On the Mechanism of Base-catalysed Alkane-forming Reactions of Simple Alkylcobaloximes

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Summary From the time dependence of the formation of monodeuterioalkanes in D_2O, and related isotopic labelling experiments, the base-catalysed alkane-forming reactions of ethyl- and methyl-(aquo)cobaloximes have been found to occur *via* different mechanisms.

RECENT publications[1–4] have pointed out substantial differences between the base-catalysed alkane-forming reactions of methyl- and ethyl-cobaloximes. Thus, while methylcobaloxime decomposes in 1·0 M aqueous KOH at 50 °C to produce 70% of methane and a base-stable, photolabile methylcobalt side-product in 30% yield,[1,2] ethylcobaloxime yields a mixture of ethane and ethene (ratio 5·6 : 1) but no side-product.[3] Furthermore, methane formation is some 22·5-fold faster than ethane formation from the alkyl(hydroxo)cobaloximes.[2,3] Also, while various N- and S-donating axial ligands depress the rate of methane formation by at least four orders of magnitude,[2] various ethyl(ligand)cobaloximes are of comparable reactivity to ethyl(hydroxo)cobaloxime,[4] the ethyl complexes being at least 100- to 650-fold more reactive towards alkane formation than the methyl complexes. These observations suggest that these reactions may occur *via* different mechanisms.

Although monodeuterioalkanes of high isotopic purity are obtained when either reaction is performed in D_2O, it is not clear whether the emerging alkyl fragments abstract an additional hydrogen from the solvent or from the cobaloxime equatorial methyl groups, the latter being known to exchange with solvent deuterons under basic conditions.[3,5,6] However, since the exchange reaction is base-dependent,[5] it should be possible to observe time dependence of monodeuterioalkane formation, if such exists.

At 50 °C in 0·10 M NaOD in D_2O,† ethylcobaloxime was found to undergo deuterium exchange with the equatorial methyl groups with a rate constant of $1{\cdot}47 \pm 0{\cdot}05 \times 10^{-4}$ s^{-1} ($t_{1/2}$ 79 min).‡ Time-resolved mass spectral analysis§ of the isotopic composition of the ethane product under these conditions (Figure, ●) shows a substantial time dependence for the formation of monodeuterioethane, the data roughly fitting an exponential function with a time constant of $1{\cdot}2 \times 10^{-4}$ s^{-1} ($t_{1/2}$ *ca.* 96 min) and a zero intercept of 0·39. This suggests that about one third of the emerging ethyl fragments are protonated by solvent, the remainder receiving their additional hydrogen atom from the equatorial methyl groups. To prove that this is the case, ethyl(aquo)cobaloxime extensively deuteriated in the equatorial methyl groups (95·5 atom-% D) was prepared¶ and decomposed in D_2O under the same conditions. The isotopic composition of the ethane product was time-independent (Figure, ■) and at an average of $92{\cdot}1 \pm 2{\cdot}1$% monodeuterioethane.

† Ionic strength 1·0 M maintained with KCl. All OD^- concentrations are for free OD^- as calculated from the added amounts of NaOD and cobaloxime and the measured dissociation constants for the alkyl(deuterioxo)cobaloximes [$0{\cdot}716 \pm 0{\cdot}0036$ M for ethyl[3] and $0{\cdot}0387 \pm 0{\cdot}0015$ M for methyl (this work)] at 50·0 °C, determined spectrophotometrically as described previously.[7]

‡ Varian T-60 n.m.r. spectrometer, determined as described previously.[3]

§ Mass spectral measurements were made on a DuPont Model 321 g.c.–m.s. system equipped with a 6 ft × 1/8 in Poropak Q column for ethane analysis or a 6 ft × 1/8 in molecular sieve 5A column for methane analysis. At a carrier flow rate of 28 ml/min, the retention times were about 5·3 min for ethane (ambient temperature) and about 2·0 min for methane (50 °C). Samples for mass spectral analysis were prepared in 1·0 ml Reactivials (Pierce) as previously described[3] and gassed with argon for 1 h at 0 °C. After sealing, the vials were incubated at 50 °C for the required time, then rapidly cooled and maintained at 0 °C until analysis the same day. Standard samples of CH_3D and CH_3CH_2D were prepared fresh daily by reaction of methylmagnesium iodide or ethylmagnesium bromide with D_2O (Merck, 99·7 atom-% D).

¶ Ethyl(aquo)cobaloxime (2·0 g) was stirred under argon at 50 °C in 40 ml of 0·35 M NaOD, ionic strength 1·0 M (KCl), for 21 h. After cooling, the solution was neutralized with 6 M DCl and evaporated to *ca.* 20 ml to produce 0·99 g of red crystals. Addition of pyridine to the supernatant produced 0·22 g of a yellow powder. The deuterium content was determined by ^{1}H n.m.r. measurements on the pyridine complex in $CDCl_3$.

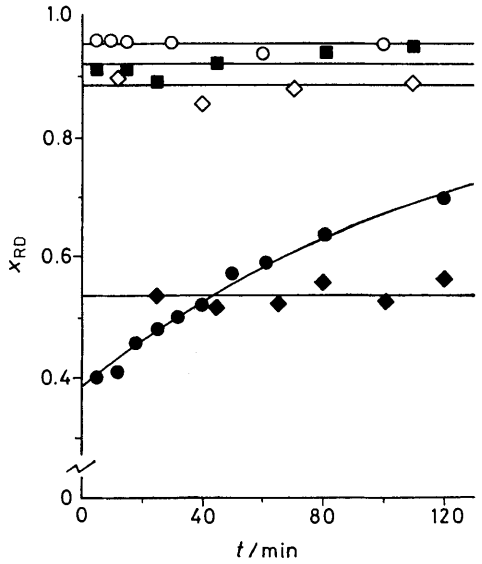

FIGURE. Plots of the mole fraction of monodeuterioalkane, x_{RD}, in the alkane product from the base-catalysed decomposition of alkyl(aquo)cobaloximes, $RCo(dmgH_2)OH_2$ (H_2dmg = dimethylglyoxime), in deuteriated solvents at 50 °C, 0·10 M NaOD, ionic strength 1·0 M (KCl), *vs.* time. ●, R = CH_3CH_2 in D_2O; ■, R = CH_3CH_2, 95·5 atom-% D in the equatorial methyl groups (see text), in D_2O; ◆, R = CH_3CH_2, 95·5 atom-% D in the equatorial methyl groups (see text), in D_2O–CH_3OD (50% v/v); ○, R = CH_3, in D_2O; ◇, R = CH_3, in D_2O–CH_3OD (50% v/v).

These data are reminiscent of Schrauzer's results on the anaerobic photolysis of methylcobaloxime in D_2O,[8] a reaction which clearly occurs *via* homolytic, or mode II,[2] carbon–cobalt cleavage. The mixtures of methane and monodeuteriomethane obtained were attributed to competition between hydrogen abstraction from the equatorial methyls and reduction of the methyl radical by the cobalt centre followed by protonation of the resulting methyl carbonion by solvent. To provide further evidence for a homolytic, or mode II, mechanism for base-catalysed ethane formation from ethylcobaloxime, the extensively deuteriated material was decomposed in 0·1 M NaOD in D_2O–CH_3OD (50% v/v). Again, the isotopic composition of the ethane product was time-independent, but the average composition was 53·7 ± 2·3% monodeuterioethane (Figure, ◆), demonstrating that solvent methyl hydrogens can successfully compete with equatorial methyls for donation of a hydrogen to the emerging ethyl fragment. It must be concluded that the reaction occurs *via* a homolytic dissociation of the carbon–cobalt bond and that the ethyl radical is converted into ethane by the competing processes of hydrogen abstraction from the equatorial ligand and/or radical reduction by the metal followed by protonation by solvent.

Under the same conditions as above, the composition of monodeuteriomethane from methylcobaloxime was found to be time-independent (Figure, ○) at an average of 95·5 ± 1·0 atom-% D despite the fact that deuterium exchange into the equatorial methyls had a half-life of 160 min‡ (*i.e.* two-fold slower than the ethyl complex). Furthermore, when decomposed in D_2O–CH_3OD (50% v/v), the isotopic purity of the resulting monodeuteriomethane was only slightly lowered to 88·1 ± 2·0% (Figure, ◇). These results are completely inconsistent with Schrauzer's results[8] for the homolytic dissociation of the carbon–cobalt bond of methylcobaloxime induced by light. It must be concluded that radicals are not involved in base-catalysed methane formation and that the reaction proceeds *via* a mode III[2] cleavage to form a methyl carbanion and a cobaloxime(III) species.

It is conceivable that the failure of methylcobaloxime to react *via* the homolytic mechanism is due to the extremely high rate of radical recombination for methyl radicals and cobaloxime(II) (k_2 *ca.* 5—8 × 10^7 mol^{-1} s^{-1} at 25 °C),[9] the relevant rate constant for ethyl radicals not having been measured. However, the failure of ethylcobaloxime to react *via* mode III cleavage is, at present, unexplainable.

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