# Concerning the Disproportionation of Cobaloximes(II) in Alkaline Media: Comments to a Paper by Simándi *et al.*

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In a recent paper appearing in This Journal [1], Simándi *et al.* reported on a failure to demonstrate the disproportionation of cobaloximes(II) on reaction with alkali in terms of reaction eq 1, where Hdmg denotes the monoanion of dimethylglyoxime:

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

Reaction eq 1 was originally discovered in 1966 [2]; it has since been used extensively for the synthesis of organocobaloximes [2–4]. Nevertheless, Simándi *et al.* are now casting doubt on the early findings and claim that a completely new interpretation of the reaction of cobaloximes(II) with base is necessary [1]. We wish to point out that the difficulties experienced by the authors could have been avoided through the selection of the proper reaction conditions. Although Co(II) acetate has been specifically recommended [2, 5] for the synthesis of diaquocobaloxime(II), Simándi *et al.* in their experiments employed cobalt(II) perchlorate instead and claimed that the cobaloxime(II) was generated *in situ* by mixing methanolic solutions of the two components. However, if the perchlorate is used, the formation of the cobaloxime(II) is quantitative in methanol only upon the addition of an equivalent amount of base! Morever, in the original demonstration [2] of a cobaloxime(II) disproportionation reaction, strong base (*e.g.* 1 *M* NaOH) was used. In contrast, the authors of Ref. [1], employed NaOH in the concentration range between $10^{-3}$ and $20 \times 10^{-3}$ *M*, too low for the disproportionation to occur to a measurable extent. It should also be noted that the cobaloxime(I) species are intrinsicly short-lived species which may decompose by spontaneous hydrogen evolution, ligand self-reduction, *etc.*

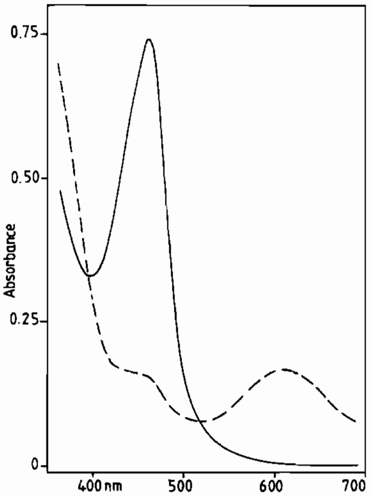

Fig. 1. Spectra of cobaloxime solutions in a 1 mm path length cuvette containing 100 μL of methanolic 5 m*M* cobalt(II) perchlorate and 100 μL methanolic 10 m*M* dimethylglyoxime. Spectra were recorded immediately after the addition of (a) 5 μL of 1 *N* NaOH (——) and (b) an additional 95 μL of 1 *N* aqueous NaOH (– – –), at 23 °C.

Figure 1 shows the spectrum of cobaloxime(II), prepared from cobalt(II) perchlorate, dimethylglyoxime and dilute base, and the spectrum recorded immediately after the addition of a sufficient amount of 1 *N* NaOH. The characteristic [6] low-energy absorptions of the cobaloxime(I) appear rapidly but gradually disappear even under strictly anaerobic conditions, for reasons stated above. From the observed absorbance near 620 nm the yields of cobaloxime(I) are quantitative in terms of the stoichiometry of eq 1.

## References

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