73687-93-1; $NiI_2(CO)(PMePh_2)_2$, 73687-94-2; $NiBr_2(CO)(PPh_3)_2$, 73687-95-3; $NiI_2(CO)(PPh_3)_2$, 73687-96-4; $NiBr_2(CO)(PEt_3)_2$, 73687-97-5; $NiI_2(CO)(PEt_3)_2$, 73687-98-6; $[NiCl(CO)(PMe_3)_3](BF_4)$, 70252-79-8; $[NiBr(CO)(PMe_3)_3](BF_4)$, 70252-77-6; $NiI_2(PMe_3)_3$, 53188-34-4; $[NiCl(PMe_3)_4](BF_4)$, 60919-88-2; $[NiBr(PMe_3)_4](BF_4)$, 60919-89-3.

Supplementary Material Available: Table III, a listing of observed and calculated structure amplitudes (3 pages). Ordering information is given on any current masthead page.

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Base-Catalyzed Bimodal Cleavage of Ethylaquocobaloxime[1,2]

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The base-catalyzed decomposition of ethylaquocobaloxime has been studied by GLC, mass spectrometry, and manometric techniques at 50.0 ± 0.1 °C in aqueous solution and in D_2O. Under all conditions, a mixture of ethane and ethylene is obtained, and no photolabile organocobalt complex is formed. In D_2O the alkane product is monodeuterioethane of high isotopic purity, but little or no deuterium is incorporated into the alkene product. Unreacted starting material recovered from partial decomposition in alkaline D_2O was found to have very little deuterium incorporated into its alkyl ligand. From the dependence of the product ratio on base concentration, the observed rate constant for decomposition in 1.0 M base and the spectrophotometrically determined dissociation constants for the hydroxo (and deuterioxo) species the specific second-order rate constants for the alkene-forming reaction (($(1.06 \pm 0.06) \times 10^{-6}$ M^{-1} s^{-1} and $(3.21 \pm 0.12) \times 10^{-6}$ M^{-1} s^{-1} for the anionic hydroxo species in H_2O and D_2O, respectively, and $(5.36 \pm 0.43) \times 10^{-7}$ M^{-1} s^{-1} and $(2.20 \pm 0.15) \times 10^{-6}$ M^{-1} s^{-1} for the neutral aquo species in H_2O and D_2O, respectively) and the alkane-forming reaction (($(6.05 \pm 0.35) \times 10^{-6}$ M^{-1} s^{-1} and $(5.87 \pm 0.73) \times 10^{-6}$ M^{-1} s^{-1} for the hydroxo species in H_2O and D_2O, respectively, and zero for the aquo species in both solvents) have been determined. The large inverse solvent deuterium isotope effects for the alkene-forming reaction are discussed in terms of a likely E2 mechanism. The mechanism of the alkane-forming reaction cannot be determined from the present data but is discussed in light of the recent results for methane formation from methylaquocobaloxime in aqueous base. It is concluded that the mechanism of the alkane-forming reaction may not be the same for the two organocobaloximes.

Introduction

In recent reports[3,4] one of us described quantitative experiments on the heterolysis of methylaquocobaloxime in aqueous base at 50 °C, evidently an example of mode III cleavage[4] of a simple, unactivated organocobalt complex. This reaction leads to the formation of methane in about 70% yield and a base-stable but photolabile methylcobalt side product in about 30% yield. Although Schrauzer[5] has stated that higher alkylcobaloximes decompose in aqueous base to form olefins and cobaloxime(I) (i.e., mode I cleavage[4]), our preliminary GLC analysis of the products of the decomposition of ethylaquocobaloxime in aqueous base showed that mixtures of ethane and ethylene were always obtained. As this reaction seemed to provide an opportunity to simultaneously study mode I and mode III cleavages as well as to extend our earlier work on the base-catalyzed mode III cleavage of simple organocobalt complexes, we undertook a quantitative study of the base-catalyzed decomposition of ethylaquocobaloxime. The present report describes the results of our study including the kinetics of ethylaquocobaloxime decomposition and the dependence of both cleavage modes on base concentration in both water and D_2O at 50 °C.

Experimental Section

Materials. Cobaltous chloride, methyl sulfide, sodium borohydride, sodium and potassium hydroxides, potassium chloride, potassium nitrate, methanol, dimethylglyoxime, ethyl bromide, and pyridine were obtained in the highest purity commercially available and used without further purification. Deuterium oxide (99.8 atom % D) and sodium deuterioxide (40% solution in D_2O, 99+ atom % D) were from Aldrich. Glass-distilled deionized water was used throughout.

$CH_3CH_2Co(D_2H_2)OH_2$ was synthesized and characterized by the procedures previously described.[6]

$CH_3CH_2Co(D_2H_2)py$ was obtained from the aquo complex as follows. A 250-mg sample of $CH_3CH_2Co(D_2H_2)OH_2$ was dissolved in about 25 mL of methanol with stirring. Upon addition of 1 mL of pyridine, the solution changed from orange to yellow immediately. After an additional 10 min of stirring, 25 mL of water was added, and the volume was reduced to about 25 mL on a rotary evaporator. After cooling of the solution in ice, the yellow solid was collected by vacuum filtration and dried over P_2O_5 under vacuum (yield 64%).

Unreacted $CH_3CH_2Co(D_2H_2)OH_2$ from partial decomposition in aqueous base was recovered as the pyridine complex in the following manner. A 0.5-g sample of $CH_3CH_2Co(D_2H_2)OH_2$ was dissolved in 25 mL of 1.0 N aqueous KOH (or 1.0 N NaOD/D_2O) which had been purged with argon for 30 min. Under continuous argon purge, the reaction mixture was heated to 50 °C in the dark for 24 h (i.e., approximately 1 half-time). The reaction mixture was then cooled in ice and neutralized with concentrated HCl (or 20% DCl in D_2O). Addition of 1 mL of pyridine caused immediate formation of a yellow precipitate which was collected by vacuum filtration and dried over P_2O_5 under vacuum.

Methods. Ethylcobaloximes were handled in dim light, and solutions were covered with aluminum foil whenever possible. Ionic strength was maintained at 1.0 M with KCl or KNO_3.

The apparent dissociation constants $K_D^{OH^-}$, for hydroxide ion from $CH_3CH_2Co(D_2H_2)OH^-$, and $K_D^{OD^-}$, for deuterioxide ion from $CH_3CH_2Co(D_2H_2)OD^-$ (eq 1 and 2), were determined spectrophotometrically at 50.0 ± 0.1 °C with an ionic strength of 1.0 M (KCl)

$$CH_3CH_2Co(D_2H_2)OH^- \underset{\pm OH^-}{\overset{K_D^{OH^-}}{\rightleftharpoons}} CH_3CH_2Co(D_2H_2)OH_2 + OH^- \qquad (1)$$

$$K_D^{OH^-} = [CH_3CH_2Co(D_2H_2)OH_2][OH^-]/[CH_3CH_2Co(D_2H_2)OH^-] \qquad (2)$$

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(1) This project was supported by the National Institutes of Health, the U.S. Public Health Service (Grant GM23215), and the Robert A. Welch Foundation, Houston, Texas (Grant Y-749).

(2) Abbreviations: $RCo(D_2H_2)L$ = alkyl(ligand)bis(dimethylglyoximato)cobalt(III) = alkyl(ligand)cobaloxime; py = pyridine.

(3) Brown, K. L. *Inorg. Chim. Acta* **1978**, *31*, L401-L403.

(4) Brown, K. L. *J. Am. Chem. Soc.* **1979**, *101*, 6600-6606.

(5) See footnote 16 in: Schrauzer, G. N.; Weber, J. H.; Beckham, T. M. *J. Am. Chem. Soc.* **1970**, *92*, 7078-7086.

(6) Brown, K. L.; Lyles, D.; Pencovici, M.; Kallen, R. G. *J. Am. Chem. Soc.* **1975**, *97*, 7338-7346.

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Table I. Data Summary for the Decomposition of Ethylaquocobaloxime in 1.0 M Base at 50.0 °C

				isotopic purity, %[c]	
solvent (base)	$10^6 k_{\mathrm{obsd}}$, s^{-1} [a]	total gas yield,[a] %	product ratio[b]	CH_2CHD	CH_3CH_2D
H_2O (KOH)	7.11 ± 0.40[d]	91.8 ± 0.6[d]	5.60 ± 0.24		
D_2O (NaOD)	9.08 ± 0.34[e]	75.3 ± 0.9[e]	1.70 ± 0.20	0.58 ± 0.43	93.8 ± 4.5

[a] From manometric experiments. [b] From GLC experiments; ratio = ethane/ethylene. [c] From mass spectral measurements. [d] Average of three determinations. [e] Average of four determinations.

on a Gilford Model 250 spectrophotometer at 470 nm by the method described previously.[7]

NMR measurements were made on a Varian T-60 NMR spectrometer with a probe temperature of 37 °C.

GLC experiments were performed on a Perkin-Elmer MKII gas chromatograph equipped with a Perkin-Elmer M-1 computing integrator and a 10 ft × $^1/_8$ in. Poropak Q column. At a column temperature of 100 °C and carrier flow rate of 37.5 mL/min, approximate retention times were 95 s for ethylene and 120 s for ethane.

Mass spectral measurements were made on a Du Pont Model 321 GC/MS system equipped with a Riber 400 Model 1000H data system and a 6 ft. × $^1/_8$ in. Poropak Q column operating at an ionizing potential of 70 eV. At ambient temperature (ca. 25 °C) and a carrier flow rate of 28 mL/min, the retention times were 3.6 min for ethylene and 5.3 min for ethane.

Manometric experiments were performed in Warburg manometers with a Precision Seven-Unit Warburg apparatus (Model 66670), with the bath temperature maintained at 50.0 ± 0.1 °C. Manometers were calibrated by using the ferricyanide-hydrazine method[8] and all reaction mixtures were purged continuously for at least 1 h with oxygen-free argon or nitrogen[9] prior to initiation of the reaction. Manometric reaction mixtures were prepared, and data were analyzed as described previously.[4]

Samples for GLC and GC/MS analysis (generally 0.5 mL in volume) contained $CH_3CH_2Co(D_2H_2)OH_2$, KOH (or NaOD), KCl or KNO_3 (when appropriate to maintain ionic strength of 1.0 M), and water (or D_2O) and were prepared in 1.0-mL Reactivials (Pierce). The vial threads were wrapped with Teflon tape, and then the vials were loosely capped with Teflon Mininert valves (Pierce). The vials were then purged with oxygen-free argon for at least 1 h (at room temperature) via a hypodermic needle inserted through the rubber septum in the valve. The valves were then tightly screwed onto the vials; the hypodermic needles were removed and the valves closed. The reaction mixtures were then incubated at 50.0 ± 0.1 °C in the dark for the required period of time. For analysis, the valves were momentarily opened, and a sample of the gas phase (5–150 μL) was removed with a gastight syringe and was immediately injected into the GLC or GC/MS septum inlet.

Pyrolysis samples, consisting of 5 mg of solid $CH_3CH_2Co(D_2H_2)py$, were similarly gassed in 1.0-mL Reactivials for at least 1 h. After the vials were sealed, the samples were pyrolyzed by heating to 225 °C in a mineral oil bath, cooled, and sampled as above.

Authentic monodeuterioethane was synthesized by allowing a few drops of dry bromoethane to react with one magnesium turning in 0.5 mL of diethyl ether in 1.0-mL Reactivials. After the reaction had subsided, the ether was evaporated by passing argon through the vials and warming them slightly. D_2O (0.5 mL) was then injected through the valve septum, and the valve was immediately closed. The gas was sampled with a gastight syringe as described above for injection into the GC/MS column inlet. The mass spectrum obtained was in excellent agreement with that of CH_3CH_2D from the literature.[10]

Results and Discussion

In 1.0 M aqueous KOH at 50 °C $CH_3CH_2Co(D_2H_2)OH_2$ decomposes with a half-time of about 24 h to yield a mixture of ethane and ethylene in a ratio of 5.6:1 (Table I). The combined yield of ethane and ethylene (determined manometrically) exceeded 90%. Unlike the case of $CH_3Co(D_2H_2)OH_2$,[3,4] subsequent photolysis of reaction mixtures did not produce any additional gaseous products. These observations indicate that no base-stable organocobalt side product is formed in this reaction.

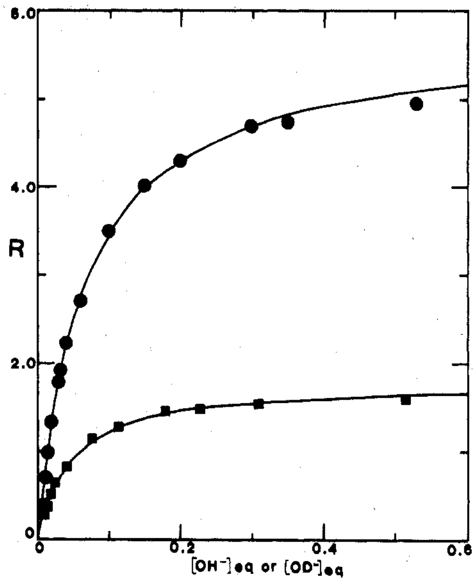

Figure 1. Plots of *R*, the ratio of ethane to ethylene, vs. the equilibrium concentration of hydroxide ion (in H_2O) (●) and the equilibrium concentration of deuterioxide ion (in D_2O) (■) for the base-catalyzed decomposition of $CH_3CH_2Co(D_2H_2)OH_2$ at 50 °C and an ionic strength of 1.0 M (KCl or KNO_3). The *solid lines* are calculated from eq 7 and the values of the rate and equilibrium constants in Table II.

In 1.0 M NaOD (in D_2O) $CH_3CH_2Co(D_2H_2)OH_2$ decomposes about 28% more rapidly (Table I), but the ratio of ethane to ethylene is significantly lowered to 1.7, indicating that one or both of the cleavage modes is subject to a substantial solvent deuterium isotope effect (see below). Although the combined product yield in D_2O was consistently lower than that in H_2O, prolonged photolysis after cessation of the base-catalyzed reaction failed to produce any additional gaseous product. The reason for the poor yield in D_2O is not understood.

Mass spectral analysis of the gaseous products from decomposition in D_2O (Table I) showed that little or no solvent deuterium is incorporated into the alkene product but that the alkane product was monodeuterioethane of high isotopic purity. The latter observation is consistent with the previous finding[3,4] of monodeuteriomethane as the product of base-catalyzed $CH_3Co(D_2H_2)OH_2$ cleavage in D_2O.

Dependence of the Product Ratio on Base Concentration. Because of the slow rate of the base-catalyzed decomposition reaction, it was not feasible to determine the dependence of the rate of the reaction on base concentration manometrically. However, the GLC assay was sufficiently sensitive to allow determination of the product ratio at various base concentrations. To ensure the validity of these determinations, we demonstrated that the product ratio showed no experimentally significant dependence on time at several base concentrations in both H_2O and D_2O. It was similarly demonstrated that substitution of KNO_3 for KCl for maintenance of ionic strength (1.0 M) had no effect on the product ratio. The

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(7) Brown, K. L. *Inorg. Chim. Acta* **1979**, *37*, L513–L516.

(8) Umbreit, W. W.; Burris, R. H.; Stauffer, J. F. "Manometric Techniques"; Burgess: Minneapolis, 1957; Chapter 4.

(9) Meites, L.; Meites, T. *Anal. Chem.* **1948**, *20*, 984–985.

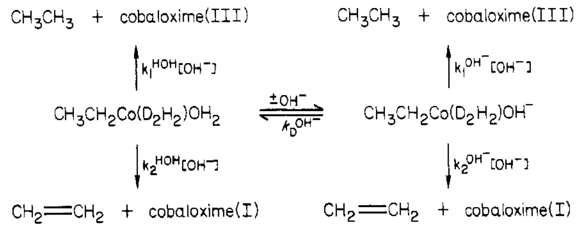
(10) Amenomiya, Y.; Pottie, R. F. *Can. J. Chem.* **1968**, *46*, 1735–1739.

Table II. Rate and Equilibrium Constants for the Base-Catalyzed Heterolysis of Ethylaquocobaloxime[a-c]

	alkane formation		alkene formation		
solvent	$10^6 k_1^{OH^-}$, $M^{-1}\ s^{-1}$	k_1^{HOH}, $M^{-1}\ s^{-1}$	$10^6 k_2^{OH^-}$, $M^{-1}\ s^{-1}$	k_2^{HOH}, $M^{-1}\ s^{-1}$	$K_D^{OH^-}$, M[d]
H_2O	6.05 ± 0.35	0	1.06 ± 0.06	(5.36 ± 0.43) × 10^{-7}	0.132 ± 0.007
D_2O	5.87 ± 0.23	0	3.21 ± 0.12	(2.20 ± 0.15) × 10^{-6}	0.0716 ± 0.0036

[a] 50.0 ± 0.1 °C, ionic strength 1.0 M. [b] See eq 1 and 2 and Scheme I for definitions of the rate and equilibrium constants. [c] Ionic strength maintained with KCl or KNO_3. [d] Determined spectrophotometrically at 470 nm.

Scheme I



results of these determinations are shown in Figure 1 as a plot of R (ratio of ethane to ethylene) vs. equilibrium base concentration (calculated from eq 2 and the measured values of $K_D^{OH^-}$ and $K_D^{OD^-}$) in both H_2O and D_2O. As seen in the figure, the dependence of R on base concentration is hyperbolic in both solvents. These data were analyzed in conjunction with Scheme I which allows for simultaneous mode III cleavage (to form the alkane and a cobalt(III) complex) and mode I cleavage (i.e., β elimination to form the alkene and a cobalt(I) complex) from both the aquo and hydroxo species of the organocobaloxime. From the law of mass action and the definition of $K_D^{OH^-}$ (eq 1 and 2) one can derive the rate laws for the apparent, pseudo-first-order rate constants for the alkane (eq 3) and alkene (eq 4) forming reactions. For parallel

$$k_1^{obsd} = (k_1^{HOH}K_D^{OH^-}[OH^-] + k_1^{OH^-}[OH^-]^2)/([OH^-] + K_D^{OH^-}) \qquad (3)$$

$$k_2^{obsd} = (k_2^{HOH}K_D^{OH^-}[OH^-] + k_2^{OH^-}[OH^-]^2)/([OH^-] + K_D^{OH^-}) \qquad (4)$$

pseudo-first-order processes the ratio of the products (R = [ethane]/[ethylene]) is equal to the ratio of the pseudo-first-order rate constants[11] so that

$$R = k_1^{obsd}/k_2^{obsd} \qquad (5)$$

and

$$R = (k_1^{HOH}K_D^{OH^-} + k_1^{OH^-}[OH^-])/(k_2^{HOH}K_D^{OH^-} + k_2^{OH^-}[OH^-]) \qquad (6)$$

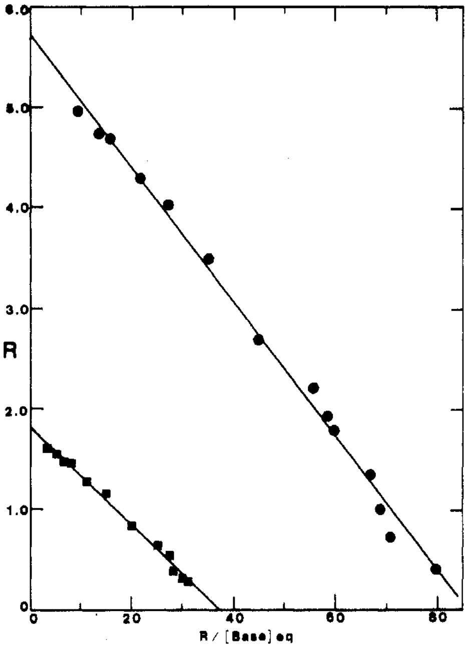


Figure 2. Plots of R, the ratio of ethane to ethylene, vs. R/[base]$_{eq}$ in H_2O (●) and D_2O (■) for the base-catalyzed decomposition of $CH_3CH_2Co(D_2H_2)OH_2$ at 50.0 °C and an ionic strength of 1.0 M (KCl or KNO_3). The *solid lines* are linear regression lines from which the values slope = −0.0667 ± 0.0015 and intercept = 5.73 ± 0.08 for H_2O and slope = −0.0490 ± 0.0013 and intercept = 1.83 ± 0.03 for D_2O were obtained.

Equation 6 may be seen to be a rectangular hyperbola with an intercept equal to k_1^{HOH}/k_2^{HOH}, a saturation factor of $k_2^{HOH}K_D^{OH^-}/k_2^{OH^-}$ and an asymptote of $k_1^{OH^-}/k_2^{OH^-}$ by arrangement to eq 7. To simplify the analysis of the data via

$$R = \{(k_1^{HOH}/k_2^{HOH})(k_2^{HOH}K_D^{OH^-}/k_2^{OH^-}) + k_1^{OH^-}[OH^-]/k_2^{OH^-}\}/\{(k_2^{HOH}K_D^{OH^-}/k_2^{OH^-}) + [OH^-]\} \qquad (7)$$

eq 7, we have assumed the intercept k_1^{HOH}/k_2^{HOH} to be zero. This assumption is justified by the clear trend of the data toward the origin in both solvents (Figure 1), the fact that the aquo species of methylcobaloxime was found to be unreactive toward methane formation,[4] and the success of the resulting treatment (see Figure 2 and below). The resulting simplified form of eq 7 may then be rearranged to the linear form of eq 8. Figure 2 shows plots of the data in both solvents according

$$R = (k_1^{OH^-}/k_2^{OH^-}) - (k_2^{HOH}K_D^{OH^-}/k_2^{OH^-})R/[OH^-] \qquad (8)$$

to eq 8. From the slopes and intercepts of the least-squares fits to these data, the terms $k_1^{OH^-}/k_2^{OH^-}$ and $k_2^{HOH}K_D^{OH^-}/k_2^{OH^-}$ were evaluated for each solvent (values are given in the legend to Figure 2). With these values, with the values for $K_D^{OH^-}$ in both solvents (determined spectrophotometrically, listed in Table II), and on the assumption that the values of the observed rate constants for $CH_3CH_2Co(D_2H_2)OH_2$ decomposition in 1.0 M base (Table I) are essentially identical with the sums of the individual rate constants for the two parallel reactions from the hydroxo complex (eq 9),[11] the system of

$$k_{obsd}(1\ M\ base) = k_1^{OH^-} + k_2^{OH^-} \qquad (9)$$

simultaneous equations may be solved. The values for the intrinsic rate constants thus obtained are listed in Table II.

Mechanism of Alkene Formation. As seen in Table II, the base-catalyzed elimination reaction of ethylcobaloxime is subject to a substantial inverse solvent deuterium isotope effect for both the aquo (k_2^{HOH}/k_2^{DOD} = 0.24 ± 0.02) and hydroxo ($k_2^{OH^-}/k_2^{OD^-}$ = 0.33 ± 0.02) complexes. Such inverse solvent deuterium isotope effects are common for base-catalyzed E2 eliminations of poor leaving groups.[12-14] To substantiate such

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[11] Frost, A. A.; Pearson, R. G. "Kinetics and Mechanism", 2nd ed.; Wiley: New York, 1961; pp 160–165.

[12] Jencks, W. P. "Catalysis in Chemistry and Enzymology"; McGraw-Hill: New York, 1969; p 272.

a mechanistic assignment, it is desirable to determine if there is any exchange of solvent deuterium into the organic ligand of the starting material during the course of the elimination reaction. Although the lack of any significant deuterium incorporation into the alkene product during the reaction suggests that such exchange does not occur to any substantial extent (Table I), experiments were performed to directly quantitate the extent of deuterium incorporation into starting material. For these experiments, $CH_3CH_2Co(D_2H_2)OH_2$ was partially decomposed by reaction for 25 h in 1.0 M aqueous KOH and in 1.0 M NaOD in D_2O, at 50 °C. Unreacted starting material was recovered in both cases following neutralization of reaction mixtures as the pyridine adduct. For determination of the extent of deuterium incorporation into the alkyl ligand, the complexes were pyrolyzed anaerobically, and the mass spectra of the resulting gases were obtained. Both samples of recovered starting material as well as untreated $CH_3CH_2Co(D_2H_2)py$ yielded principally ethylene (95.9 ± 0.3%) with lesser amounts of ethane (4.1 ± 0.3%) in substantial agreement with the results of Schrauzer and co-workers.[15] The pyrolysis products obtained from the complex recovered after partial base-catalyzed decomposition in D_2O were found to be enriched in deuterium to the extent of 0.15 ± 0.37% for ethylene (as $CH_2{=}CHD$) and 2.38 ± 1.50% for ethane (as CH_3CH_2D). These values surely must overestimate the extent of deuterium incorporation into the alkyl ligand since the ethane pyrolysis product probably arises via thermal homolysis of the carbon–cobalt bond followed by abstraction of a hydrogen atom from the equatorial ligand system.[15] Since all of the hydrogens in the equatorial ligand system exchange with solvent deuterium in 1.0 M OD^- at 50.0 °C substantially faster than the complex decomposes (see below), additional incorporation of deuterium into the ethane pyrolysis product above that due to actual exchange of deuterium into the alkyl ligand during the base-catalyzed reaction is to be expected. Nonetheless, if all of the deuterium found in the pyrolysis products is assumed to be due to base-catalyzed exchange into the β position of the alkyl ligand, the $CH_3CH_2Co(D_2H_2)py$ recovered after partial decomposition in D_2O was at most 0.24% enriched in deuterium. Consequently an upper limit of 2.67×10^{-8} M^{-1} s^{-1} can be set on the rate constant for the base-catalyzed exchange reaction. As this value is slightly more than two orders of magnitude lower than the rate constant for elimination from the deuterioxo complex in D_2O (Table II), the mechanism must either be E2 or E1cB with an extremely low rate of reprotonation of the intermediate carbanion. Since solvent deuterium isotope effects for E1cB eliminations are generally much smaller (0.77–0.87)[16] than those seen in the present work, the mechanism is most likely E2.

The magnitude of the inverse solvent deuterium isotope effects observed is, however, larger than expected for such eliminations. While deuterioxide ion is about twofold more basic than hydroxide ion at 50.0 °C,[14,17] the elimination reaction is about threefold faster in D_2O than in H_2O for the hydroxo species and about fourfold faster for the aquo species. Thornton's detailed derivation of solvent deuterium isotope effects[14,18] shows that all such measured effects are a composite of two terms: the actual thermodynamic isotope effect and a term representing the solvation or "medium" isotope effect which is normally expected to be small.[18] However, in the present case, substantial exchange of deuterium into the leaving group occurs, leading to the complication of secondary deuterium isotope effects. It is clear that both of the oxime-bridged hydrogens[19] and the axial ligand hydrogens of the organocobaloxime substrate must rapidly exchange with solvent deuterium. In addition, it has been shown that all 12 of the equatorial methyl hydrogens of methylcobaloximes exchange with solvent deuterons in basic media.[4,20,21] In order to determine if ethylcobaloximes undergo such exchange rapidly enough to complicate the observed isotope effect of the base-catalyzed elimination reaction, we measured the ^1H NMR spectrum of $CH_3CH_2Co(D_2H_2)OH_2$ in 1.0 M NaOD in D_2O–methanol-d_4 (50% v/v) as a function of time at 37 °C. Figure 3 shows a semilogarithmic plot of the relative intensity of the ^1H NMR integral for the equatorial methyl groups (ca. 2.1–2.3 ppm downfield of Me_4Si) vs. time, the slope of which gives a rate constant of $(9.57 \pm 0.22) \times 10^{-5}$ M^{-1} s^{-1} for the exchange reaction. Hence solvent deuterium exchange into the equatorial methyls is about 30-fold faster at 37 °C than the elimination reaction at 50 °C (Table II), at least in 1.0 M base. Consequently, throughout most of the course of the decomposition reaction of $CH_3CH_2Co(D_2H_2)OH_2$ in D_2O, the cobaloxime(I) leaving group is completely deuterated (15 positions in the hydroxo species, 16 in the aquo species). If we assume that the "medium effect" contribution to the observed isotope effect is small,[18] then we must conclude that the deuterated cobaloxime moieties are some 1.5–2.0-fold better leaving groups (for the hydroxo and aquo species) than the corresponding hydrogenated species.

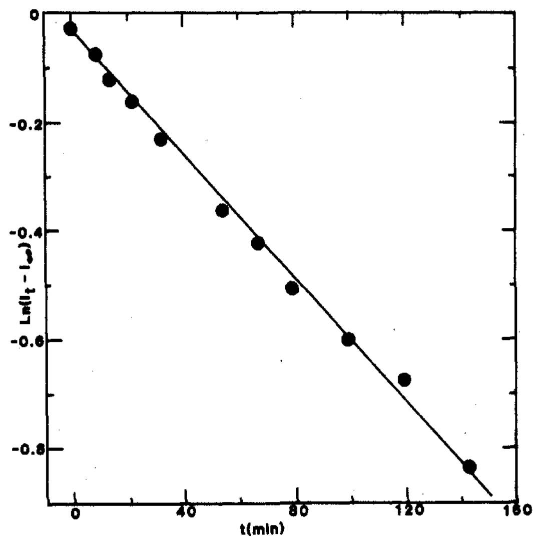

Figure 3. Plot of the natural logarithm of the equatorial methyl group ^1H NMR integral at time t minus the integral at t = 48 h vs. time for $CH_3CH_2Co(D_2H_2)OH_2$ in 1.0 M NaOD in D_2O–methanol-d_4 (50% v/v) at 37 °C. The *solid line* is a linear regression line, the slope of which is $(-5.74 \pm 0.13) \times 10^{-3}$ min^{-1}.

Mechanism of Alkane Formation. As was the case for the base-catalyzed formation of methane from methylaquocobaloxime,[3,4] the alkane product obtained in D_2O media in the present study is essentially completely monodeuterated (Table I). This observation is consistent with either a radical mechanism (i.e., mode II cleavage) in which the alkyl radical generated abstracts a hydrogen from the equatorial methyl groups [which become deuterated more rapidly than the

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(13) Saunders, W. H.; Cockerill, A. F. "Mechanisms of Elimination Reactions"; Wiley: New York, 1973; Chapter 2.

(14) Steffa, L. J.; Thornton, E. R. *J. Am. Chem. Soc.* **1967**, *89*, 6149–6156.

(15) Schrauzer, G. N.; Sibert, J. W.; Windgassen, R. J. *J. Am. Chem. Soc.* **1968**, *90*, 6681–6688.

(16) Reference 13, Chapter 1.

(17) Pentz, L.; Thornton, E. R. *J. Am. Chem. Soc.* **1967**, *89*, 6931–6938.

(18) Thornton, E. K.; Thornton, E. R. In "Isotope Effects in Chemical Reactions"; Collins, C. J., Bowman, N. S., Eds.; Van Nostrand: New York, 1970; Chapter 4.

(19) Birk, J. P.; Chock, P. B.; Halpern, J. *J. Am. Chem. Soc.* **1968**, *90*, 6959–6963.

(20) Cartāno, A. V.; Ingraham, L. L. *Bioinorg. Chem.* **1977**, *7*, 351–357.

(21) Brown, K. L.; Jinkerson, D. *J. Organomet. Chem.* **1979**, *164*, 203–209.

complex decomposes for either complex (see above and ref 4)] or a mode III heterolytic mechanism in which the emerging carbanion is protonated by solvent. For the latter possibility, two kinetically indistinguishable mechanisms have been discussed:[4] mechanism I in which dissociation of an equatorial methyl proton leads to a dianionic intermediate which decomposes to yield an alkyl ligand carbanion and mechanism II in which hydroxide ion directly attacks the equatorial ligand system leading to concerted expulsion of the organic ligand as a carbanion. Although these two mechanisms could presumably be distinguished by their solvent deuterium isotope effects, the complications arising from secondary isotope effects due to extensive deuteration of the cobaloxime moiety and the very small magnitude of the observed isotope effect ($k_1^{OH^-}/k_1^{OD^-} = 1.03 \pm 0.07$) make such a distinction impossible.

It is surprising to find that $CH_3Co(D_2H_2)OH^-$[4] is 22.5-fold more reactive in the alkane forming reaction than $CH_3CH_2Co(D_2H_2)OH^-$ (Table II), considering the small difference in electron inductive effect for the two organic ligands ($\sigma^* = 0$ for CH_3, $\sigma^* = -0.10$ for CH_3CH_2[22]). This result strongly suggests either that one of the two complexes is anomalously reactive or that the mechanism of alkane formation is not the same for both complexes. The lack of any significant formation of side product in the $CH_3CH_2Co(D_2H_2)OH^-$ case also seems to support the latter conclusion. Further experiments are in progress to attempt to clarify this question.

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Registry No. $CH_3CH_2Co(D_2H_2)OH_2$, 26025-30-9; $CH_3CH_2Co(D_2H_2)OH^-$, 73926-34-8; CH_3CH_3, 74-84-0; $CH_2{=}CH_2$, 74-85-1; $CH_3CH_2Co(D_2H_2)py$, 25360-57-0.

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(22) Taft, R. W. In "Steric Effects in Organic Chemistry"; Newman, M. S., Ed.; Wiley: New York, 1956; Chapter 13.

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Enthalpy of Combustion of a Copper Complex. Standard Enthalpy of Formation of Bis(nitrato)(1,4,8,11-tetraazacyclotetradecane)copper(II)

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The standard energy of combustion of bis(nitrato)(1,4,8,11-tetraazacyclotetradecane)copper(II) has been determined by oxygen aneroid rotating-bomb calorimetry. Nitric acid was used as solvent for the solid products of combustion in order to produce a well-defined homogeneous final solution of copper(II) nitrate in excess nitric acid. The work reported is the first known application of rotating-bomb calorimetry to an organocopper compound. A standard enthalpy of formation, $\Delta H_f°(C_{10}H_{24}N_6O_6Cu(c)) = -639.4 \pm 4.0$ kJ mol^{-1}, was derived from the experimental data and was used, together with enthalpy of solution data, to derive the enthalpy of formation of the complex ion in aqueous solution. This latter value was in close agreement with a direct calorimetric value.

Introduction

The phenomenon that some macrocyclic ligands in aqueous solution form more stable complexes with metal ions than the analogous open-chain ligands with the same donor groups has been termed the macrocyclic effect.[1] Since the first reported example of this effect, which involved the copper complex of a hexamethyl derivative of a 14-membered tetraaza macrocycle,[1] a great deal of interest has been shown in the thermodynamic origins of this extra stability. Early conflicting studies assigned the extra stability to wholly entropy[2] or wholly enthalpy[3] terms based on enthalpy values obtained from temperature-dependent stability constant studies. More recently[3-7] direct calorimetric determinations of enthalpy values have shown that the entropy term is always favorable and that the enthalpy term is dependent on the matching of the size of the macrocyclic ligand aperture to that of the metal ion. For the octahedral complexes of copper(II) and nickel(II) with 1,4,8,11-tetraazacyclotetradecane (L_1) and 1,4,8,11-tetraazaundecane (L_2), ΔH values for the metathetical reaction

$$ML_2^{2+}(aq) + L_1(aq) = ML_1^{2+}(aq) + L_2(aq) \qquad (1)$$

which represents the macrocyclic effect are −19.7[6] and −20.5 kJ mol^{-1},[7] respectively. These values have been obtained from the calorimetrically determined enthalpy change associated with the formation reactions, namely

$$M^{2+}(aq) + L(aq) = ML^{2+}(aq) \qquad (2)$$

which were measured for both ligands, L_1 and L_2. The experimental conditions used in the determinations were extreme (pH 14), and some collaboration of the results seemed desirable especially since they did not agree with ΔH values obtained indirectly. We decided, therefore, to determine the standard enthalpies of formation of both ligands and their copper complexes, in the form of their nitrate salts, by oxygen aneroid bomb calorimetry and by combining these data with the corresponding enthalpies of solution to obtain an independent value for the macrocyclic enthalpy.

The standard enthalpies of formation and solution of both ligands, L_1 and L_2, have been reported in ref 8. Here we report the determination of the standard enthalpy of formation of bis(nitrato)(1,4,8,11-tetraazacyclotetradecane)copper(II) ($CuL_1(NO_3)_2$). The authors believe that this is the first re-

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(1) S. K. Cabbiness and D. W. Margerum, *J. Am. Chem. Soc.*, **91**, 6540 (1969).

(2) M. Kodma and E. Kimura, *J. Chem. Soc., Dalton Trans.*, **116**, 2341 (1976).

(3) F. P. Hinz and D. W. Margerum, *Inorg. Chem.*, **13**, 2941 (1974).

(4) A. Anichini, L. Fabbrizzi, P. Paoletti, and R. M. Clay, *J. Chem. Soc., Chem. Commun.*, 244 (1977).

(5) A. Anichini, L. Fabbrizzi, P. Paoletti, and R. M. Clay, *Inorg. Chim. Acta*, **22**, L25 (1977).

(6) A. Anichini, L. Fabbrizzi, P. Paoletti, and R. M. Clay, *J. Chem. Soc., Dalton Trans.*, 577 (1978).

(7) L. Fabbrizzi, P. Paoletti, and R. M. Clay, *Inorg. Chem.*, **17**, 1042, (1978).

(8) R. M. Clay, M. Micheloni, P. Paoletti, and W. V. Steele, *J. Am. Chem. Soc.*, **101**, 4119 (1979).

0020-1669/80/1319-2414$01.00/0