999 (1967).
(19) E. Bamberger and F. Brady, *Ber.*, *33*, 271 (1900).

benzene dimer or condensation after initial reduction of the monomer. (Oxygen abstraction leading to a nitrene seems very unlikely).[20,21] A mechanism involving reduction of the dimer is attractive in that an NN bond already exists. It would also account for the fact that 4-nitroso-N,N-dimethylaniline, which does not dimerize, is not reduced to azoxy or azo compounds. However if the nitrosobenzene dimer were readily reduced, formation of $(\mathrm{PhNO})_2^{\cdot -}$ would be expected; this species does not appear to have been detected for example by e.s.r. spectroscopy in situations where it would have been formed if at all feasible.

As sodium borohydride reduces nitrosobenzene to azoxybenzene readily,[7] it is not clear whether the cobalt species act as catalysts. However cobalt(I) provides a one elctron reductant for the process, $\mathrm{PhNO} \rightarrow \mathrm{PhNO}^{\cdot -}$, which is known to occur in basic solution.[22] Work[23] on the condensation of nitrosobenzene and phenylhydroxylamine indicates that the radical anion, once formed, will dimerize and give azoxybenzene:

either

$$2(\mathrm{PhNO}^{\cdot -}) \rightleftharpoons (\mathrm{PhNO}^-)_2 \xrightarrow{\mathrm{H}^+} \xrightarrow{\mathrm{OH}^-} \mathrm{PhN{:}N(O)Ph}$$

or

$$\mathrm{PhNO}^{\cdot -} \underset{}{\overset{\mathrm{H}^+}{\rightleftharpoons}} \mathrm{PhNOH}^{\cdot} \xrightarrow{\mathrm{PhNO}^{\cdot -}}$$

$$\mathrm{PhN(O^-)N(OH)Ph} \xrightarrow{-\mathrm{OH}^-} \mathrm{PhN{:}N(O)Ph}$$

There is no need to invoke formation of phenylhydroxylamine in the main reactions, as the nitrosobenzene radical anion is favoured very much in the equilibria:[23]

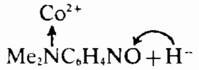
$$2(\mathrm{PhNO}^{\cdot -}) \rightleftharpoons \mathrm{PhNO} + \mathrm{PhNO}^{2-}$$

$$\mathrm{PhNO}^{2-} + 2\mathrm{H}^+ \rightleftharpoons \mathrm{PhNHOH}$$

Presumably the small amounts of aniline produced in the reaction of nitrosobenzene are formed by reduction of phenylhydroxylamine.

4-nitroso-N,N-dimethylaniline is different from nitrosobenzene in forming 4-amino-N,N-dimethylaniline on reduction rather than an azoxy or azo compound. Unlike the parent compound, 4-dimethylamino substituted azo compounds are reduced, so that some mechanism involving formation of azo compounds could occur whether this substituent is present or not. However the experiments performed on the 4-dimethylamino compounds under the following conditions suggest otherwise. Use of only a limited quantity of borohydride yields no 4-dimethylamino-azo compounds (for which the acidification procedure mentioned in the Experimental Section provides a very sensitive test). Therefore either they are not formed or else the azo groups are reduced very much more rapidly than the nitroso, which would be surprising. Reduction in the presence of a limited amount of cobalt bromide gives no azo compound. Again this would be surprising if azo compound were formed, as a relatively large quantity of cobalt bromide is needed for its reduction to be complete.

Invoking the donor character of the dimethylamino group illustrates how the possible paths suggested for the reduction of nitrosobenzene could be modified. The species $\mathrm{Me_2NC_6H_4NO}^{\cdot -}$ will be less stable than $\mathrm{PhNO}^{\cdot -}$, so that the radical anion dimerization process leading to an azoxy compound is less probable. It is tempting to suggest an alternative mechanism involving hydride atack on the cobalt(II) complexes:



$$\overset{\mathrm{Co}^{2+}}{\uparrow}\!\!\!\mathrm{Me_2NC_6H_4NO} + \mathrm{H}^-$$

followed by rapid protonation giving 4-dimethylaminophenylhydroxylamine and its subsequent rapid reduction to amine.

All the azo compounds which are reduced contain at least one donor group on one of their benzene rings (for the hydroxyl groups will be ionized under the conditions used). In these cases, cobalt complexes may be formed in which the azo group is more readily reduced. Support for this idea is provided by the fact that at least 1 mole of cobalt ion is needed for complete reduction of 1 mole of dimethylaminoazobenzene. The first cobalt ion reacts with the amino group giving a cobalt(II) ammine complex, while the second is responsible for attack on the azo group.

## Experimental Section

Several of the compounds studied are available commercially. 4,4′-bis-(N,N-dimethylamino)azobenzene was prepared by reduction of 4-nitroso-N,N-dimethylaniline with lithium aluminium hydride.[24] The remaining azo compounds were prepared by coupling of the appropriate compound with the diazotized aniline or aniline derivative.

Finely divided cobalt metal was prepared by the reduction of cobalt oxide with carbon monoxide at a temperature of about 700°C. Cobalt boride[5] was prepared by the action of sodium borohydride on an aqueous solution of cobalt(II) bromide. It was separated by means of a centrifuge, washed well with water, and ethanol, and stored under ethanol.

Reductions were carried out as follows. A methanolic solution of nitrogen containing compound was treated with a methanolic solution of cobalt compound and then with solid sodium borohydride (or vice versa). The order of mixing reactants did not affect the products significantly nor did substitution of ethanol for methanol. It seemed immaterial whether anhydrous $\mathrm{CoBr_2}$ or $\mathrm{CoBr_2 . 6H_2O}$ was used. In the oxime systems, cobalt was added as *trans*[aquobromobis(dimethylglyoximato)]cobalt(III). After about five minutes 20% aqueous sodium hydroxide was added and the mixture filtered where necessary. Organic products were extracted into chloroform or

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(23) G. A. Russell, E. J. Geels, F. J. Smentowski, K. Y. Chang, J. Reynolds, and G. Kaupp, *J. Amer. Chem. Soc.*, *89*, 3821 (1967)

(24) Organic Reactions, ed. by R. Adams, VI p. 506.

ether which was removed under vacuum, and identified by NMR and in some cases gas phase chromatography.

A sensitive test for the substituted azo compounds was provided by their indicator properties: in acid solution they absorb strongly between 500 and 700 mμ,[25] producing a colour and spectrum quite distinct from that of any cobalt(II) species.

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