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Base-Catalyzed Heterolysis of Methyl(aquo)cobaloxime

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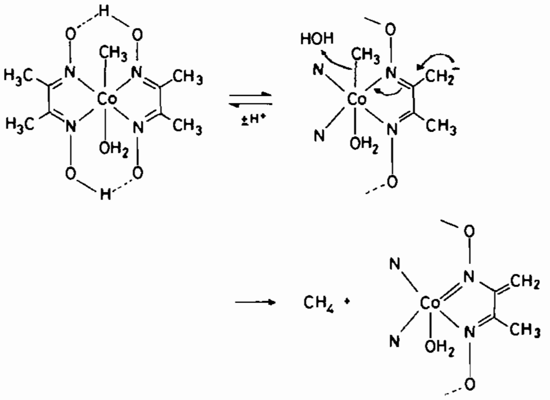
In previous publications [1, 2] it was reported that $CH_3Cl(D_2H_2)HOH$ [1, 3] and, in fact, all simple alkyl(aquo)cobaloximes [2, 3] undergo uv and visible spectra changes in aqueous base indicative of carbon–cobalt bond cleavage to yield a cobalt(III) complex. I would now like to report that the organic product of this reaction for $CH_3Co(D_2H_2)HOH$ is methane. Methane was detected in the atmosphere above samples containing *ca.* 1.67 × 10^{-3} *M* $CH_3Co(D_2H_2)HOH$ in 1.0*N* aqueous KOH at 50 °C both by glpc [4] and mass spectral analysis [5]. When the reaction was run in D_2O (1.0*N* in NaOD) the product was monodeuteromethane of high isotopic purity (Table). When $CD_3Co(D_2H_2)HOH$ [6] was decomposed in 1.0*N* aqueous KOH the product was trideuteromethane while in D_2O (1.0 *N* in NaOD) tetradeuteromethane was obtained (Table).

This base catalyzed heterolysis was quantitated manometrically using Warburg manometers [8, 9]. In all cases (Table) the yield of methane was less than stoichiometric, the average yield for the decomposition of $CH_3Co(D_2H_2)HOH$ in aqueous KOH being 68.8 ± 2.6% (average of nine determinations). The yield was independent of cobaloxime concentration over the range *ca.* 5.0 × 10^{-4} to 5.0 × 10^{-3} *M*. Lowering the temperature to 25.0 °C also had little or no effect on the yield of methane. However, in all cases, subsequent photolysis of the reaction mixtures [10] after completion of the base catalyzed reaction produced an additional quantity of methane [11] such that the combined base-catalyzed and photolytic yields were essentially stoichiometric (Table). These observations indicate that the base-catalyzed reaction does not convert significant amounts of the organic ligand to any product other than methane.

Significant amounts of methane were detected (by glpc [4]) above samples incubated under air effectively ruling out a homolytic carbon–cobalt cleavage mechanism leading to methyl radicals, although other radical processes cannot be ruled out by these observations. Cartaño and Ingraham [12] have shown that the equatorial methyl groups of $CH_3Co(D_2H_2)HOH$ are acidic and undergo exchange with solvent protons in alkaline DMSO–d_6–D_2O mixtures at 35 °C at a rate that is twice as fast as methane formation at 50 °C. These results suggest the following heterolytic mechanism for methane formation although other heterolytic mechanisms are, of course, possible.



To obtain evidence regarding the involvement of equatorial methyl proton dissociation in methane formation an attempt was made to decompose methyl bis(diphenylglyoximato)aquocobalt(III) [13]. After 284 hr at 50 °C in 1.0*N* KOH, 20.0 ± 2.0 μl of gas were evolved or 9.4 ± 1.0% (based on cobalt, average of two samples). However, the boron difluoride bridged derivative, $CH_3Co(D_2B_2F_4)HOH$, reacted to produce a 78.1 ± 1.8% yield of methane with an apparent first order rate constant of 3.03 ± .08 × 10^{-6} s^{-1} under the same conditions. While these observations are consistent with the mechanism shown above, other explanations are also possible.

To my knowledge this is the first example of an apparent heterolytic carbon–cobalt solvolysis to a cobalt(III) complex and a carbanion-like organic fragment for a simple organo-cobalt complex. In all previous examples of this mode of carbon–cobalt cleavage the organic ligand is activated either by the presence of a leaving group on the β-carbon (in which case olefins are formed) [16] or a keto group on the β-carbon (so that enols may be formed) [17].

The nature of the yield-limiting side reaction is not yet clear, although the results in the Table show that it is *not* second order in cobaloxime and apparently does *not* lead to carbon–cobalt bond cleavage. Presumably some base-induced alteration of the equatorial ligand system renders a significant fraction of the organocobalt complex inert to the base-catalyzed heterolysis, either by preventing equatorial ionization or deactivating the carbon–cobalt bond for heterolytic cleavage.

The effects of various axial ligands on the base-catalyzed heterolysis described herein as well as the nature of the yield-limiting side reaction are currently under investigation and will be the subject of a forthcoming report.

TABLE. Products, Yields and Rate Constants for the Formation of Methane from Methyl(aquo)cobaloxime in 1.0 *N* Aqueous Base.

Compound	Concentration (*M*)	Temperature (°C)	Base (solvent)	Product	Min. Isotopic[a] Purity (%)	k_{obs}[b] (s^{-1})	Base-Cat.[c] Yield (%)	Photolysis[c] Yield (%)	Total[d] Yield (%)
$CH_3Co(D_2H_2)HOH$	1.68×10^{-3}	50	KOH (H_2O)	CH_4	–	$1.86 \pm .14 \times 10^{-4}$ [e]	68.6 ± 2.7[e]	23.8 ± 2.0[f]	92.4 ± 4.7
$CH_3Co(D_2H_2)HOH$	4.97×10^{-3}	50	KOH (H_2O)	CH_4	–	$1.84 \pm .09 \times 10^{-4}$	73.1 ± 2.4	–	–
$CH_3Co(D_2H_2)HOH$	5.00×10^{-3}	50	KOH (H_2O)	CH_4	–	$1.82 \pm .03 \times 10^{-4}$ [f]	68.7 ± 3.0[f]	23.3 ± 0.9	92.0 ± 3.9
$CH_3Co(D_2H_2)HOH$	1.67×10^{-3}	25	KOH (H_2O)	CH_4	–	$2.55 \pm .08 \times 10^{-5}$	66.6 ± 2.0	–	–
$CH_3Co(D_2H_2)HOH$	1.67×10^{-3}	50	NaOD (D_2O)	CDH_3	94	$7.76 \pm 0.34 \times 10^{-5}$ [f]	77.1 ± 1.4[f]	19.4 ± 0.7	96.5 ± 2.1
$CD_3Co(D_2H_2)HOH$	1.67×10^{-3}	50	KOH (H_2O)	CD_3H	95	$1.47 \pm .06 \times 10^{-4}$	69.7 ± 1.7	27.3 ± 3.5	97.0 ± 5.2
$CD_3Co(D_2H_2)HOH$	1.67×10^{-3}	50	NaOD (D_2O)	CD_4	94	$1.13 \pm .02 \times 10^{-4}$	70.5 ± 0.4	27.9 ± 1.9	98.4 ± 2.3

[a] By mass spectral analysis. See footnote 5. [b] Slope of plots of ln ($V_\infty - V_t$) *vs.* time, where V_∞ is the volume of CH_4 liberated (STP) after completion (at least six half-times) and V_t is the volume of CH_4 (STP) liberated at time t. [c] From manometric experiments. [d] Sum of the base catalyzed and photolysis yields. [e] Average of 5 determinations. [f] Average of 2 determinations.

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3 Abbreviations: $CH_3Co(D_2H_2)HOH$ = methyl(aquo)bis(dimethylglyoximato)cobalt = methyl(aquo)cobaloxime; $CD_3Co(D_2H_2)HOH$ = trideuteromethyl(aquo)cobaloxime.

4 10 ft. × 1/8 inch porapak Q, column temperature 50 °C, carrier flow 37.5 ml/min, retention time for methane was 52s.

5 Mass spectral samples (total vol 10 ml) contained 1.67×10^{-3} *M* cobaloxime and 1.0*N* aqueous base. They were placed in glass bulbs fitted with teflon stopcocks, frozen in liquid nitrogen, evacuated to 5×10^{-3} Torr, sealed, and allowed to thaw. The freeze–pump–thaw cycle was repeated twice. The samples were then incubated in the dark at 50 °C for 16 hr, frozen in liquid nitrogen and the atmosphere vented directly into the gas inlet of a Finnigan 3200 GC/MS (ionizing potential 70 electron volts).

6 Synthesized from CD_3I (99.5% D, Sohler Isotopes) by the procedure of Crumbliss and Gaus [7],

7 A. L. Crumbliss and P. L. Gaus, *Inorg. Chem., 14,* 486 (1975).

8 W. W. Umbreit, R. H. Burris, and J. F. Stauffer, "Manometric Techniques", 3rd ed., Burgess, Minneapolis, Minnesota (1957) Chapters 1, 4, 5.

9 Manometric samples were flushed with O_2-free N_2 for 60 min before initiation of the reaction.

10 275 watt tungsten lamp at 10 cm.

11 Methane was confirmed as the photolysis product in the following experiment. Two samples (10 ml, 3.41×10^{-3} *M* in cobaloxime, 1.0*N* in KOH) were prepared as described in footnote 5 and incubated for 19 hr at 50 °C in the dark. The samples were then frozen in liquid nitrogen, evacuated to 1×10^{-2} Torr, sealed, and allowed to thaw. The freeze–pump–thaw cycle was repeated twice. One of the samples was then photolyzed [10] for 25.5 hr while the other was kept dark at room temperature. Mass spectral analysis (inlet pressure 5×10^{-7} Torr) showed large amounts of methane in the atmosphere above the photolyzed sample while the dark control contained just a trace of methane.

12 A. V. Cartaño and L. L. Ingraham, *Bioinorg. Chem., 7,* 351 (1977).

13 Synthesized as its pyridine derivative using the procedure described by Schrauzer [14] for the analogous cobaloxime; C, H, N, NMR ($CDCl_3$) δ_{Me_4Si}; 1.44 (s, 3.1H), 6.95–9.08 (m, 25H, including pyridine). The aquo complex was obtained by hydrolysis of the pyridine complex with Bio-Rad AG 50W-X8 ion exchange resin (H^+ form) as has been described for the cobaloximes [15]. C, H, N, NMR (py-d_5) δ_{Me_4Si}; 1.80 (s, 2.8H), 7.02–7.59 (m, 20H).

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