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Effect of Axial Ligands on the Base-catalyzed Cleavage of Ethylcobaloxime

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In recent publications [1–3] we have described the base-catalyzed carbon–cobalt cleavage reactions of simple alkylcobaloximes in aqueous solution pointing out substantial differences between the reactions of methyl- and ethylcobaloximes. For example, methyl(aquo)cobaloxime decomposes in 1.0 *M* KOH at 50 °C under anaerobic conditions with a half-time of about one hour to form methane in about 70% yield and a base-stable but photolabile methyl cobalt derivative in about 30% yield, subsequent photolysis of the latter product yielding additional methane [1, 2]. In contrast, ethyl(aquo)cobaloxime, under the same conditions, decomposes with a half-time of about 27 hr to yield a mixture of ethane and ethylene in a ratio of 5.6 to 1.0 with no detectable formation of a base-stable organocobalt side product [3]. We would now like to describe yet another substantial difference between these two reactions, namely, the dependence of the alkane forming reaction on added axial ligands.

Figure 1 shows the dependence of R, the ratio of ethylene/ethane, for the base-catalyzed cleavage of ethylcobaloxime at 50 °C and 1.0 *M* KOH on the equilibrium concentration of added pyridine*,**. The data show a substantial dependence of R on $[py]_{eq}$ from a value of 0.175 in the absence of pyridine [3] to 1.54 in *ca.* 0.2 *M* pyridine. These data may be analyzed in terms of the scheme, showing base-catalyzed pathways for ethylene and ethane formation from both the hydroxo- and ligand-complexes of ethylcobaloxime and the communicating axial ligation equilibrium†. For such a scheme of parallel pseudo-first-order reaction pathways, one can readily show that the ratio of products is time-independent and is equal to the ratio of the pseudo-first-order rate constants for formation of each product [5]. It can then be shown that the dependence of the product ratio on the equilibrium concentration of ligand is given by eqn. 2, which can be linearized to eqn. 3 for convenience in the data treatment. Figure 2 shows a plot of $(R - k_2^{OH^-}/k_1^{OH^-})$ *vs.* $(R - k_2^{OH^-}/k_1^{OH^-})/[L]_{eq}$ for the data in Fig. 1,

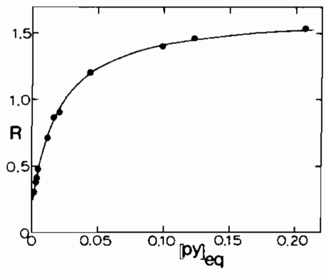

Fig. 1. Plot of R, the ratio of ethylene to ethane, from the base-catalyzed cleavage of ethylcobaloxime, 50 °C, 1.0 *M* KOH, *vs.* the equilibrium concentration of pyridine. The solid line was calculated from eqn. 2 and the rate and equilibrium constants listed in the Table.

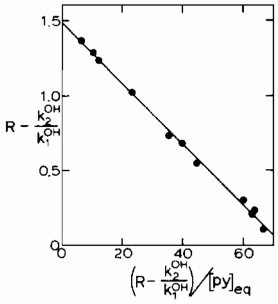

Fig. 2. Replot of the data in Fig. 1 according to eqn. 3. The solid line is the least-squares regression line, slope = −0.0202 ± 0.0004 *M*, intercept = 1.487 ± 0.016.

$$R = k_2^{obs}/k_1^{obs} \tag{1}$$

$$R = \frac{(k_2^{OH^-}/k_1^{OH^-})(k_1^{OH^-}K_D^L/k_1^L) + [L]_{eq}(k_2^L/k_1^L)}{(k_1^{OH^-}K_D^L/k_1^L) + [L]_{eq}} \tag{2}$$

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*Dissociation constants, K_D^L, for all ligands employed were measured spectrophotometrically at 50 °C in 1.0 *M* KOH by the method previously described.† Equilibrium concentrations of ligand were calculated from these measured dissociation constants and the added concentrations of ligand and cobaloxime.

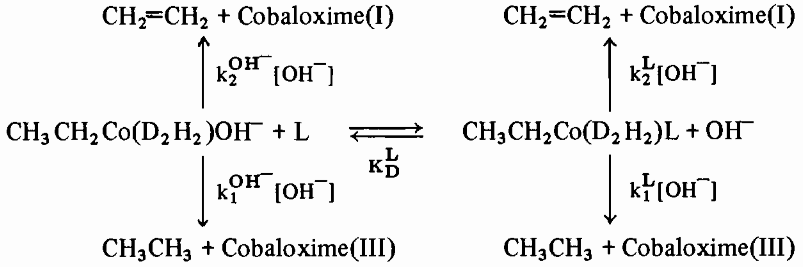
**Anaerobic reaction samples were prepared in 1.0 ml Reactivials (Pierce) sealed with Teflon minimert valves (Pierce) as described previously [3]. Gaseous product ratios were found to be time-independent and were determined on a Perkin-Elmer MK II gas chromatograph equipped with a 10 ft × 1/8 in. Poropak Q column and a Perkin-Elmer M-1 Computing Integrator. At a carrier flow of 37.5 ml/min and 100 °C column temperature retention times were 97 sec and 123 sec for ethylene and ethane, respectively.

†Under the conditions employed, the ligation equilibria are achieved rapidly compared to the rate of carbon–cobalt bond cleavage.

TABLE I. Rate and Equilibrium Constants for the Base-Catalyzed Cleavage of Ethyl(ligand)cobaloximes, 50.0 °C, Ionic Strength 1.0 M.[a]

L	K_D^L (M)[b]	k_1^L (M^{-1} s^{-1})	k_2^L (M^{-1} s^{-1})
OH^- [c]	0.132 ± 0.007	$6.05 \pm 0.35 \times 10^{-6}$	$1.06 \pm 0.06 \times 10^{-6}$
py	0.0107 ± 0.0002	$3.20 \pm 0.20 \times 10^{-6}$	$5.32 \pm 0.34 \times 10^{-6}$
SMME	0.200 ± 0.008	$1.14 \pm 0.09 \times 10^{-6}$	$5.14 \pm 0.43 \times 10^{-7}$
CN^-	$1.57 \pm 0.08 \times 10^{-6}$ [d]	$8.82 \pm 0.92 \times 10^{-6}$	$2.55 \pm 0.31 \times 10^{-6}$

[a] See the scheme for definitions of the rate and equilibrium constants. [b] Determined spectrophotometrically as described in reference 4. [c] Data from reference 3. [d] Determined spectrophotometrically [4] using 10 cm pathlength cells.



Scheme

$$(R - k_2^{OH^-}/k_1^{OH^-}) = (k_2^L/k_1^L - k_2^{OH^-}/k_1^{OH^-}) - (k_1^{OH^-}K_D^L/k_1^L)(R - k_2^{OH^-}/k_1^{OH^-})/[L]_{eq} \quad (3)$$

using the previously determined value of 0.175 for $k_2^{OH^-}/k_1^{OH^-}$ [3]. From the slope and intercept of this plot (by the method of least squares), the independently measured value of K_D^L* and the previously determined value of $k_1^{OH^-}$ ($6.05 \pm 0.35 \times 10^{-6}$ M^{-1} s^{-1} [3]) the values of k_1^L and k_2^L were calculated. The success of the treatment is indicated by the agreement of the raw data (Fig. 1) with the solid line which was calculated from eqn. 2 and the rate and equilibrium constants determined as described.

The rate constants thus determined and the value of K_D^L are listed in Table I along with those for the ligands S-methyl mercaptoethanol (SMME) and CN^-, which were determined in an analogous manner from similar data (not shown). The second-order rate constants for alkane formation, k_1^L, show a slight tendency to increase with increasing proton basicity of the ligand, although the trend is not strictly monotonic and the dependence is quite small considering the meager proton basicity of S-methyl sulfides [6]. Such trends are also likely to be complicated by variations in metal-to-ligand π bonding which is not, of course, related to proton basicity. There is no apparent trend of k_2^L with either proton basicity or expected π-accepting ability of L.

The most important feature of these data is that the rate constants for the alkane forming reaction (k_1^L) for L = py, SMME and CN^- are all of the same order of magnitude as that for L = OH^-. This is in striking contrast to our previous results for methylcobaloxime for which four axial ligands (including N- and S-donors with affinity for the cobalt center varying from 6.0 to 3500 M^{-1}) were shown to depress the rate of methane formation by at least four orders of magnitude compared to the hydroxo- complex [2]. In fact, all values of k_1^L determined for methylcobaloximes were experimentally indistinguishable from zero with the exception of L = OH^-. These results represent yet another major difference between the reactivities of the methyl- and ethylcobalt complexes and tend to support our earlier conjecture [3] that the mechanisms of the base-catalyzed alkane forming reactions of these two complexes may well be basically dissimilar.

Acknowledgements

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*See note on page L115.