*Journal of Organometallic Chemistry*, 287 (1985) 377–394
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

# MECHANISM OF ACID-INDUCED DECOMPOSITION OF 2-HYDROXYETHYL- AND 2-ALKOXYETHYL-COBALOXIMES

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(Received October 31st, 1984)

## Summary

The decomposition of hydroxyethyl-, ethoxyethyl- and phenoxyethyl(aquo)cobaloximes in sulfuric acid/water mixtures to produce ethylene has been studied spectrophotometrically and manometrically. Definitive kinetic evidence for formation of an intermediate which is common to all three starting complexes and accumulates at acidities greater than 7.3 $M$ $H_2SO_4$ has been obtained. A complete rate law which accounts for all of the ionizations of starting materials and intermediate has been derived and fit to the rate data. The rate-determining step for product formation is decomposition of the intermediate at all acidities: the intermediate accumulates in strong acid because of a shift in the equilibrium for its formation due to the reduced activity of water in strongly acidic media. Activation parameters for the decomposition of the intermediate, which may be formulated as an ethylene-cobaloxime(III) $\pi$-complex or as a $\sigma$-bonded ethyl carbonium ion, have been obtained. $^1H$ and $^{13}C$ NMR observations of the intermediate and its deuterated analog (from 1,1,2,2-tetradeuterio-2-hydroxyethyl(aquo)cobaloxime) have led to the conclusion that it is probably a $\sigma$-bonded ethyl carbonium ion which may be stabilized by $\sigma$–$\pi$ hyperconjugation.

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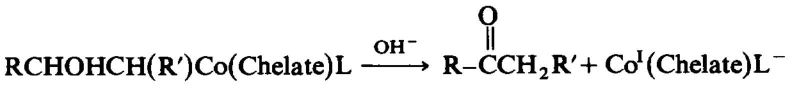
## Introduction

There has long been interest in 2-hydroxyalkylcobalt complexes which are well known to decompose in aqueous base to aldehydes or ketones (eq. 1) [1,2] and in



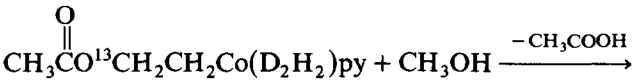
$$\mathrm{RCHOHCH(R')Co(Chelate)L} \xrightarrow{OH^-} \mathrm{R{-}\overset{\overset{\displaystyle O}{\|}}{C}CH_2R'} + \mathrm{Co^I(Chelate)L^-} \quad (1)$$

aqueous acid to olefins (eq. 2) [1]. Cationic intermediates, which may be formulated as

$$\mathrm{RCHOHCH(R')Co(Chelate)L} \xrightarrow{H^+} \mathrm{RCH{=}CHR'} + \mathrm{Co^{III}(Chelate)L^+} \quad (2)$$

0022-328X/85/$03.30

cobalt σ-bonded alkyl carbonium ions or cobalt(III)-olefin π-complexes, have long been suspected to occur in the latter reaction based mostly on indirect evidence. Golding and coworkers first postulated such intermediates in the alcoholysis of 2-acetoxyalkylcobaloximes [3,4] which has been shown to occur with scrambling of the label of 2-$^{13}$C-2-acetoxyethyl(pyridine)cobaloxime (eq. 3) [5]. Similar evidence



$$CH_3\overset{\overset{O}{\|}}{C}O^{13}CH_2CH_2Co(D_2H_2)py + CH_3OH \xrightarrow{-CH_3COOH}$$

$$CH_3O^{13}CH_2CH_2Co(D_2H_2)py + CH_3OCH_2{}^{13}CH_2Co(D_2H_2)py \qquad (3)$$

has come from the observation of acid-catalyzed rearrangements of 2-hydroxy-n-propyl- and 2-hydroxy-i-propylcobaloximes [6,7], the synthesis of organocobalt complexes via reactions of vinyl ethers and related olefins with cobalt(III) complexes [8–13], and the effective trapping of such intermediates with nucleophiles [14–18] to form new organocobalt complexes. Such intermediates are of potentially great interest due to the possible intermediacy of similar species in the 1,2-rearrangement catalyzed by adenosylcobalamin-requiring enzymes [5,10].

In the acid-induced decomposition of 2-hydroxyethyl(aquo)cobaloxime such an intermediate, if present, would be expected to form upon the presumably reversible loss of water from the 2-hydroxy protonated starting material (eq. 4). However,

$$H_2O^+CH_2CH_2Co(D_2H_2)OH_2 \xrightleftharpoons[\pm H_2O]{} \text{intermediate} \rightarrow$$

$$CH_2{=}CH_2 + Co^{III}(D_2H_2)(OH_2)_2 \qquad (4)$$

studies in dilute perchloric acid ($\leqslant 0.200\ M$) [7] have shown the kinetics of the decomposition of $HOCH_2CH_2Co(D_2H_2)OH_2$ to be strictly first order, indicating that the intermediate, if present, does not accumulate under these conditions. However, in more concentrated solutions of mineral acids, the activity of water is significantly reduced [19–21], leading to the possibility that the formation of the intermediate from protonated starting material may become irreversible. In addition, the known first equatorial protonation of alkylcobaloximes (eq. 5) [22–24] and

$$RCo(D_2H_2)L \pm H^+ \rightleftarrows RCo(D_2H_3)L^+ \qquad (5)$$

anticipated second equatorial protonation (eq. 6) may alter the specific rate con-

$$RCo(D_2H_3)L^+ + H^+ \rightleftarrows RCo(D_2H_4)L^{2+} \qquad (6)$$

stants for formation and decomposition of the intermediate so as to allow its accumulation and characterization. We have consequently undertaken a study of the kinetics of the decomposition of $HOCH_2CH_2Co(D_2H_2)OH_2$ and the related ethoxyethyl- and phenoxyethylcobaloximes, whose decomposition would be expected to proceed via the same intermediate, in sulfuric acid/water mixture. Preliminary studies [25] have, in fact, shown that an intermediate accumulates in strongly acidic mixtures. This report provides an analysis of the complete acidity function-rate profiles of these cobaloximes and a characterization of the intermediate by NMR spectroscopy.

## Experimental section

Hydroxyethyl(aquo)cobaloxime was obtained by reaction of ethylene oxide with diaquocobaloxime(II) in methanol under hydrogen gas at 45°C [1,6]. In the absence of a strongly donating axial ligand, yields are limited to about 50% due to self-reduction of hydrido(aquo)cobaloxime [26–28]. C, H, N; $^1$H NMR (CDCl$_3$/methanol-$d_4$) $\delta$(Me$_4$Si) 1.60 (t, 2H, $J$ 7.2 Hz), 2.24 (s, 12H), 2.87 (t, 2H, $J$ 7.2 Hz); $^{13}$C NMR (CDCl$_3$/methanol-$d_4$) $\delta$(Me$_4$Si) 12.130 (equatorial-CH$_3$), 64.640 (CH$_2$OH), 152.570 (C=N). The $\alpha$-carbon $^{13}$C resonance is not observed due to excessive broadening due to quadrapolar relaxation by the cobalt nucleus [29–31]. 1,1,2,2-Tetradeuterio-2-hydroxyethyl(aquo)cobaloxime was similarly obtained from tetradeuterioethylene oxide (Merck, 98 Atom-% D).

Ethoxyethyl- and phenoxyethyl(aquo)cobaloximes were obtained by reductive alkylation of diaquocobaloxime(II) with bromoethylethyl ether and bromoethylphenyl ether as previously described for methyl(aquo)cobaloxime [32]. $CH_3CH_2OCH_2CH_2Co(D_2H_2)OH_2$: C, H, N; $^1$H NMR (CDCl$_3$/methanol-$d_4$) $\delta$(Me$_4$Si) 1.04 (t, 3H, $J$ 7.0 Hz), 1.51 (t, 2H, $J$ 8.4 Hz). 2.23 (s, 12H), 2.87 (t, 2H, $J$ 8.4 Hz), 3.33 (q, 2H, $J$ 7.0 Hz); $^{13}$C NMR (CDCl$_3$/methanol-$d_4$) $\delta$(ME$_4$Si) 12.059 (equatorial-CH$_3$), 15.284 (CH$_2$$C$H$_3$), 65.559 ($C$H$_2$OCH$_2$CH$_3$), 71.876 (O$C$H$_2$CH$_3$), 151.795 (C=N). $C_6H_5OCH_2CH_2Co(D_2H_2)OH_2$: C, H, N; $^1$H NMR (CDCl$_3$/methanol-$d_4$) $\delta$(Me$_4$Si) 1.66 (t, 2H, $J$ 7.5 Hz), 2.21 (s, 12H), 3.40 (t, 2H, $J$ 7.5 Hz), 6.57–7.41 (m, 5H); $^{13}$C NMR (CDCl$_3$/methanol-$d_4$) $\delta$(Me$_4$Si) 12.124 (equatorial-CH$_3$), 69.246 (CH$_2$O), 114.342, 120.161, 129.329, 158.681 (C$_6$H$_5$), 152.054 (C=N). Electronic grade sulfuric acid and glass distilled deionized water were used throughout. All manipulations of organocobaloximes were carried out in the dark or under dim illumination (flashlights).

Spectrophotometric kinetic measurements were made on a Cary 219 or Gildford Model 250 spectrophotometer with sample compartments thermostatted to 25.0 ± 0.1°C or other appropriate temperatures. First order rate constants were obtained from the slopes of plots of $\ln|A_\infty - A_t|$ vs. time. Manometric kinetic measurements were made in Warburg manometers thermostatted to 25.0 ± 0.1°C as previously described [32]. All manometric rate measurements were shown to be free of complications due to phase transfer of the gaseous product by demonstrating independence of the observed rates of product formation on the rate of manometer shaking. Acidities of spectrophotometric or manometric samples were determined by titration of duplicate aliquots (100–500 $\mu$l) with standard KOH to a phenolphthalein endpoint. All such duplicate titrations agreed to within 1%. Values of acidity functions were obtained from the determined sulfuric acid molarities from literature data [33–36], interpolating between literature data points when necessary.

$^1$H NMR measurements were made on a Varian T-60 or Nicolet NT-200 wide bore NMR spectrometer operating at 60.0 and 200.068 MHz, respectively. $^{13}$C NMR measurements were made on the Nicolet instrument at 50.311 MHz. $^1$H NMR spectra of the intermediate were obtained on the Nicolet instrument in D$_2$SO$_4$/D$_2$O solution at various temperatures between −15 and +35°C. $^{13}$C NMR spectra of the intermediate were obtained in 70% HClO$_4$ at −30°C using CD$_2$Cl$_2$ in a concentric insert (Wilmad) for deuterium lock.

A typical experiment in which $HOCH_2CH_2Co(D_2H_2)OH_2$ was obtained from partial decomposition of the alkoxyethylcobaloximes was performed as follows: 1.7 g (4.47 mmol) of $CH_3CH_2OCH_2CH_2Co(D_2H_2)OH_2$ was decomposed for 50 min at 25.0 ± 0.1°C in 500 ml of 0.0213 $M$ H$_2$SO$_4$ ($H_0 = 1.50$). The solution was neutralized with 4.6 $N$ KOH and concentrated to about 35 ml. Addition of pyridine and cooling in ice produced a yellow precipitate which proved to be unreacted

$CH_3CH_2OCH_2CH_2CO(D_2H_2)py$ (by TLC and $^1H$ NMR). Additional organo(pyridine)cobaloximes were extracted with chloroform and separated by chromatography on a 2.5 × 18.5 cm column of silica gel. Additional $CH_3CH_2OCH_2CH_2Co(D_2H_2)py$ was eluted with ethyl acetate while $HOCH_2CH_2Co(D_2H_2)py$ (TLC, $^1H$ NMR) was eluted with acetone. Final yields were 0.84 mmol (18.8%) $CH_3CH_2OCH_2Co(D_2H_2)py$ and 0.25 mmol (5.7%) $HOCH_2CH_2Co(D_2H_2)py$.

## Results and discussion

At all acidities below about 6.0 $M$ $H_2SO_4$ (i.e. $H_0 <$ ca. $-3.0$), the decomposition of $HOCH_2CH_2Co(D_2H_2)OH_2$(I) is strictly first order, as previously found by Espenson and Wang [7], when measured spectrophotometrically at 255 or 445 nm or when the formation of ethylene is measured manometrically. Examples of first-order plots for all three types of measurements are shown in Fig. 1 at 0.0124 $M$ $H_2SO_4$ ($H_0 = 1.70$). The decomposition of $CH_3CH_2OCH_2CH_2Co(D_2H_2)OH_2$ (IIIa) and $C_6H_5OCH_2CH_2Co(D_2H_2)OH_2$ (IIIb) under the same conditions shows a distinct lag followed by a first-order region whether measured spectrophotometrically or manometrically (Fig. 1). At all acidities below 6.0 $M$ $H_2SO_4$, the apparent first-order rate constans increase in the order IIIb < IIIa < I. In more strongly acidic media ($[H_2SO_4] > 7.3$ $M$) all three compounds show a "burst" of absorbance change followed by a slower first-order change which is identical for all three compounds whether measured spectrophotometrically or manometrically (see Fig. 2, for example, at ca. 10.0 $M$ $H_2SO_4$). The latter observation is crucial in that it demonstrates that the rapid proces (too fast to quantitate under these conditions) leads to formation of a species which is common to all three starting materials and is on the pathway to ethylene, the final organic product. These results suggest that Scheme 1 (abbreviated to omit, temporarily, ionizations of the starting materials and inter-

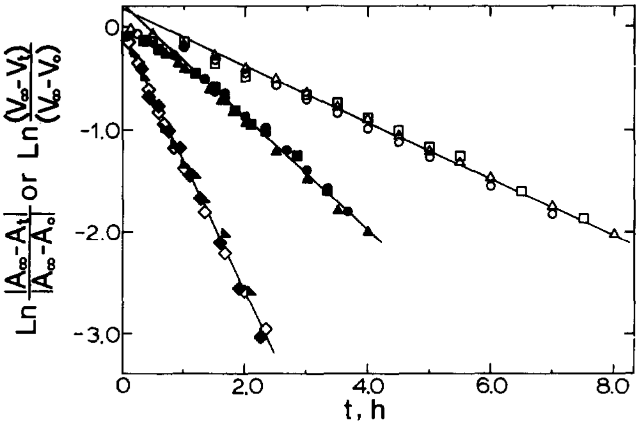
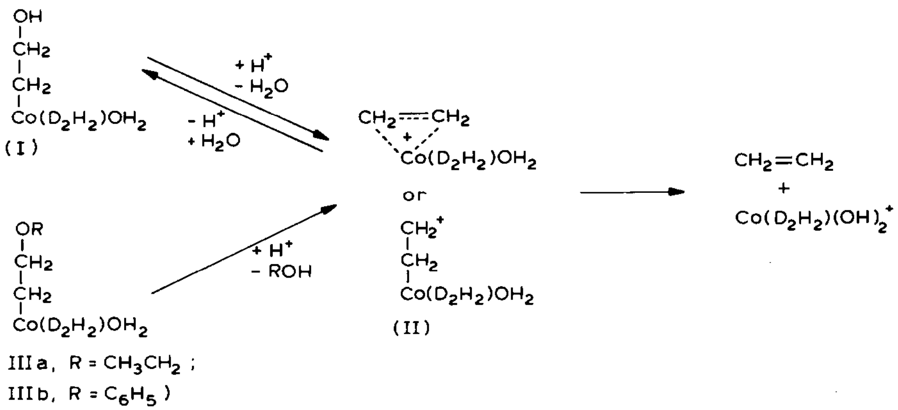


Fig. 1. Normalized, semilogarithmic plots of the UV (255 nm), visible (445 nm) and manometric kinetics of the decomposition of hydroxyethyl- and alkoxyethyl(aquo)cobaloximes in 0.0124 $M$ $H_2SO_4$, 25.0 ± 0.1°C. IIIb, UV (○), visible (△), manometric (□), $k_{obs}$ $7.65 \pm 0.18 \times 10^{-5}$ $s^{-1}$; IIIa, UV (●), visible (▲), manometric (■), $k_{obs}$ $1.53 \pm 0.04 \times 10^{-4}$ $s^{-1}$; I, UV (◆), visible (◇), manometric (◣), $k_{obs}$ $3.53 \pm 0.05 \times 10^{-4}$ $s^{-1}$.

SCHEME 1



mediate) is operative. Additional evidence has also been obtained to support this reaction scheme. The irreversibility of the loss of the leaving group alcohol from the starting materials IIIa and IIIb is indicated by the lack of any effect of added ethanol or phenol ($3.7 \times 10^{-5}$ to $3.7 \times 10^{-2}$ *M*) on the kinetics of decomposition of IIIa and IIIb, respectively. The scheme also suggests that the lag in the kinetics of decomposition of IIIa and IIIb is due to the establishment of steady state concentrations of the intermediate, II, and of I, assuming that the loss of water from I is reversible. These features of the decomposition scheme are supported by the

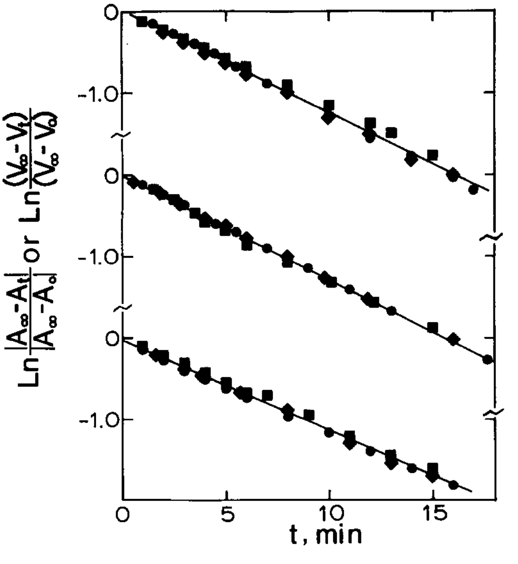


Fig. 2. Normalized, semilogarithmic plots of the decomposition of I (●), IIIa (◆), and IIIb (■) in ca. 10.0 *M* $H_2SO_4$, 25.0±0.1°C. Upper plots, UV (255 nm), $[H_2SO_4]$ 9.991 *M*, $k_{obs}$ $2.08 \pm 0.03 \times 10^{-3}$ $s^{-1}$; center plot, visible (445 nm), $[H_2SO_4]$ 9.934 *M*, $k_{obs}$ $2.12 \pm 0.03 \times 10^{-3}$ $s^{-1}$; lower plot, manometric, $[H_2SO_4]$ 10.068 *M*, $k_{obs}$ $1.85 \pm 0.03 \times 10^{-3}$ $s^{-1}$.

observation that initiation of the decomposition of either IIIa or IIIb in the presence of admixtures of I, strongly effect both the duration and severity of the lag, as well as the observed first-order rate constant. In addition, Scheme 1 is further supported by the observation that I may be obtained from reaction mixtures in which IIIa or IIIb is partially decomposed in mildly acidic solution. For example, when $4.46 \times 10^{-3}$ mol of IIIa was decomposed for 50 min (ca. one half-time) at 25.0°C in 0.0217 *M* $H_2SO_4$, $0.84 \times 10^{-3}$ mol of unreacted IIIa (or 18.8%) (as its pyridine complex, see Experimental) and $0.25 \times 10^{-3}$ mol of I (5.7%) were obtained after separation by silica gel chromatography.

Complete acidity function-rate profiles for all three starting materials have been obtained and are shown in Fig. 3. A generalized acidity function (eq. 7) due to Cox and Yates [36] has been utilized

$$-H = m^{\star}X + \log C_{H^+} \qquad (7)$$

where X is the so-called excess acidity of sulfuric acid, $C_{H^+}$ is the concentration of hydrogen ion, and $m^{\star}$ is a parameter characteristic of the type of weak base which is being protonated and indicative of the fact that all known acidity functions are linearly related to one another [36–38]. For the present work, the value of $m^{\star}$ has been set equal to 1.25 by a method which will be described presently.

The *H*-rate profile of I is characterized by a region of first-order dependence on hydrogen ion activity ($H >$ ca. 1.25) followed by an apparent inflection near $H = 0.50$, which is similar to the reported values (0.67–0.00 [23,24]) for the $pK_a$'s for the first equatorial protonations of alkyl(aquo)cobaloximes (eq. 5). Prior to the attainment of the anticipated second first-order limb (i.e., for monoprotonated I) a leveling-off occurs at about $H = -1.0$, which apparently indicates achievement of

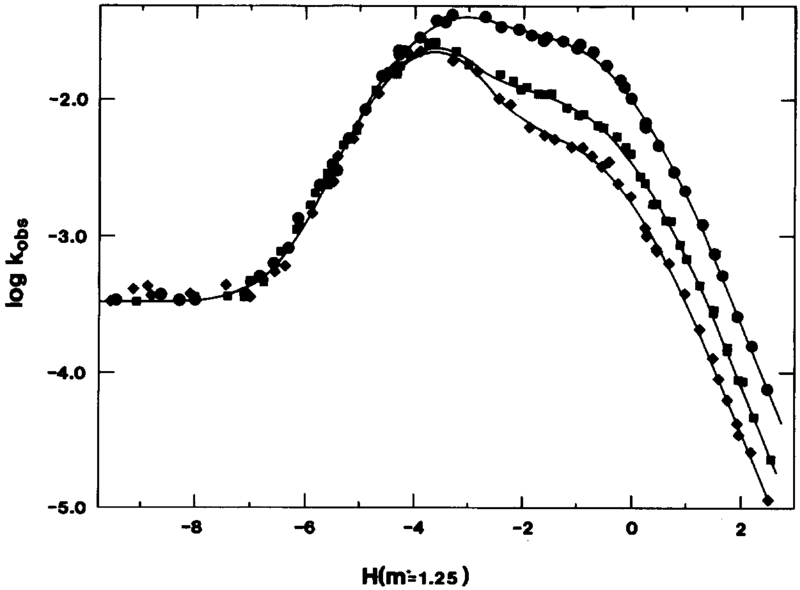


Fig. 3. Plots of $k_{obs}$ for the decomposition of I (●), IIIa (■), and IIIb (◆) in aqueous sulfuric acid at 25.0±0.1°C, vs. *H*, eq. 7, at $m^{\star} = 1.25$ (see text). The solid lines have been calculated from eq. 8 (upper line) and eq. 17 using the least-squares parameter values in Table 1.

equilibrium protonation of the $\beta$-hydroxyl group. At higher acidities there is a small increase in $k_{\text{obs}}$ which may be attributed either to the decrease in the activity of water at these acidities or to the second equatorial protonation of I (eq. 6) followed by a large decrease in $k_{\text{obs}}$ to an acidity-independent region at $H > -7.5$. The $H$-rate profiles for IIIa and IIIb are similar in shape except that for all acidities above $H = -4.5$ $k_{\text{obs}}$ decreases in the order I > IIIa > IIIb. At acidities stronger than $H = -4.5$, the observed rate constants, following the burst, are identical for all three starting materials.

The complete decomposition scheme for $HOCH_2CH_2Co(D_2H_2)OH_2$ including all anticipated ionizations of starting material and intermediate is shown in Scheme 2. This scheme includes nine ionic species and 18 parameters, of which 16 are independent. Application of the law of mass action and the steady state assumption on the sum of the concentrations of the ionic species of the intermediate leads to the rather complicated rate law of eq. 8 in which $a_{\text{H}^+}$ represents the activity of hydrogen

$$\begin{aligned} k_{\text{obs}} = {} & \Big\{\big(k_1K'_{\text{I}_1}K'_{\text{I}_2}a_{\text{H}^+} + k'_1K'_{\text{I}_2}a^2_{\text{H}^+} + k''_1a^3_{\text{H}^+}\big)\big(k_2K_{\text{II}_1}K_{\text{II}_2} + k'_2K_{\text{II}_2}a_{\text{H}^+} + k''_2a^2_{\text{H}^+}\big)\Big\}\Big/ \\ & \Big\{\Big[K_\text{a}K'_{\text{I}_1}K'_{\text{I}_2} + \big(K'_{\text{I}_1} + K'_\text{a}\big)K'_{\text{I}_2}a_{\text{H}^+} + \big(K'_{\text{I}_2} + K''_\text{a}\big)a^2_{\text{H}^+} + a^3_{\text{H}^+}\Big]\Big[\big(k_{-1}K_{\text{II}_1}K_{\text{II}_2} + \\ & \quad k'_{-1}K_{\text{II}_2}a_{\text{H}^+} + k''_{-1}a^2_{\text{H}^+}\big)a_{\text{H}_2\text{O}} + k_2K_{\text{II}_1}K_{\text{II}_2} + k'_2K_{\text{II}_2}a_{\text{H}^+} + k''_2a^2_{\text{H}^+}\Big] \\ & + \big(K_{\text{II}_1}K_{\text{II}_2} + K_{\text{II}_2}a_{\text{H}^+} + a^2_{\text{H}^+}\big)\big(k_1K'_{\text{I}_1}K'_{\text{I}_2}a_{\text{H}^+} + k'_1K'_{\text{I}_2}a^2_{\text{H}^+} + k''_1a^3_{\text{H}^+}\big)\Big\}^{-1} \end{aligned} \tag{8}$$

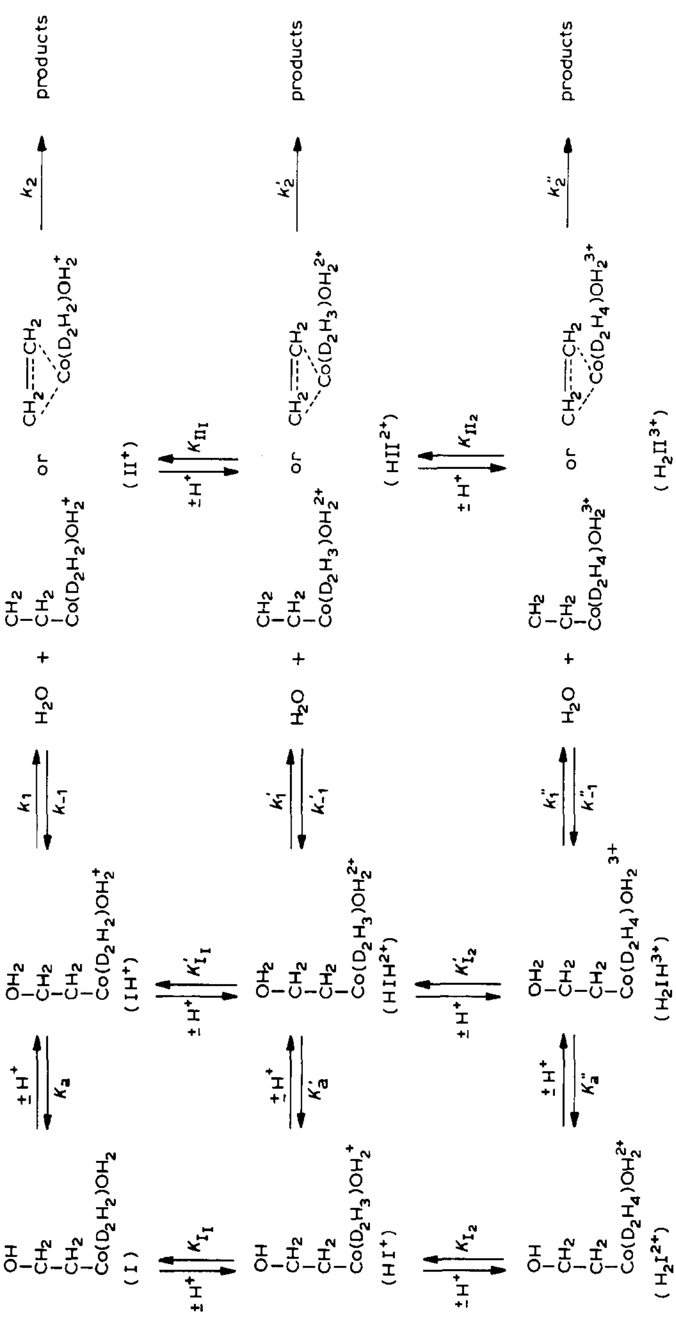
ion, and $a_{\text{H}_2\text{O}}$ the activity of water. Although this 14 parameter equation may, in fact, be fit to the rate data for $HOCH_2CH_2Co(D_2H_2)OH_2$ using a weighted least squares method and a simplex minimization routine, experience shows that despite the extensive amount of data the large number of parameters involved leads to multiple, false convergences indicating that at least some of the parameters are very poorly determined when this many degrees of freedom are involved. However, as it is absolutely necessary to demonstrate that the observed H-rate profile may be accurately generated from the rate law (eq. 8) based on Scheme 2 with chemically reasonable values for all of the parameters involved we have constrained eq. 8 and reduced the number of parameters to be determined as follows.

(1) The data for the descending limb at $H < -4.5$ for all three compounds represents the decomposition of the intermediate as it undergoes its final equatorial protonation (species $\text{HII}^{2+}$ and $\text{H}_2\text{II}^{3+}$, Scheme 2). The data in this region for all three compounds (52 data points) were consequently fit to the abbreviated rate law of eq. 9, to provide values of $k'_2$, $k''_2$ and $K_{\text{II}_2}$. These data were also used to

$$k_{\text{obs}}(H < -4.5) = \frac{k'_2K_{\text{II}_2} + k''_2a_{\text{H}^+}}{a_{\text{H}^+} + K_{\text{II}_2}} \tag{9}$$

determine the appropriate value of $m^\star$ to be used in conjunction with the generalized acidity function (eq. 7). The approach was to fit these data to eq. 9 calculating hydrogen ion activity from eq. 7 using an arbitrary value of $m^\star$. The precision of the fit was evaluated from the magnitude of the sums of the squares of the deviations of the calculated values from the observed values. This procedure was repeated for additional values of $m^\star$ until the minimum in the sum of the squares of the

SCHEME 2



deviations was found at $m^* = 1.25$. This value of $m^*$ was used for all further work. Values of the parameters from eq. 9 at this $m^*$ ($k_2'$ $2.42 \times 10^{-2}$ $s^{-1}$; $k_2''$ $3.33 \times 10^{-4}$ $s^{-1}$; $K_{II_2}$ $4.25 \times 10^4$) were then incorporated into the rate law of eq. 8 to reduce its dimensionality to 11.

(2) The previously mentioned features of the $H$-rate profile at $H = 0.50$ and $H = -1.0$ are clearly related to ionizations of the starting material and may be used to estimate values for macroscopic p$K_a$'s of the starting material. From the ionization scheme for $HOCH_2CH_2Co(D_2H_2)OH_2$ (Scheme 2) three macroscopic p$K_a$'s may be defined as in eqs. 10–15.

$$G_1 = \frac{([HIH^{2+}] + [H_2I^{2+}])a_{H^+}}{[H_2IH^{3+}]} \tag{10}$$

$$G_1 = K'_{I_2} + K''_a \tag{11}$$

$$G_2 = \frac{([HI^+] + [IH^+])a_{H^+}}{([HIH^{2+}] + [H_2I^{2+}])} \tag{12}$$

$$G_2 = \frac{K_{I_2}(K'_a + K'_{I_1})}{K_{I_2} + K'_a} \tag{13}$$

$$G_3 = \frac{[I]a_{H^+}}{([IH^+] + [HI^+])} \tag{14}$$

$$G_3 = \frac{K_a K'_{I_1}}{K'_{I_1} + K'_a} \tag{15}$$

From the data near the inflection point at about $H = 0.50$ (data in the region $H = -0.15$ to $+2.50$) the value of $G_3$ was estimated to be 0.34 and from the data near the leveling off at $H$ ca. $-1.0$ (data in the region $H = -0.15$ to $-2.43$) $G_2$ was estimated to be 2.04. These values of $G_2$ and $G_3$ were used to further reduce the dimensionality of eq. 8 to nine.

(3) The rate law of eq. 8 can be seen to be first order in hydrogen ion activity in sufficiently dilute acid, i.e.

$$\lim_{a_{H^+} \to 0} k_{obs} = \frac{k_1 k_2 a_{H^+}}{K_a(k_{-1}a_{H_2O} + k_2)} \tag{16}$$

Since the activity of water at these acidities is 1.00, $k_1k_2/K_a(k_{-1} + k_2)$ can be estimated from the data at low acidity. Values of $k_{obs}/a_{H^+}$ were found to be acidity-independent in the region $H = 1.5$ to 2.5 and the average value ($2.38 \pm 0.16 \times 10^{-2}$ $M^{-1}$ $s^{-1}$) was used to reduce the dimensionality of eq. 8 to eight.

(4) In order to insure a fit of the data to eq. 8 which behaves properly outside the range of acidities over which data was available, the first derivative of eq. 8 was constrained to be zero at $H < -9.5$ and to equal $2.38 \times 10^{-2}$ $M^{-1}$ $s^{-1}$ at $H > 2.5$.

(5) Experience with attempted fits at this point showed that one additional parameter had to be fixed since the remaining eight parameters had a tendency to "blow up" although their ratios remained reassuringly constant. It was thus necessary to assume that the value of $K'_{I_2}$ (Scheme 2) was identical to the previously determined value of $K_{II_2}$ ($4.25 \times 10^4$). This is reasonable in that both of these constants govern

equatorial proton dissociations from fully protonated tricationic cobaloximes and, in fact, the two species undergoing ionizations ($H_2IH^{3+}$ and $H_2II^{3+}$) differ only by the presence of water $\beta$ to the cobalt atom.

The resulting seven parameter equation converges firmly to generate the upper solid line in Fig. 3 and the chemically reasonable parameter values listed in Table 1. Considering the number of approximations and constraints required to obtain this fit, it seems prudent to question the accuracy of the absolute values of the parameters determined. Some confidence in the accuracy of these parameters is obtained from the value of the $pK_a$ for the first equatorial protonation of the intermediate ($pK_{II_1} = -0.16$) which is very reasonable compared to known values for this $pK_a$ for other organo(aquo)cobaloximes (+0.67 to 0.00 [23,24]) considering the dicationic nature of the protonated species. Unfortunately, no other data exists in the literature to which these parameters can be directly compared. However, experience gained by observing the behavior of the parameters during the process of reducing the dimensionality of the rate equation gives us considerable confidence in the relative values of the various rate parameters so that conclusions based on trends in the values seem well founded. Consequently, we note that the values for the rate constants for attack of water on the intermediate to reform protonated starting material increase monotonically as the intermediate becomes increasingly cationic due to equatorial protonation (i.e., $k_{-1} < k'_{-1} < k''_1$) as would be expected. Interestingly, the effect of equatorial protonation on the rate of decomposition of the intermediate ($k_2$, $k'_2$, $k''_2$, Table 1) is much larger than the effect of such protonation on the rate of attack of water on the intermediate, an effect to which we will return

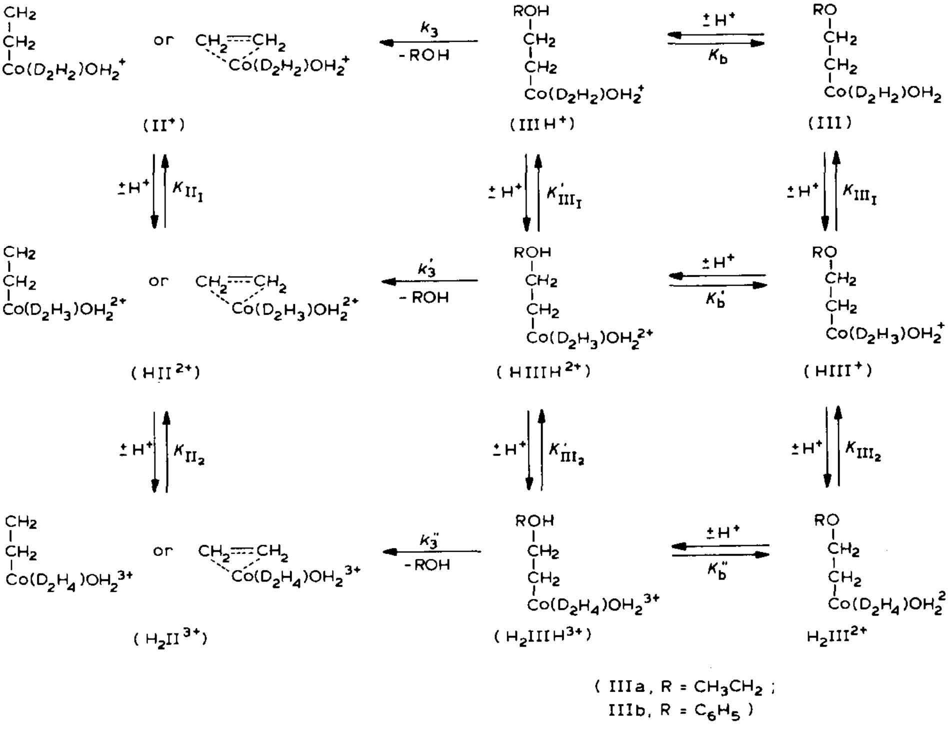
TABLE 1

RATE AND EQUILIBRIUM PARAMETERS FOR ACID-INDUCED DECOMPOSITION OF $ROCH_2CH_2Co(D_2H_2)OH_2$ IN $H_2SO_4/H_2O$, 25.0±0.1°C

| Parameter | R | | |
|---|---|---|---|
| | H | $CH_2CH_2$ | $C_6H_5$ |
| $k_1K'_{I_1}K'_{I_2}$ | $9.59\times10^5\ M^2\ s^{-1}$ | | |
| $k'_1K'_{I_2}$ | $2.96\times10^5\ M\ s^{-1}$ | | |
| $k''_1$ | $3.88\times10^5\ s^{-1}$ | | |
| $k_2$ | $1.58\times10^2\ s^{-1}$ | | |
| $k'_2$ | $2.42\times10^{-2}\ s^{-1}$ | | |
| $k''_2$ | $3.33\times10^{-4}\ s^{-1}$ | | |
| $K_{II_2}$ | $4.25\times10^4\ M$ | | |
| $K_{II_1}$ | $1.45\ M$ | | |
| $K_aK'_{I_1}K'_{I_2}$ | $2.94\times10^4\ M^3$ | | |
| $K'_{I_2}(K'_{I_1}+K'_a)$ | $8.67\times10^4\ M^2$ | | |
| $K'_{I_2}+K''_a$ | $4.25\times10^4\ M$ | | |
| $k_{-1}$ | $2.15\times10^4\ M^{-1}\ s^{-1}$ | | |
| $k'_{-1}$ | $8.39\times10^4\ M^{-1}\ s^{-1}$ | | |
| $k''_{-1}$ | $1.50\times10^5\ M^{-1}\ s^{-1}$ | | |
| $k_3K'_{III_1}K'_{III_2}$ | | $4.12\times10^1\ M^2\ s^{-1}$ | $8.67\ M^2\ s^{-1}$ |
| $k'_3K'_{III_2}$ | | $1.27\times10^2\ M\ s^{-1}$ | $2.61\times10^1\ M\ s^{-1}$ |
| $k''_3$ | | $1.87\times10^{-1}\ s^{-1}$ | $1.26\times10^{-1}\ s^{-1}$ |
| $K_bK'_{III_1}K'_{III_2}$ | | $4.68\times10^3\ M^3$ | $2.31\times10^3\ M^3$ |
| $(K'_{III_1}+K'_b)K'_{III_2}$ | | $2.85\times10^4\ M^2$ | $1.24\times10^4\ M^2$ |
| $(K'_{III_2}+K''_b)$ | | $7.22\times10^3\ M$ | $4.00\times10^3\ M$ |

later. It is also interesting to note that the rate-determining step for decomposition of $HOCH_2CH_2Co(D_2H_2)OH_2$ is apparently always decomposition of the intermediate as the rate of attack of water on the intermediate to reform protonated

SCHEME 3



starting material always exceeds that of decomposition of the intermediate (i.e., $k_{-1}a_{H_2O} > k_2$, $k'_{-1}a_{H_2O} > k'_2$, $k''_{-1}a_{H_2O} > k''_2$ at all acidities). Consequently, the intermediate does not accumulate in strong acid due to a change in rate-determining step but instead, accumulates because of a shift in the apparent equilibrium constant for its formation from protonated starting material due at least in part to the reduced activity of water at high acidities (i.e., $k''_{-1}a_{H_2O} < k''_1$ at all water activities, but at $H < -6$ where $a_{H_2O} < 0.07$, $k''_{-1}a_{H_2O} \ll k''_1$).

The complete scheme for the decomposition of IIIa and IIIb includes all of the ionic species of I and II shown in Scheme 2 in addition to the ionic species of III shown in Scheme 3. The necessary combination of Schemes 2 and 3 contains 28 rate and equilibrium parameters of which 24 are independent. Application of the law of mass action and the steady state assumption to both the sum of the concentrations of the various ionic species of the intermediate (i.e., II) and the sum of the concentrations of the various ionic species of $HOCH_2CH_2Co(D_2H_2)OH_2$ (i.e., I, Scheme 2) leads to the rate law of eq. 17.

$$k_{\mathrm{obs}} = \left(k_1K'_{\mathrm{I}_1}K'_{\mathrm{I}_2}a_{\mathrm{H}^+} + k'_1K'_{\mathrm{I}_2}a^2_{\mathrm{H}^+} + k''_1a^3_{\mathrm{H}^+}\right)\left(k_3K'_{\mathrm{III}_1}K'_{\mathrm{III}_2}a_{\mathrm{H}^+} + k'_3K'_{\mathrm{III}_2}a^2_{\mathrm{H}^+} + k''_3a^3_{\mathrm{H}^+}\right)$$

$$\times\left(k_2K_{\mathrm{II}_1}K_{\mathrm{II}_2} + k'_2K_{\mathrm{II}_2}a_{\mathrm{H}^+} + k''_2a^2_{\mathrm{H}^+}\right)/\left\{\left[\left(K_{\mathrm{a}}K'_{\mathrm{I}_1}K'_{\mathrm{I}_2} + \left(K'_{\mathrm{I}_1} + K'_{\mathrm{a}}\right)K'_{\mathrm{I}_2}a_{\mathrm{H}^+}\right.\right.\right.$$

$$
\begin{aligned}
&+\left(K'_{\mathrm{I}_2}+K''_{\mathrm{a}}\right)a^2_{\mathrm{H}^+}+a^3_{\mathrm{H}^+}\Big)\left(k_{-1}K_{\mathrm{II}_1}K_{\mathrm{II}_2}+k'_{-1}K_{\mathrm{II}_2}a_{\mathrm{H}^+}+k''_{-1}a^2_{\mathrm{H}^+}\right)\\
&\times\left(k_3K'_{\mathrm{III}_1}K'_{\mathrm{III}_2}a_{\mathrm{H}^+}+k'_3K'_{\mathrm{III2}}a^2_{\mathrm{H}^+}+k''_3a^3_{\mathrm{H}^+}\right)\Big]a_{\mathrm{H_2O}}\\
&+\left(k_1K'_{\mathrm{I}_1}K'_{\mathrm{I}_2}a_{\mathrm{H}^+}+k'_1K'_{\mathrm{I}_2}a^2_{\mathrm{H}^+}+k''_1a^3_{\mathrm{H}^+}\right)\left(K_{\mathrm{II}_1}K_{\mathrm{II}_2}+K_{\mathrm{II}_2}a_{\mathrm{H}^+}+a^2_{\mathrm{H}^+}\right)\\
&\times\left(k_3K'_{\mathrm{III}_1}K'_{\mathrm{III}_2}a_{\mathrm{H}^+}+k'_3K'_{\mathrm{III}_2}a^2_{\mathrm{H}^+}+k''_3a^3_{\mathrm{H}^+}\right)+\left(k_1K'_{\mathrm{I}_1}K'_{\mathrm{I}_2}a_{\mathrm{H}^+}+k'_1K'_{\mathrm{I}_2}a^2_{\mathrm{H}^+}+k''_1a^3_{\mathrm{H}^+}\right)\\
&\times\left(k_2K_{\mathrm{II}_1}K_{\mathrm{II}_2}+k'_2K_{\mathrm{II}_2}a_{\mathrm{H}^+}+k''_2a^2_{\mathrm{H}^+}\right)\left(K_{\mathrm{b}}K'_{\mathrm{III}_1}K'_{\mathrm{III}_2}\right)\\
&+\left(K'_{\mathrm{III}_1}+K'_{\mathrm{b}}\right)K'_{\mathrm{III}_2}a_{\mathrm{H}^+}+\left(K'_{\mathrm{III}_2}+K''_{\mathrm{b}}\right)a^2_{\mathrm{H}^+}+a^3_{\mathrm{H}^+}\Big)\Big\} \qquad (17)
\end{aligned}
$$

Fortunately 14 of the 20 parameters in eq. 17 are identical to the 14 parameters either fixed or obtained in the fit of the $HOCH_2CH_2Co(D_2H_2)OH_2$ *H*-rate profile to eq. 8. These 14 parameters were consequently fixed at the values given in Table 1 and the remaining six were fit to the *H*-rate profiles of IIIa and IIIb by an iterative least-squares procedure to produce the middle and lower solid lines in Fig. 3, and the parameter values also listed in Table 1. If one is willing to assume that the values of the $\mathrm{p}K_\mathrm{a}$'s for equatorial protonation of IIIa and IIIb are very close to those for I it is possible to estimate the ratio of the rate constants for formation of the intermediate from $\beta$-oxy protonated III to those of I (i.e., $k_3/k_1$, $k'_3/k'_1$ and $k''_3/k''_1$) from these results. These estimates show that $\beta$-oxy protonated IIIa is some three to six orders of magnitude less reactive than I, while IIIb is about one order of magnitude less reactive than IIIa.

We have also investigated the temperature dependence of the rate of decomposition of I in the acid-independent region at $H = -8.05$ which surely must represent

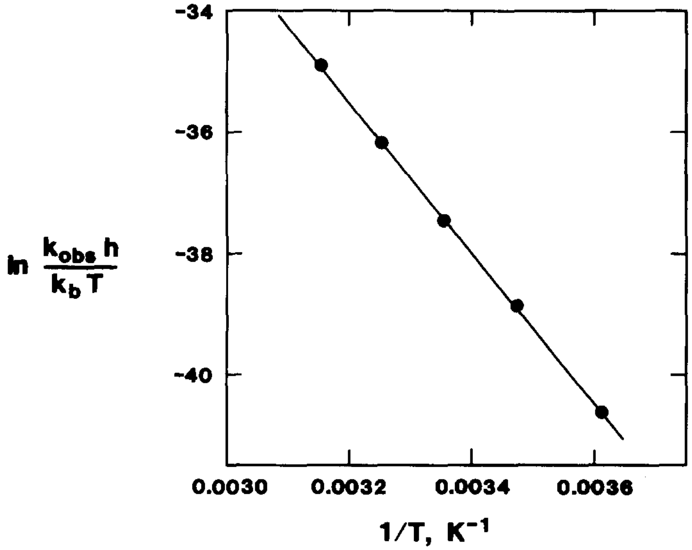


Fig. 4. Plot of $\ln(k_{\mathrm{obs}}h/k_{\mathrm{b}}T)$ vs. $1/T$ for I at $H = -8.05$. The solid line is a least-squares line, slope $= -1.244 \pm 0.017 \times 10^4$ K, intercept $= 4.309 \pm 0.562$.

the temperature dependence of the rate of decomposition of the fully protonated intermediate ($k''_2$, Scheme 2). Figure 4 shows a plot of $\ln(k_{obs}h/k_bT)$ vs. $1/T$ (where $h$ is Planck's constant and $k_b$ is Boltzmann's constant) from which values of $\Delta H^\ddagger$ 24.7 ± 0.3 kcal mol$^{-1}$ and $\Delta S^\ddagger$ 8.6 ± 1.1 eu were obtained. Although a positive entropy of activation is expected for the dissociation of the intermediate into products, the enthalpy of activation is surprisingly large. This leads to a substantial influence of temperature on the rate of intermediate decomposition so that the half-time of about 30 min at 25°C is increased to 14.8 h at 5°C. Assuming the activation parameters to be constant over the necessary temperature range, the calculated half-time for intermediate decomposition in this acidity range at −30°C is one year. Consequently, characterization of the intermediate by NMR spectroscopy at low temperature is clearly feasible.

Figure 5A shows the $^1$H NMR spectrum of the intermediate generated from I in 73% $D_2SO_4/D_2O$ ($H$ ca. −8) at −5°C. Similar spectra may be obtained from IIIa and IIIb except these contain additional resonances due to the alcohol leaving groups. The spectrum consists of a 12 proton singlet at 2.15 ppm representing the four equivalent equatorial methyl groups and two broad singlets of nearly equal intensity at 2.76 and 2.92 ppm integrating to a total of 4 protons. The latter two resonances may be assigned to the ethyl ligand fragment of the intermediate since they are missing from the spectrum of the intermediate generated from $HOCD_2CD_2Co(D_2H_2)OH_2$ (Fig. 5B). Careful examination of these resonances shows no evidence of any coupling and continuous wave irradiation of either resonance caused no change in shape of the other. It should be pointed out, however,

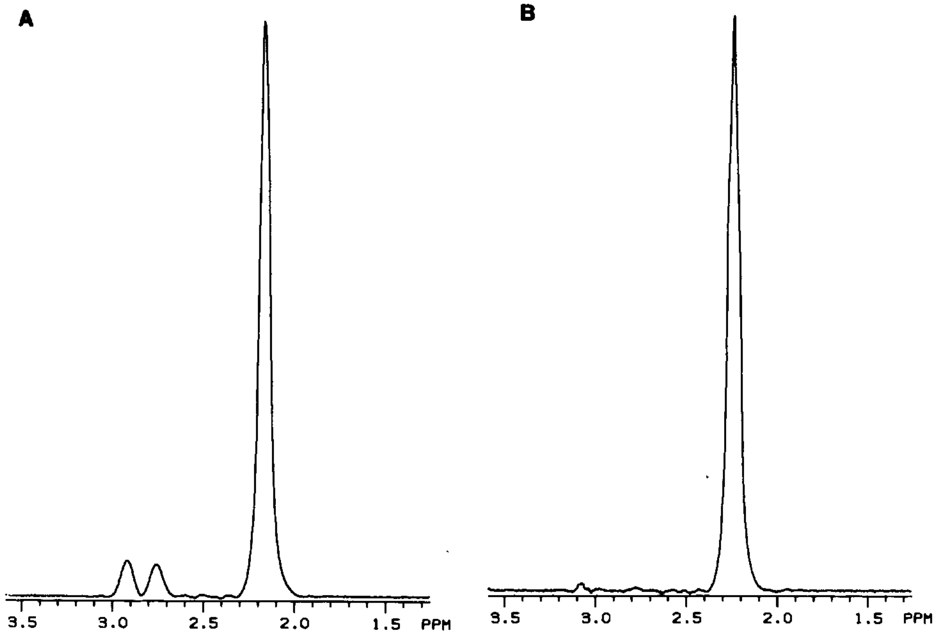


Fig. 5. 200 MHz $^1$H NMR spectra of the intermediate generated from $HOCH_2CH_2Co(D_2H_2)OH_2$ (A) or $HOCD_2CD_2Co(D_2H_2)OH_2$ (B) in 73% $D_2SO_4/D_2O$, −5°C. Chemical shifts are relative to external TMS.

that the high viscosity of the solvent must be at least partly responsible for the broadness of all three resonances and could obscure some fine structure in the organic ligand resonances. In a preliminary report on this work [25] we reported that the relative intensity of the two resonances from the organic ligand appeared to change as a function of increasing temperature. A careful examination of the $^1H$ NMR spectra of the intermediate at six temperatures between $-15$ and $+35°C$ has now shown that this effect, if real, is far too small to be the basis of any conclusions regarding the nature of the intermediate. However, the separation between the two resonances does decrease monotonically from 32.5 Hz at $-15°C$ to 25.4 Hz at $+35°C$ apparently indicating a tendency to collapse to a single resonance with increasing temperature. When observed at 60 MHz and 32°C the organic ligand resonance of the intermediate was a broad singlet ($w_{1/2}$ ca. 15 Hz) at 2.84 ppm. These spectral features are consistent with a cobaloxime(III)-ethylene $\pi$-complex intermediate if it exists as an equilibrium pair of conformers, one with the ethylene protons pointing towards the equatorial methyls and one with the ethylene protons pointing towards the equatorial oxygens (Fig. 6) if the conformers are in relatively slow (on the NMR time scale) exchange and the enthalpy of activation for rotation of the ethylene fragment is extremely small so that collapse of the resonances cannot be achieved over a 50°C temperature range. These spectral results are, however, also consistent with the formulation of the intermediate as a $\sigma$-bonded ethylcobalt carbonium ion if it is undergoing a relatively slow (on the NMR time scale) topoisomerism and the activation enthalpy for this process is also suitably low. The requirement of relatively slow topoisomerism does not conflict with the labeling studies of Golding and Sakrikar [4] and Silverman, et al. [5] (eq. 3) since the rate of trapping of the intermediate is apparently quite slow in solvent alcohols [39].

We have found 70% $HClO_4$ ($H = -8.84$ at $m^* = 1.25$ [36]) to be a more satisfactory solvent for natural abundance $^{13}C$ NMR than $D_2SO_4/D_2O$ mixtures due to extreme broadening of NMR resonances at temperatures below $-15°C$ in the latter solvent because of its high viscosity. Figure 7A shows the $^{13}C$ NMR spectrum of the intermediate generated from $HOCH_2CH_2CO(D_2H_2)OH_2$ in 70% $HClO_4$ at $-30°C$. The spectrum consists of sharp, relatively intense resonances at 15.104 and 176.465 ppm assignable to the equatorial methyls and quaternary carbons, respectively [29] and two much less intense and broader resonances at 25.744 ppm ($w_{1/2}$ ca. 9.3 Hz) and 66.846 ppm ($w_{1/2}$ ca. 7.7 Hz). The latter two resonances are readily assigned to the organic ligand since they are missing from the spectrum generated

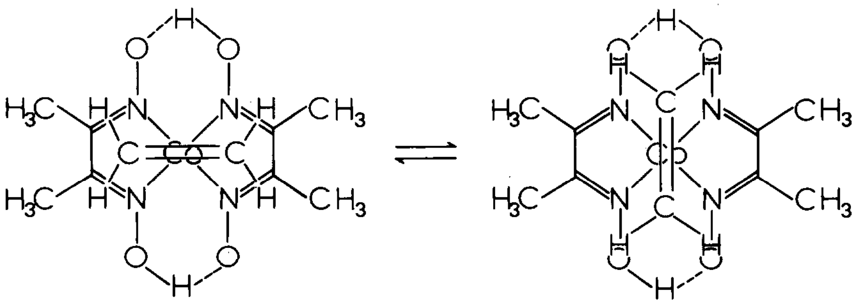


Fig. 6. Hypothetical conformational equilibrium of the cobaloxime(III)ethylene $\pi$-complex intermediate.

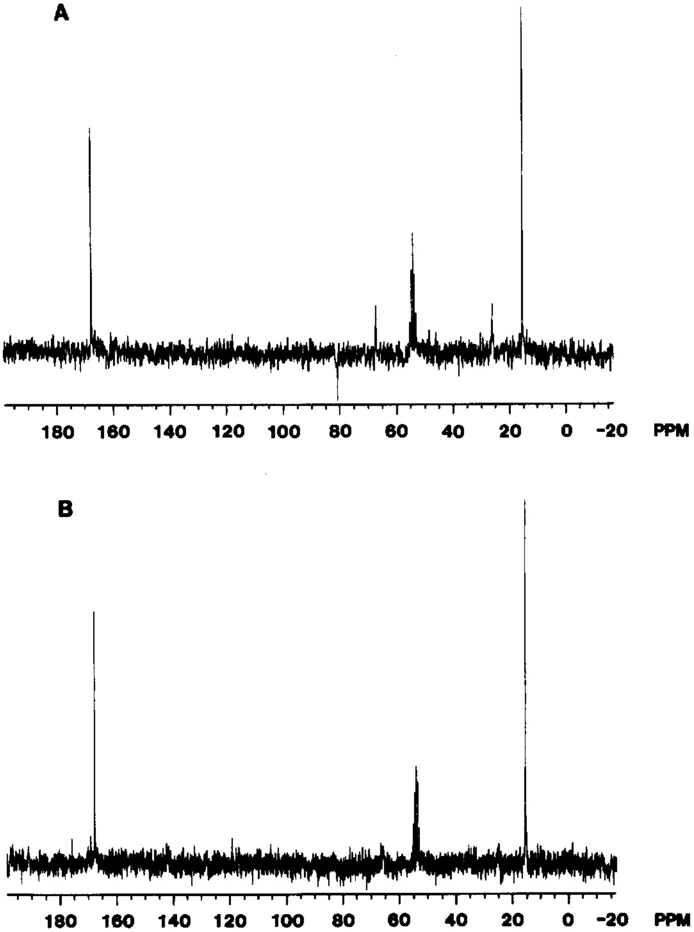
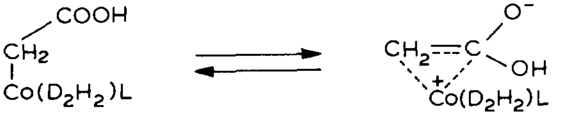


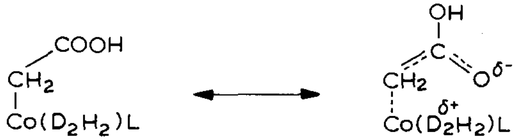
Fig. 7. 50.31 MHz $^{13}C$ NMR spectra of the intermediate generated from $HOCH_2CH_2Co(D_2H_2)OH_2$ (A) or $HOCD_2CD_2Co(D_2H_2)OH_2$ (B) in 70% $HClO_4/H_2O$, −30°C. Chemical shifts are relative to external TMS. The multiplets at 54 ppm are due to $CD_2Cl_2$ in a concentric insert to provide a deuterium lock signal.

from $HOCD_2CD_2Co(D_2H_2)OH_2$ under the same conditions (Fig. 7B). Again, virtually identical spectra can be generated from IIIa and IIIb except that these contain additional, expected resonances from the alcohol leaving groups. A very similar spectrum was also obtained from I in 73% $D_2SO_4/D_2O$ (not shown) at −5°C, except that the resonances occurred at slightly different positions (12.030, 22.904, 71.527 and 164.213 ppm). These spectra are incompatible with a formulation of the intermediate as an ethylene-cobaloxime(III) $\pi$-complex since it seems highly unlikely that the $^{13}C$ chemical shifts of the ethylene carbons of the two $\pi$-complex conformers (Fig. 6) could differ by as much as 41 ppm. We consequently conclude that the intermediate is probably a $\sigma$-bonded ethylcobaloxime carbonium ion which is probably significantly stabilized by lyate ion pairing. The differences in $^{13}C$ chemical shift between the intermediate generated in $H_2SO_4/H_2O$ and $HClO_4/H_2O$ mixtures (which may, in part, be due to differences in the extent of protonation of the intermediate in the two media) suggest significant ion pairing between the mineral acid anions and the highly cationic intermediate generated at these acidities. In addition, extensive rate measurements (not shown) of the decomposition of I in $HClO_4/H_2O$ mixtures have shown that the *H*-rate profile in this medium is similar in shape to that in $H_2SO_4/H_2O$ but that the observed rate constants are from 1.3 to about 6-fold faster in $HClO_4/H_2O$ mixtures, the difference increasing with increasing acidity [40]. These observations support the the idea that significant ion pairing between lyate ion and the cationic species of intermediate (and starting material) occurs in such strongly acidic media [41].

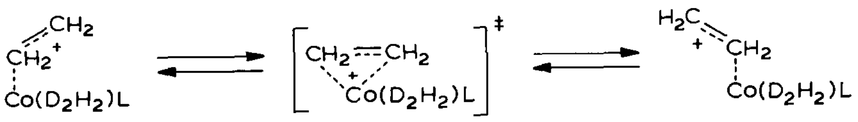
The cationic center of the intermediate may also be significantly stabilized by $\sigma$–$\pi$ hyperconjugation from the Co–C bond [42,43] as originally suggested by Golding, et al. [3]. This latter idea is particularly attractive on several counts. In our recent study of the $\beta$-effect in 1-carboxyalkylcobaloximes [43] we specifically considered the competing possibilities of valence tautomerization (eq. 18, i.e. equilibrium formation


(18)

of a cobaloxime(III)-enediolate $\pi$-complex) and hyperconjugation (eq. 19) as explanations for the feeble acidity of these carboxylic acids.


(19)

We were able to firmly conclude that hyperconjugation was in fact responsible for the $\beta$-effect in such complexes. This work demonstrates the ability of the evidently very polarizable Co–C $\sigma$-bond to participate in hyperconjugation. In addition, a hyperconjugated carbonium ion intermediate provides a handy rationalization for the very large decrease in the rate constant for intermediate dissociation to products upon sequential protonation of the equatorial ligand (i.e., $k_2 \gg k'_2 \gg k''_2$, Table 1 and Scheme 2). Hence, as the cobalt center of the intermediate becomes increasingly cationic due to equatorial protonation the tendency of the Co–C $\sigma$-bond to donate electron density to stabilize the carbonium ion center will decrease, thus increasing the localized electron density in the Co–C bond and stabilizing it with respect to dissociation of the organic ligand. Hyperconjugation may also provide an explanation for the apparently very low enthalpy of activation for topoisomerism of the intermediate as it would seem that a symmetrical transition state for topoisomerization (a $\pi$-complex?) could be reached with very little bond breaking from the ground state (eq. 20) and that the enthalpic effect of that amount of bond breaking which


(20)

must occur may be compensated for by bond making in such a symmetrical transition state.

With these thoughts in mind, it may well be time to conclude that cobalt(III)-olefinic $\pi$-complexes are not, in fact, involved in organocobalt chemistry to any significant extent and that hyperconjugated ionic species are much more common. The evidently high polarizability of Co–C $\sigma$-bonds and the consequent tendency of chelated cobalt centers to participate in hyperconjugation appears to be a general property of organocobalt species. Our recent study of the acidities of carboxyalkylcobalamins and cobinamides [44] has shown that substantial hyperconjugation occurs in these corrin chelates as well.

## Acknowledgements

This research was supported by the Robert A. Welch Foundation, Houston, Texas, Grant No. Y-749 (K.L.B.) and No. Y-743 (D.S.M.) and the Organized Research Fund of the University of Texas at Arlington. The authors would like to thank Cathy Smith Bacquet, Lien Truong and Wendy Van Dusen for technical assistance.

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39 Golding, et al. [3] report a first-order rate constant of $4.37 \times 10^{-6}$ $s^{-1}$ ($t_{\frac{1}{2}}$ 44 h) for the alcoholysis of 2-acetoxyethyl(pyridine)cobaloxime in absolute ethanol at 25°C.

40 Such effects are common. See C.H. Rochester, Acidity Functions, Academic Press, New York, 1970, Chapter 5.

41 In the limit, the intermediate could, in fact, be a covalent lyate ion ester ($HO_3SOCH_2$-$CH_2Co(D_2H_n)OH_2$). However, this possibility seems remote in that it is unlikely that such a species would show the dynamic behavior demonstrated for the ethyl moiety by $^1H$ NMR spectroscopy.

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