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Disproportionation *vs.* Covalent Hydration of Cobaloxime(II) in Alkaline Media. A Reply to Comments by Schrauzer and Grate

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In a recent letter published in this Journal [1], Schrauzer and Grate commented on an earlier paper [2] in which a hitherto-unknown transformation of cobaloxime(II) in the presence of OH^- ions had been reported. This novel reaction is the covalent hydration of the C=N bond in coordinated dimethylglyoxime. The comments of Schrauzer and Grate reflect their failure to distinguish between experimental conditions leading to disproportionation and covalent hydration.

The main features of the two reactions will now be illustrated by uv–vis spectra recorded at different NaOH concentrations under otherwise identical conditions.

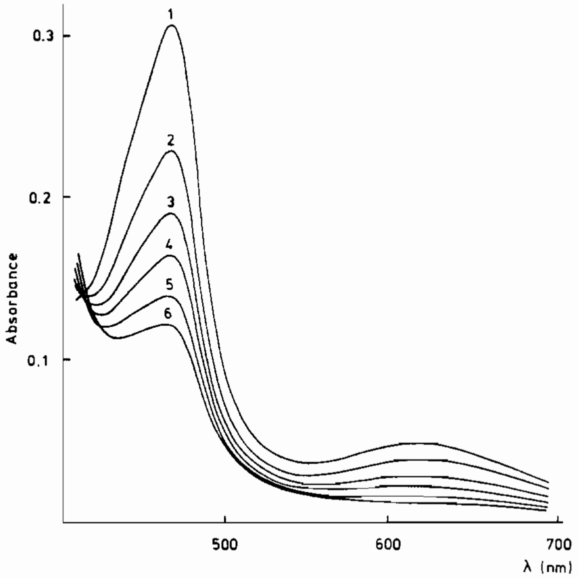

Fig. 1. Spectral changes for a 1×10^{-3} mol dm^{-3} cobaloxime(II) solution at 0.1 mol dm^{-3} NaOH (disproportionation observable). Solvent MeOH, room temperature, 1 mm cells, Ar atmosphere, scanning speed 4 nm/s. The scans were started at the following times after mixing: 1, 1 min; 2, 4.5 min; 3, 8.2 min; 4, 12 min; 5, 18 min; 6, 24.6 min.

Disproportionation of Cobaloxime(II)

Figure 1 shows the series of successive spectra obtained for 1×10^{-3} mol dm^{-3} $Co(Hdmg)_2$ in MeOH in the presence of 0.1 mol dm^{-3} NaOH. $Co(Hdmg)_2$, where $Hdmg^-$ is the monoanion of dimethylglyoxime, was prepared *in situ* from cobalt(II) perchlorate, dimethylglyoxime and the required amount of NaOH under Ar atmosphere in a suitable vessel, one arm of which was a spectrophotometric cell. Excess NaOH was added to the vessel, then the cell was sealed and transferred into a Beckman ACTA MIV spectrophotometer. The first spectrum reveals a wide band at *ca.* 620 nm, characteristic of cobaloxime(I) formed via disproportionation of cobaloxime(II):

$$2Co^{II}(Hdmg)_2 + OH^- \longrightarrow Co^{I}(Hdmg)_2^- + Co^{III}(Hdmg)_2OH \qquad (1)$$

Subsequently, both the 620 nm band and the one at 470 nm, characteristic of cobaloxime(II), decrease. The crossing of spectra at about 410 nm is not a true isosbestic point, consequently at least one additional process other than reaction (1) is occurring. Since the first scan of the 620 nm band took place *ca.* 1.5 min after mixing, the maximum transient cobaloxime(I) concentration is higher than that reflected by spectrum 1 in Fig. 1. The disappearance of cobaloxime(I) is too fast to be assigned to the hydrogenation of coordinated $Hdmg^-$, a reaction analyzed in detail earlier [4]. Only extremely small amounts of hydridocobaloxime(III) can be present in strongly basic solutions. Upon neutralization, hydridocobaloxime(III) is formed from all cobaloxime(I) via fast protonation, but due to its instability, it rapidly decomposes [3, 4] to H_2 and cobaloxime(II):

$$Co^{I}(Hdmg)_2^- + H^+ \longrightarrow HCo^{III}(Hdmg)_2 \longrightarrow 1/2H_2 + Co^{II}(Hdmg)_2 \qquad (2)$$

Thus, disproportionation (1) can be unambiguously detected by observing the 620 nm band and the blue-green colour of the solution. It takes place if the excess of NaOH is *ca.* 0.1 mol dm^{-3} or higher.

Covalent Hydration of Cobaloxime(II)

Figure 2 illustrates the series of successive spectra for 1×10^{-3} mol dm^{-3} $Co(Hdmg)_2$ in MeOH under Ar, containing 0.039 mol dm^{-3} NaOH. The very weak absorbance in the vicinity of 620 nm clearly shows that only minor amounts of cobaloxime(I) are formed. Strong changes are, however, observed in the 470 nm band and a well-defined isosbestic point

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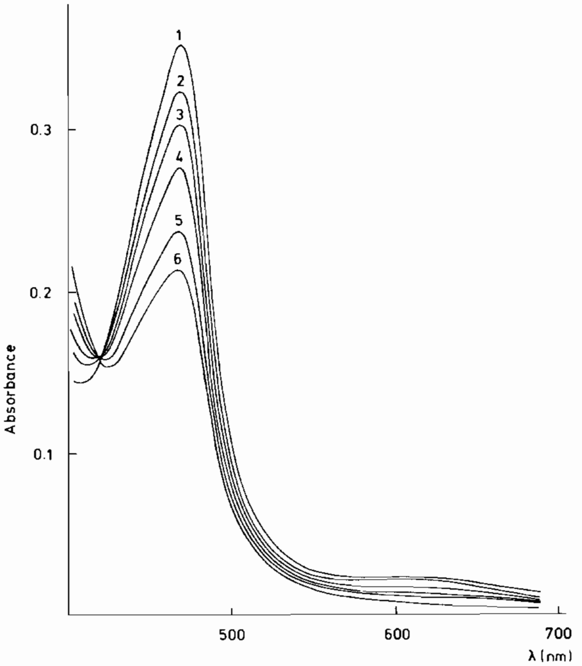

Fig. 2. Spectral changes for a 1×10^{-3} mol dm^{-3} cobaloxime(II) solution at 0.039 mol dm^{-3} NaOH (disproportionation *not* observable). Solvent MeOH, room temperature, 1 mm cells, Ar atmosphere, scanning speed 4 nm/s. The scans were started at the following times after mixing: 1, 1 min; 2, 4 min; 3, 8 min; 4, 17 min; 5, 38 min; 6, 61 min.

appears at 420 nm. The spectra of Figs. 1 and 2 unequivocally demonstrate that the character of spectral changes depends on the NaOH concentration. Disproportionation is not detectable at $(4.0–20.0) \times 10^{-3}$ mol dm^{-3} NaOH [2], but the cobaloxime(II) spectrum nevertheless changes with time. The behaviour reflected in Fig. 2 has been subjected to kinetic analysis [2] and interpreted in terms of covalent hydration of the C=N bond in coordinated $Hdmg^-$:

$$Co^{II}(Hdmg)_2 + OH^- + H_2O \longrightarrow [Co^{II}(Hdmg)(Hdmg,H_2O)OH]^- \qquad (3)$$

where $(Hdmg, H_2O)$ denotes the ligand $[HO{-}N{=}C(CH_3){-}\underset{OH}{\underset{|}{C}}(CH_3){-}NH{-}O]^-$, a monoanion formed from $Hdmg^-$ via addition of H_2O across one of the C=N bonds [2]. Covalent hydration has been reported for coordinated phenanthroline and bipyridine [5]. Neutralization of the solution after reaction (3) has gone to completion leads to immediate regeneration of more than 98% of the starting $Co(Hdmg)_2$. The absence of significant losses shows that no cobaloxime(III) has been formed, *i.e.* eqn. 3 is consistent with the experimental results. Additional evidence in favour of (3) is provided by the gradual replacement of the characteristic ESR spectrum of cobaloxime(II) by a spectrum indicating decreased symmetry. Also product *A*, being a cobalt(II) derivative is sensitive to dioxygen, as witnessed by the colour change upon exposure to air. Reaction (3) takes place to some extent also under the conditions of Fig. 1, resulting in the blurring of the isosbestic point.

Upon neutralization, *A* reacts as follows:

$$A \xrightarrow{H^+} Co^{II}(Hdmg)_2 + 2H_2O \qquad (4)$$

Careful comparison of the conditions used in refs. [2] and [1] makes it abundantly clear that different reactions occur under the two sets of conditions. Characteristically, the NaOH concentration used in ref. [1] to produce disproportionation was 0.33 mol dm^{-3} at a cobaloxime(II) concentration of 1.66×10^{-3} mol dm^{-3}. It is not surprising that the nearly 15 times lower NaOH concentrations employed in ref. [2] lead to a profound change in the reaction pattern observed.

The authors of ref. [1] incorrectly assume that the sole objective in ref. [2] was to reproduce the procedure recommended by Schrauzer and Windgassen [6] for the preparation of diaquacobaloxime(II) using cobalt(II) acetate. Cobalt(II) perchlorate is equally suitable for *in situ* preparations, as confirmed by the results of Schrauzer and Grate [1]. The difference in anions has nothing to do with the different behaviour observed in refs. [2] and [6].

Additionally, the authors of the comments [1] mistakenly seem to believe that no base was added for the conversion of H_2dmg to $Hdmg^-$ in ref. [2]. In fact, the reaction was carried out with an excess of NaOH present. The starting spectrum in Fig. 1 of ref. [2] clearly shows full formation of cobaloxime(II), which is only possible if the required amount of base is present.

The different reactions observed in refs. [2] and [1, 6] are due to the different concentrations of excess NaOH rather than to the assumed nonconformity with the suggested procedures.

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