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Kinetics and Mechanism of Alkali-induced Decomposition of 2-Alkoxyethylcobaloximes*

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Abstract

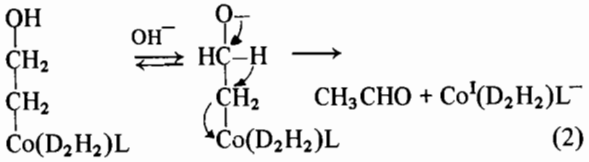
Kinetics of the base-induced decomposition of five 2-alkoxyethyl(aquo)cobaloximes, $ROCH_2CH_2Co(D_2H_2)OH_2$ ($R = C_6H_5$, CF_3CH_2, CH_3, CH_3CH_2, $(CH_3)_2CH$), have been studied manometrically in aqueous base, ionic strength 1.0 M (KCl) at 25.0 ± 0.1 °C under an argon atmosphere. For the complexes with good leaving group alkoxide substituents ($R = C_6H_5$ and CF_3CH_2) the reactions are first-order in cobaloxime and first-order in hydroxide ion and produce stoichiometric amounts of ethylene and leaving group alcohol (ROH). NMR observation of decomposing solutions and workup of cobalt chelate products show that the reaction is initiated by hydroxide ion attack on an equatorial quaternary carbon leading to formation of an altered cobaloxime product in which one of the Schiff's base linkages has become hydrated. For the remainer of the complexes the yield of ethylene is less than stoichiometric and pH-dependent, and the ethylene evolving reaction is second-order in hydroxide ion activity. The yield-limiting side reaction is shown to be base-catalyzed formation of a base-stable but photolabile alkoxyethylcobaloxime analog in which a Schiff's base linkage of the chelate has become hydrated. β-Elimination to form alkyl vinyl ethers was not observed for any of the alkoxyethylcobaloximes. The second-order dependence of ethylene formation on hydroxide ion activity for $R = CH_3$, CH_2CH_3, and $CH(CH_3)_2$ is discussed at some length, but is not well understood at present.

Introduction

Our continuing interest in the mechanism of carbon–cobalt bond cleavage reactions of organocobalt chelates [1–7] has lead us to a consideration of the mechanism of base-induced acetaldehyde formation from 2-hydroxyethyl-cobaloximes (eqn. (1)). Schrauzer and Sibert [8] originally proposed

$$HOCH_2CH_2Co(D_2H_2)L \xrightarrow{OH^-} CH_3CHO + Co^I(D_2H_2)L^- \quad (1)$$

a 1,2-hydride shift mechanism (eqn. (2)) for this reaction. The major competing mechanism for this



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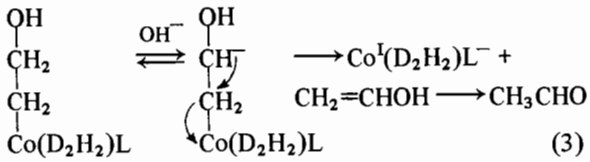
reaction is base-catalyzed β-elimination (eqn. (3)). Since acetaldehyde undergoes rapid exchange with



(3)

solvent deuterons in basic D_2O [8], Schrauzer and Sibert were unable to carry out the critical experiment of measuring the isotopic composition of acetaldehyde formed from 2-hydroxyethylcobaloxime in basic D_2O to distinguish between the two mechanisms. These authors subsequently ruled out the β-elimination mechanism based on the qualitative observation that 2-ethoxyethyl(pyridine)cobaloxime seemed completely alkali-resistant [8]. While this complex is indeed much more resistant to alkali than the corresponding hydroxyethyl derivative, it seemed unlikely that it could be completely alkali-resistant, considering that even methyl- and higher alkylcobaloximes undergo slow Co–C bond cleavage in strong alkali [1–5, 9–11]. Ethylcobaloxime is

*Abbreviations: $RCo(D_2H_2)L$ = alkyl(ligand)bis(dimethylglyoximato)cobalt(III) = alkyl(ligand)cobaloxime.

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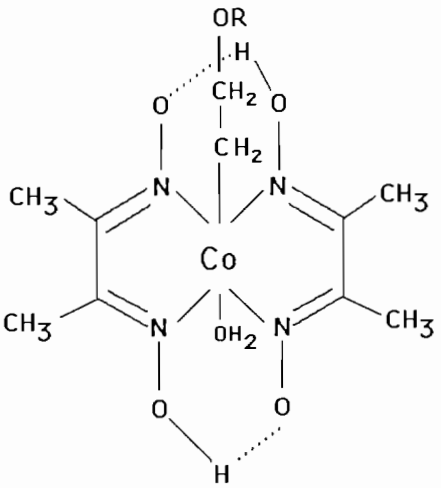
especially interesting in this context as it undergoes (among other reactions) β-elimination in aqueous base [3, 4, 12].

We accordingly decided to investigate the reactions of 2-alkoxyethylcobaloximes in greater detail. To eliminate the inhibiting effects of axial bases, we synthesized and studied the reactions of a series of 2-alkoxyethyl(aquo)cobaloximes [**Ia–e**] with alkali. It soon became apparent that rather than β-elimination (eqn. (4)), the complexes decomposed with ethylene formation apparently according to eqn. (5). While this work was in progress a paper appeared by



Ia, R = C_6H_5
Ib, R = CF_3CH_2
Ic, R = CH_3
Id, R = CH_3CH_2
Ie, R = $(CH_3)_2CH$

$$ROCH_2CH_2Co(D_2H_2)OH_2 \xrightarrow{OH^-}$$

$$ROCH{=}CH_2 + Co^{I}(D_2H_2)OH_2^- \qquad (4)$$

$$ROCH_2CH_2Co(D_2H_2)OH_2 \xrightarrow{OH^-}$$

$$CH_2{=}CH_2 + ROH + Co^{III}(D_2H_2)(OH_2)_2 \qquad (5)$$

Mock and Bieniarz [13] also showing that olefins were formed by base-induced decomposition of 2-alkoxyalkylcobaloximes. However, as these authors neither quantitated the olefins produced in their reactions nor looked for formation of vinyl ethers the question regarding the lability of such complexes toward base-catalyzed β-elimination remains unanswered. In addition, as several of our kinetic observations and the interpretation thereof differ considerably from those of Mock and Bieniarz a thorough reevaluation of the mechanism of the base-induced decomposition of 2-alkoxyethylcobaloximes seems in order. The current report details the results of our kinetic and mechanistic study of the decomposition of **Ia–e** in aqueous base and shows conclusively that β-elimination (eqn. (4)) is not a significant pathway for the decomposition of these complexes.

Experimental

Materials

Cobaltous chloride, cobaltous acetate, sodium borohydride, potassium hydroxide, potassium phosphates, potassium chloride, organic solvents and reagents were obtained in the highest purity commercially available and used without further purification. Deuterated solvents and sodium deuteroxide (40% solution in D_2O, 99+ atom% D) were from Aldrich. Glass distilled deionized water was used throughout.

The 2-alkoxyethyl(aquo)cobaloximes were prepared by standard reductive alkylation methods [2, 14] using the appropriate 2-alkoxyethyl bromides as alkylating agents. Cobaloximes **Ia** [6, 7], **Ic** [9] and **Id** [6, 7] have previously been described. The previously unreported derivatives were characterized as follows.

$CF_3CH_2OCH_2CH_2Co(D_2H_2)OH_2$ (Ib)

Anal. C, H, N, F [15] NMR (methanol-d_4): δ_{Me_4Si} 1.450 (t, 2H, J = 7.8 Hz), 2.240 (s, 12H), 3.010 (t, 2H, J = 7.7 Hz), 3.675 (q, 2H, J_{H-F} = 9.0 Hz).

$(CH_3)_2CHOCH_2CH_2Co(D_2H_2)OH_2 \cdot 4H_2O$ (Ic)

Anal. C, H, N [15]. NMR ($CDCl_3$): δ_{Me_4Si} 1.000 (d, 6H, J = 6.2 Hz), 1.430 (t, 2H, J = 8.0 Hz), 2.175 (s, 12H), 2.821(t, 2H, J = 8.0 Hz), 3.434 (septuplet, 1H, J = 6.1 Hz).

The 2-alkoxyethylbromide alkylating agents for **Ia** (2-phenoxyethyl bromide), and **Id** (2-ethoxyethyl bromide) were obtained from Eastman. 2-Methoxyethyl bromide was obtained by bromination of 2-methoxyethanol (Eastman) with phosphorus tribromide in pyridine by the method of Palomaa and Kenetti [16]. 2-Isopropoxyethanol was obtained by reaction of sodium isopropoxide with 2-chloroethanol in dry isopropanol [17] and converted to the bromide with PBr_3 [16]. 2,2,2-Trifluoroethoxyethanol was prepared as follows: 66 g powdered KOH and 30 g sodium iodide were added to 100 g 2,2,2-trifluoroethanol (Aldrich) and the mixture was stirred mechanically in a three-necked round-bottomed flask fitted with a reflux condenser and pressure equilizing addition funnel. 2-Chloroethanol (67 ml) was added dropwise while the reaction mixture was maintained at 25 °C with the aid of an ice bath. Following the addition, the mixture was stirred for 2 h at room temperature then carefully heated to 50 °C for 1 h. The reaction mixture was filtered by suction, dried over sodium

sulfate and the product purified by fractional distillation; boiling point 144–145 °C (1 atm), yield 36.1 g (25%). The product was converted to the bromide by reaction with PBr_3 [16]: boiling point 131–135 °C (1 atm), yield 36%.

Methods

All manipulations with organocobaloximes were performed in dim light and solutions were covered with aluminium foil whenever possible. Ionic strength was maintained at 1.0 M with potassium chloride throughout. NMR measurements were made on a Varian T-60 NMR spectrometer (60 MHz) or a Nicolet NT-200 superconducting NMR spectrometer (200.068 MHz).

The apparent proton dissociation constants, pK_a for the axial water ligand of **Ia–e** (eqns. (6) and (7))

$$ROCH_2CH_2Co(D_2H_2)OH_2 \rightleftharpoons ROCH_2CH_2Co(D_2H_2)OH^- + H^+ \quad (6)$$

$$K_a = [ROCH_2CH_2Co(D_2H_2)OH^-][H^+]/[ROCH_2CH_2Co(D_2H_2)OH_2] \quad (7)$$

were determined spectrophotometrically at wavelengths of 450–455 nm on a Cary 219 Spectrophotometer (cell compartment thermostatted to 25.0 ± 0.1 °C) by the method previously described [18]. Values for the apparent hydroxide ion dissociation constant, $K_D^{OH^-}$, from the hydroxo complexes (eqns. (8) and (9)) were calculated from the

$$ROCH_2CH_2Co(D_2H_2)OH^- \rightleftharpoons ROCH_2CH_2Co(D_2H_2)OH_2 + OH^- \quad (8)$$

$$K_D^{OH^-} = [ROCH_2CH_2Co(D_2H_2)OH_2][OH^-]/[ROCH_2CH_2Co(D_2H_2)OH^-] \quad (9)$$

values of pK_a via eqn. (10), where K_w is the ion product of water.

$$K_D^{OH^-} = K_w/K_a \quad (10)$$

Quantitation of ethylene and kinetic measurements of its evolution under an argon atmosphere were performed in Warburg manometers thermostatted at 25 ± 0.1 °C. Manometers were calibrated by the ferricyanide–hydrazine method [19] and samples were prepared, measurements made, and data analyzed as previously described [2]. All reactions were followed to completion, the slowest reactions quantitated having half-times of about 30 h. pH was maintained with KOH or phosphate buffers (for pH < 12.0). In general, duplicate or triplicate measurements were made at each pH and the results averaged to provide the best estimates of ethylene yield and observed rate constants. Although most kinetic runs employed cobaloximes **Ia–Ie** at $1-2 \times 10^{-3}$ M, experiments in which cobaloxime concentration was varied between 5×10^{-4} M and 2.5×10^{-3} M showed that both the ethylene yield and observed decomposition rate constants were independent of starting cobaloxime concentration.

Samples for gas chromatography-mass spectral analysis (general 0.5 ml in volume) were prepared in 1.0 ml Reactivials (Pierce). The vial threads were wrapped with Teflon tape and the vials were loosely covered with Teflon Mininert valves (Pierce). The vials were purged with argon at 0 °C for at least one hour via hypodermic needles inserted through the rubber septa. After purging the valves were tightly screwed on, the purging needles removed and the valves closed. The vials were then incubated at 25 °C in the dark until the reaction was complete (at least $6 \times T_{1/2}$). For ethylene analysis the valves were momentarily opened, a sample of the gas phase was removed with a gastight syringe and immediately injected into a DuPont Model 321 GC/MS system equipped with a Riber 400 Model 1000H data system and a 6 ft × 1/8 in Poropak Q column. At a column temperature of 40 °C and a carrier flow rate of 28 ml/min the retention time of ethylene was about 3.5 min. For analysis of leaving group alcohols, the vials were opened and the samples neutralized by addition to a sufficient volume of 2.0 M monobasic potassium phosphate to create a buffer in the pH range of 6.8–8.0. A sample (1–2 μl) of the aqueous solution was analyzed on the DuPont GC/MS system. Samples for analysis of ethyl vinyl ether contained 0.1 M **Id** in 0.5 ml of 0.5 M KOH in aqueous methanol (10% methanol by volume). Samples were prepared and purged with argon as above, then incubated at 25 °C for 48 h ($9.3 \times T_{1/2}$) in the dark. For analysis, 0.25 ml heptane was injected into the vial, the vial was shaken vigorously, and the heptane layer was sampled (*ca.* 0.5 μl) through the valve septum. Analyses were performed on a Ribermag R10-10C mass spectrometer equipped with a PDP8A data system and a Carlo Erba 4160 gas chromatograph. An SE54 30 m × 0.32 mm capillary column was used with a temperature program of 30 °C for 1 min followed by a 5 °C/min increase to 150 °C. Under these conditions the retention time for ethyl vinyl ether was 1.1 min and for heptane 3.1 min. Controls in which 0.1 M ethyl vinyl ether was substituted for **Id** showed both that ethyl vinyl ether survived the reaction conditions and was readily extracted into heptane. For photolysis experiments samples of **Id** prepared and incubated as above (or prepared in the absence of KOH for neutral photolysis) were illuminated with a 275 watt tungsten lamp at a distance of 20 cm for 5.5 h while

the samples were cooled with a stream of air provided by a small fan. The samples were assayed for ethyl vinyl ether as described above.

Cobalt-containing products were worked up as follows.

$CH_3CH_2OCH_2CH_2Co(D_2H_2)OH_2$

25 ml of 0.5 N aqueous KOH was purged with argon in a 50 ml three-necked round-bottomed flask for 1.5 h with magnetic stirring. 0.5 g of **Id** was added and the solution stirred at room temperature for 3 days ($14 \times T_{1/2}$) under argon. The pH of the solution was adjusted to 6.3 with 5.0 N H_2SO_4, the solution was evaporated to dryness, then dried over P_2O_5 *in vacuo*. The dry residue was continuously extracted with 300 ml chloroform for 15 h and then with 200 ml methanol. The chloroform extract (dry wt. 0.33 g) contained unreacted starting material (by TLC) and a product apparently identical (by TLC) to the product in the methanol extract (dry wt. 0.16 g). The chloroform extract was resolved on a 30×3 cm column of silica gel (elution with 50% acetone/methanol (*v/v*)) into 0.13 g starting material (*i.e.*, **Id**, identified by NMR) and 0.13 g of product which was combined with the product from the methanol extract for a total of 0.29 g of **II** (identified by NMR and conversion to the dichlorocobaloxime acid, $H[Co(D_2H_2)Cl_2]$ [2]).

$CF_3CH_2OCH_2CH_2Co(D_2H_2)OH_2$

0.20 g of **Ib** was similarly decomposed at pH 13.31 for 2.5 h ($10 \times T_{1/2}$) under argon and worked up to provide a small amount of unreacted **Ib** (*ca.* 15 mg) and 0.17 g of **II**, identifed as above. Dealkylated cobalt-containing products (*i.e.*, **II**) were converted to the dichlorocobaloxime acid, $H[Co(D_2H_2)Cl_2]$ [20] as described previously [2], and this product was positively identified by comparison of its NMR spectrum to authentic material [20].

Results and Discussion

Values of pK_a, the proton dissociation constants of the axial water ligand of the alkoxyethyl(aquo)-cobaloximes (eqns. (6) and (7)), are listed in Table I along with the calculated values of $K_D^{OH^-}$ (eqns. (8) and (9)) and literature values for the pK_a of the conjugate acid of the alkoxide ion substituent (pK_{ROH}). The overall range of pK_a values throughout the series of five compounds is quite small (0.24) as would be expected since the substituent R is five bonds removed from the axial water oxygen. However, the trend in pK_a within the series is not as anticipated. Although the basicity of the alkoxide in RO^-, increases with increasing inductive electron donation of the alkyl group, R (with the exception of $R = C_6H_5$ due to resonance effects on pK_{ROH}) [25, 26], the anticipated increase in pK_a with increasing inductive donation of the organic ligand [9, 18] is not observed as a regular trend throughout the series. If we consider the complexes to fall into two groups, **Ia** and **Ib**, and **Ic–Ie**, then there is a tendency for pK_a to increase between the first and second groups, but the trend within each group is inverse. Interestingly, the kinetic behavior of the complexes with respect to base-induced decomposition places them in the same two groups while the reactivity decreases monotonically with increasing pK_{ROH} (see below).

As the kinetics of alkali-induced decomposition of **Ia** and **Ib** differed significantly from those of **Ic–Ie**, these results will be discussed separately, beginning with **Ia** and **Ib**. Both **Ia** and **Ib** decomposed cleanly in aqueous base with first-order kinetics to produce stoichiometric amounts of ethylene, the presence of which in the gas phase above reaction mixtures was confirmed by mass spectrometry. **Ia** decomposition was monitored over the pH range 10.78 ($T_{1/2}$ 79 min) to 12.54 ($T_{1/2}$ 3.3 min) and the average yield of ethylene was 100.0 ± 5.5%, while **Ib** decomposition was studied over the pH range 11.35 ($T_{1/2}$ 35 h) to 13.85 ($T_{1/2}$ 2.9 min) and the average ethylene yield was 97.3 ± 4.7%. Ethylene yields and observed rate constants were independent of cobaloxime concentration over the range 5×10^{-4} M to 2.5×10^{-3} M. The leaving group alcohols (phenol for **Ia** and 2,2,2-trifluoroethanol for **Ib**) were positively identified in reaction mixtures by

TABLE I. pK_a Values for the Alkoxyethylcobaloximes[a]

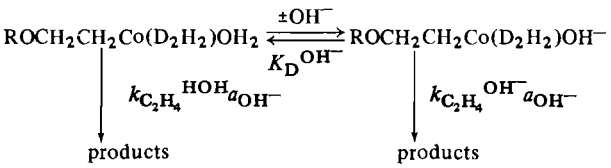
Compound	R	pK_a[b]	$K_D^{OH^-}$[c]	pK_{ROH}[d]
Ia	C_6H_5	12.02 ± 0.08[e]	$1.05 \pm 0.19 \times 10^{-2}$	9.95[f]
Ib	CF_3CH_2	11.95 ± 0.02	$8.91 \pm 0.14 \times 10^{-3}$	12.43[g]
Ic	CH_3	12.19 ± 0.02	$1.55 \pm 0.07 \times 10^{-2}$	15.54[h]
Id	CH_3CH_2	12.10 ± 0.01	$1.26 \pm 0.03 \times 10^{-2}$	16.0[h]
Ie	$(CH_3)_2CH$	12.06 ± 0.02	$1.15 \pm 0.05 \times 10^{-2}$	17.1[i]

[a]25.0 ± 0.1 °C, ionic strength 1.0 M (KCl). [b]Eqns. (6) and (7). [c]Eqns. (8) and (9) calculated from pK_a and eqn. (10). [d]Proton dissociation constant for the conjugate acid of the alkoxide substituent. [e]Ref. 18. [f]Ref. 21. [g]Ref. 22. [h]Ref. 23. [i]Ref. 24.

mass spectrometry, confirming that the only significant mode of decomposition of these two complexes is that represented by eqn. (5). Allowing for reactivity of both the aquo and hydroxo complexes of **Ia** and **Ib** [2] the rate law of eqn. (11), where

$$k_{obs} = (k_{C_2H_4}^{OH^-}(a_{OH^-})^2 + k_{C_2H_4}^{HOH}K_D^{OH^-}a_{OH^-})/(K_D^{OH^-} + a_{OH^-}) \quad (11)$$

k_{obs} is the observed rate of ethylene evolution and a_{OH^-} is the activity of hydroxide ion, is readily derived from Scheme 1 and the definition of $K_D^{OH^-}$.



Scheme 1. (**Ia** or **Ib**)

Division of k_{obs} by a_{OH^-} and substitution of α, the fraction of cobaloxime as the hydroxo species (eqn. 12)) provides eqn. (13), a linear equation of k_{obs}/a_{OH^-} in α. Plots of k_{obs}/a_{OH^-} *versus* α for **Ia** and **Ib**

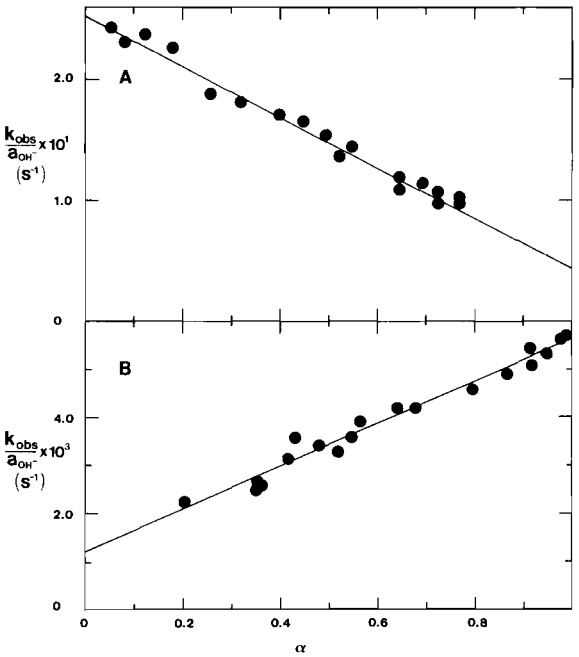


Fig 1. (a) Plot of k_{obs}/a_{OH^-} *vs* α for $C_6H_5OCH_2CH_2Co(D_2H_2)OH_2$ (**Ia**), 25.0 ± 0.1 °C, ionic strength 1.0 M (KCl). The solid line is a least squares fit to eqn. (13) slope = −0.209 ± 0.008 M^{-1} s^{-1} intercept = 0.253 ± 0.004 M^{-1} s^{-1} (b) Plot of k_{obs}/a_{OH^-} *vs.* α for $CF_3CH_2OCH_2CH_2Co(D_2H_2)OH_2$ (**Ib**), 25.0 ± 0.1 °C, ionic strength 1.0 M (KCl). The solid line is a least squares fit to eqn. (13), slope = 0.00454 ± 0.00013 M^{-1} s^{-1}, intercept = 0.00110 ± 0.00010 M^{-1} s^{-1}.

TABLE II. Rate Constants for Base-Induced Decomposition of 2-Alkoxyethylcobaloximes[a]

Compound	R	$K_{C_2H_4}^{HOH}$ (M^{-1} s^{-1})	$K_{C_2H_4}^{OH^-}$ (M^{-1} s^{-1})	$K_{C_2H_4}^{HOH}$ (M^{-2} s^{-1})	$k_{C_2H_4}^{OH^-}$ (M^{-2} s^{-1})	k_{sp}^{HOH} (M^{-1} s^{-1})	$k_{sp}^{OH^-}$ (M^{-1} s^{-1})	pK_{ROH}
Ia	C_6H_5	2.53 ± 0.04 × 10^{-1}	4.40 ± 1.2 × 10^{-2}					9.95[b]
Ib	CF_3CH_2	1.10 ± 0.10 × 10^{-3}	5.64 ± 0.23 × 10^{-3}					12.43[c]
Ic	CH_3			5.88 ± 0.36 × 10^{-3}	2.95 ± 0.08 × 10^{-4}	2.43 ± 0.19 × 10^{-4}	1.00 ± 0.41 × 10^{-4}	15.54[d]
Id	CH_3CH_2			1.07 ± 0.16 × 10^{-3}	1.18 ± 0.04 × 10^{-4}	4.70 ± 69.3 × 10^{-6}	3.87 ± 0.18 × 10^{-5}	16.0 [d]
Ie	$(CH_3)_2CH$			2.64 ± 8.21 × 10^{-5}	5.28 ± 0.18 × 10^{-5}	8.49 ± 4.10 × 10^{-5}	1.57 ± 0.08 × 10^{-5}	17.1 [e]

[a]25.0 ± 0.1 °C, ionic strength, 1.0 M. [b]Ref 21. [c]Rf. 22. [d]Ref. 23. [e]Ref. 24.

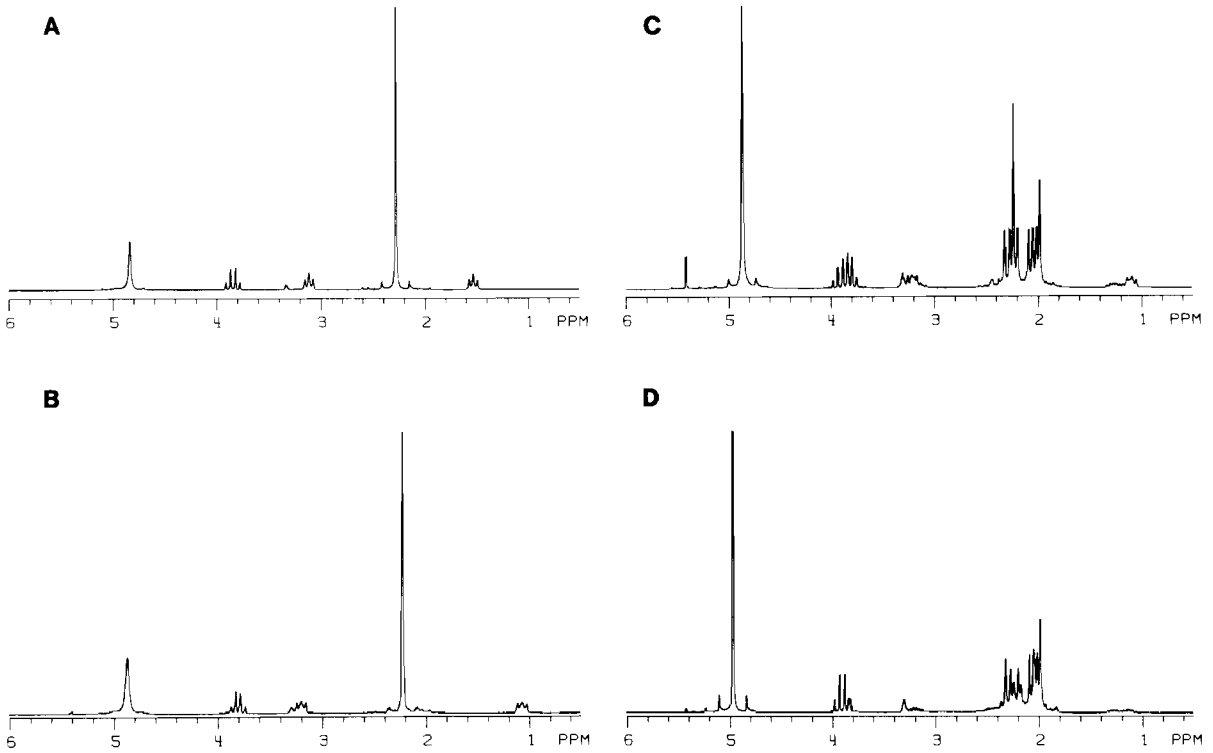


Fig. 2(a) 200 MHz ^{1}H NMR spectra of $CF_3CH_2OCH_2CH_2Co(D_2H_2)OH_2$ (**Ib**), *ca.* 0.10 M in D_2O/methanol-d_4 (*ca.* 3:1 *v/v*). (b) Spectrum of the sample of A, immediately after addition of 10 μl of 40% NaOD/D_2O (final $[OD^-]_{tot}$ *ca.* 0.2 M, approximately 90% conversion of **Ib** to the hydroxo complex). (c) Same, but 1 h after NaOD addition. (d) Same, but 19 h 20 min after NaOH addition.

$$\alpha = a_{OH^-}/(a_{OH^-} + K_D^{OH^-}) \quad (12)$$

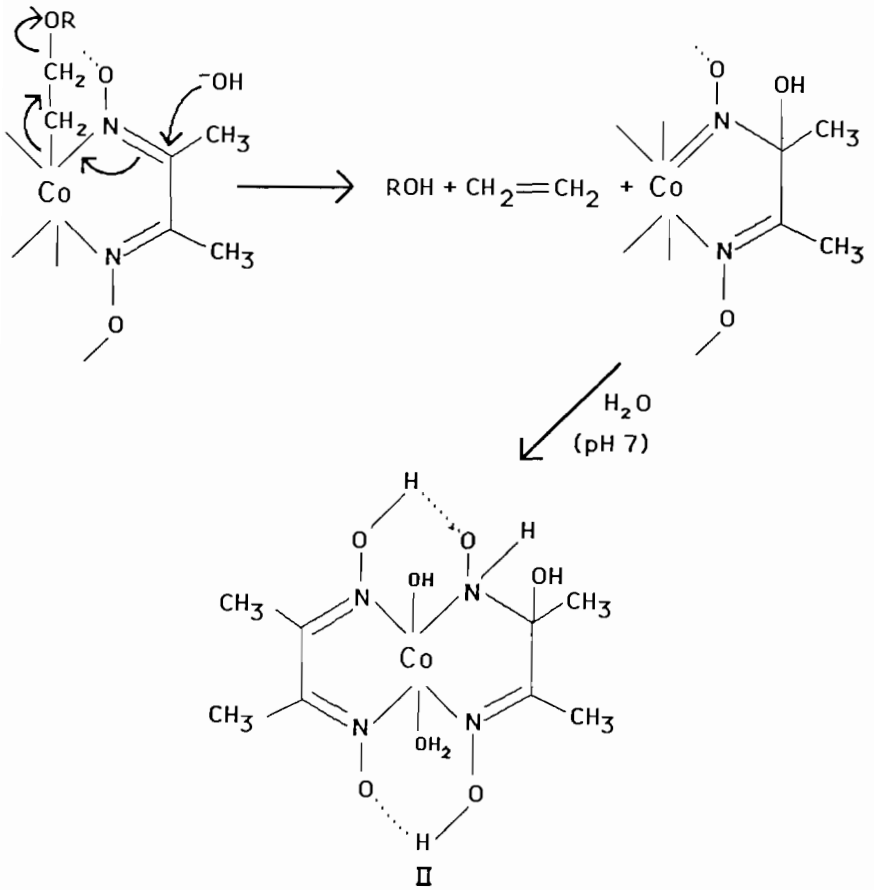
$$k_{obs}/a_{OH^-} = k_{C_2H_4}^{HOH} + \alpha(k_{C_2H_4}^{OH^-} - k_{C_2H_4}^{HOH}) \quad (13)$$

are shown in Fig. 1a and 1b, respectively, and can be seen to be satisfactorily linear. From the slopes and intercepts of least squares fits to these data sets, values of the second-order rate constants for ethylene formation from the aquo and hydroxo complexes of **Ia** and **Ib** were obtained and these are listed in Table II. The reactivity of these complexes can be seen to be strongly affected by the leaving ability of the alkoxide group (as indicated by the proton dissociation constant of the conjugate acid of the alkoxide ion, pK_{ROH}), the effect, however, being very much larger for the aquo complexes than for the hydroxo complexes. Thus, an increase in proton basicity of the leaving alkoxide ion of some 300-fold (*i.e.*, from $C_6H_5O^-$, pK_{ROH} = 9.95 to $CF_3CH_2O^-$, pK_{ROH} = 12.43) results in a 230-fold decrease in reactivity of the aquo complexes but only a 7.8-fold difference in reactivity for the hydroxo complexes. Fortuitously this leads to the curious situation in which the aquo complex of **Ia** is more reactive than the hydroxo complex (by 5.8-fold) while the reverse is true for **Ib**. While the cause of this differential sensitivity of the aquo and hydroxo complexes to the basicity of the leaving group is not immediately obvious, consideration of the mechanism of this reaction (below) suggests an explanation to which we shall return shortly.

In order to consider the mechanism of this reaction, a solution of **Ib** was observed by ^{1}H NMR during decomposition. Figure 2a shows the spectrum of the starting material (*ca.* 0.1 M) in D_2O/methanol-d_4 (*ca.* 3:1 *v/v*). The spectrum consists of a sharp singlet at 2.267 ppm assignable to the four magnetically equivalent equatorial methyl groups, a triplet (2H) at 1.522 ppm for the α-methylene group, a triplet (2H) at 3.103 ppm for the β-methylene group, and a quartet at 3.834 ppm for the alkoxide methylene group. The signal at 4.829 ppm is due to solvent. Upon addition of 10 μl of 40% NaOD/D_2O (final $[OD^-]_{tot}$ *ca.* 0.2 M) the complex is converted about 90% to the hydroxo species (Fig. 2b, acquired immediately after the addition). The conversion is accompanied by slight upfield shifts of the equatorial methyls (to 2.206 ppm) and alkoxide methylene (to 3.795 ppm) but the α- and β-methylene groups move in opposite directions, the

former upfield to 1.058 ppm and the latter downfield to 3.190 ppm. This curious phenomenon is apparently a consequence of the anisotropic dipolar shielding due to the induced dipole of the cobalt atom [27–29]. Evidently one of the methylene groups lies in the shielding region of the cobalt dipole while the other lies in the deshielding region so that the change in magnetic anisotropy of the cobalt dipole upon ionization of the axial water ligand causes the two resonances to move in opposite directions. The electronic effect of the ligand substitution on these resonances must, of course, be superimposed on the dipolar effect.

The decomposition reaction was subsequently monitored by successive NMR scans after the addition of NaOD (the half-time was about 40 min). As an example, the spectrum shown in Fig. 2c was acquired 1 h after base addition. It clearly shows a decline in the relative intensites of the α- and β-methylene signals at 1.058 and 3.190 ppm, respectively, and the growth of a signal at 5.407 ppm due to ethylene. In addition, the quartet at 3.795 ppm due to the methylene group of the 2,2,2-trifluoroethoxy substituent is seen to decline in intensity as a new quartet, with which it partially overlaps, grows at 3.905 ppm, the precise position of the methylene quartet of 2,2,2-trifluoroethanol in the same media. Most interestingly, the resonance near 2.2 ppm for the equatorial methyls can be seen to fragment into a multiplet as the reaction progresses, suggesting that the equatorial methyl groups are becoming non-equivalent due to a loss of symmetry. The final spectrum (Fig. 2d, taken 19 h, 20 min after base addition) simply shows completion of the time-dependent changes alluded to above, and clearly shows the non-equivalence of the equatorial methyls of the product chelate. This latter observation suggests that, as was the case with the base-induced decomposition of methyl(aquo)cobaloxime [2], the decomposition reaction is the consequence of attack of hydroxide ion on the equatorial ligand, leading to formation of a dealkylated cobalt chelate product in which one Schiff's base linkage has been hydrated (Scheme 2), which is subsequently converted to the aquohydroxocobalt(III) complex, **II**, upon neutralization. Further support for this mode of cobaloxime reactivity comes from observations of base-induced hydration of the equatorial ligand of diaquocobaloxime-(II) in alkaline solution [30] leading to the cobalt(II) analog of **II**. It must be pointed out that attack of



Scheme 2.

hydroxide ion on the equatorial ligand can occur either from above or below the equatorial ligand thus leading to formation of a pair of stereoisomers. These will be diastereomers and not enantiomers since the two halves of the bis(dimethylglyoximate) unit are not expected to be coplanar as is well known from many X-ray crystal structures of cobaloximes [31]. Consequently eight equatorial methyl resonances are expected. Careful inspection of Fig. 2d shows that all eight resonances have been resolved (a small ninth peak apparently being due to the persistence of a small amount of unreacted starting material). **II** has also been worked up from alkali-induced decomposition of **Ib** (see Experimental) and was apparently identical to the product previously obtained from alkali-induced decomposition of methyl(aquo)cobaloxime [2], and like this latter product, was convertible to the dichlorocobaloxime acid by stirring with 20% HCl (eqn. (14)). Improved ^{1}H NMR spectra of **II** (at 200 MHz) show an ex-

$$\mathbf{II} \xrightarrow{20\%\ HCl} HCo(D_2H_2)Cl_2 \qquad (14)$$

changeable one proton resonance at 1.33 ppm (the equatorial OH proton) and seven of the eight anticipated methyl resonances, one of which is considerably more intense than others and presumable represents a superposition of two resonances. Further confirmation of the structure of **II** and the mechanism of Scheme 2 comes from ^{13}C NMR observation of **Ib** before and after decomposition in base. Prior to decomposition the ^{13}C NMR spectrum (D_2O/CD_3OD, 3:1 (*v*/*v*)) was typical of organocobaloximes [7, 32]. The equatorial methyls and equatorial C=N carbons appeared as singlet resonances at 15.19 and 156.10 ppm, respectively, the CF_3 and CH_2 carbons of the trifluoroethoxy groups both appeared as quartets at 125.50 ppm (J_{FC} = 280.6 Hz) and 68.23 ppm (J_{FCC} = 35.2 Hz), respectively, and the β-carbon of the organic ligand appeared as a singlet at 75.56 ppm. As is always the case in natural abundance ^{13}C spectra of alkylcobaloximes the α-carbon of the organic ligand was not observed due to excessive broadening from quadrupolar relaxation by the cobalt nucleus [32–34]. After decomposition in NaOD the trifluoroethanol product (which is partially ionized under these conditions) had resonances at 63.19 ppm ($CF_3\mathit{CH}_2OH$, J_{FCC} = 32.2 Hz) and 128.16 ppm (CF_3CH_2OH, J_{FC} = 281.3 Hz). Seven of the eight anticipated methyl resonances were resolved (at 13.02, 13.34, 13.45, 13.54, 13.78, 13.92, and 14.01 ppm) and the downfield region showed six lines (for the three equatorial C=N carbons of each diastereomer) at 160.25, 156.60, 155.49, 155.17, 154.29 and 153.74 ppm. The two resonances for the equatorial C–OH carbon of the two diastereomers appeared at 138.96 and 126.11 ppm.

We conclude that the mechanisms of the alkali-induced decomposition of **Ia**, **Ib** and methyl(aquo)-cobaloxime are the same. The much higher reactivity of the alkoxyethylcobaloximes is most likely an entropic effect, *i.e.*, stabilization of the transition state by incipient fragmentation to three (rather than two) products, although increased rate of attack of hydroxide ion due to greater electron withdrawal by the organic ligand may also contribute to the difference in reactivity.

In light of this mechanism, the question of the differential sensitivity of the aquo and hydroxo complexes to leaving group basicity (Table I) may now be addressed. The reaction would be expected to show a large dependence on leaving group basicity since expulsion of increasingly basic alkoxide ions must require placing increasing negative charge on the alkoxide oxygen atom hence destabilizing the transition state. We would anticipate that the transition state would adjust to reduce the charge which must be placed on the alkoxide oxygen by becoming increasingly early (*i.e.*, less O–C and Co–C bond breaking) as the leaving group becomes more basic, leading to less entropic stabilization of the transition state. However, for the anionic hydroxo complexes, attack of hydroxide ion should be discouraged by electrostatic repulsion while expulsion of the leaving group as an alkoxide ion should be enhanced. As the leaving group becomes more basic the increased concentration of charge on the β-oxygen of the organic ligand enhances the expulsion of the alkoxide ion due to charge repulsion but the increased electron donation to the metal atom simultaneously decreases the rate of attack of hydroxide ion on the equatorial ligand. The two competing effects may thus lead to a leveling of the effect of leaving group basicity on reactivity.

Both the kinetics and stoichiometry of the alkali-induced decomposition of **Ic**, **Id** and **Ie** differed substantially from those of **Ia** and **Ib**. For the former three complexes the yields of ethylene (confirmed in the gas phase by mass spectrometry) were less than stoichiometric at all levels of pH and the yields were significantly dependent on pH. Again, kinetic results were unaffected by five-fold variation in cobaloxime concentration. In addition, since the reactions were much slower, data could only be collected over a narrower range of pH (and hence α values). For example, for **Id**, data were obtained from pH 13.9 (α = 0.984, $T_{1/2}$ = 1.75 h, yield = 78%) to pH 13.2 (α = 0.923, $T_{1/2}$ = 20 h, yield = 50%). However, leaving group alcohols, ROH, were detected by mass spectrometry in the reaction mixtures indicating that a reaction similar to eqn. (5) remains a major pathway for decomposition. This situation is quite reminiscent of the alkali-induced decomposition of methyl(aquo)cobaloxime [2] in which methane yields were also less than stoichiometric

and pH-dependent. In this case, methane yields were found to be limited by competition of the decomposition reaction with base catalyzed formation of the methyl-cobalt analog of **II**, which was apparently base-stable but remained photolabile. Its presence was inferred from generation of additional amounts of methane upon anaerobic photolysis of alkaline reaction mixtures subsequent to completion of the alkali-induced decomposition and from its dehydration to form methyl(aquo)cobaloxime upon neutralization of reaction mixtures (it could not be isolated). However in the present case, caution must be exercised in extrapolating from the results for methyl(aquo)cobaloxime since the competing reaction could be β-elimination (eqn. (4)) which now competes successfully with ethylene formation due to the poor leaving ability of the alkoxide ions.

For **Ic–Ie** the observed rate constants for the base-induced reaction, k_{obs}, are readily resolved into observed rate constants for ethylene formation, $k_{C_2H_4}^{obs}$, and observed rate constant for side product formation, k_{sp}^{obs}, since, for the parallel pseudo-first order system [35] ethylene formation is governed by the rate law of eqn. (15), and the observed rate constant must be equal to the sum of the rate cons-

$$[CH_2{=}CH_2] = k_{C_2H_4}^{obs}([ROCH_2CH_2Co(D_2H_2)OH_2]/k_{obs})(1 - e^{-k_{obs}t}) \quad (15)$$

tants for the two processes (eqn. (16)). Hence $k_{C_2H_4}^{obs}$ and k_{sp}^{obs} could be obtained from the slopes and intercepts of semilogarithmic plots of the mano-

$$k_{obs} = k_{C_2H_4}^{obs} + k_{sp}^{obs} \quad (16)$$

metric kinetic data at each pH. Despite the limited range of values over which data dould be collected, plots of $k_{C_2H_4}^{obs}/a_{OH^-}$ *vs.* α (*i.e.* eqn. (13)) were distinctly curved upward as shown in Fig. 3 for **Ic** and **Id**. This suggests that the ethylene forming reaction for **Ic–Ie** is, in fact, second order in hydroxide ion as shown in Scheme 3. From Scheme 3 and the definition of $K_D^{OH^-}$ (eqn. (9)) eqn. (17) is readily derivable for the dependence of $k_{C_2H_4}^{obs}$ on hydroxide ion activity. Although plots of $k_{C_2H_4}^{obs}/$

$$k_{C_2H_4}^{obs} = (k_{C_2H_4}^{OH^-}(a_{OH^-})^3 + k_{C_2H_4}^{HOH}K_D^{OH^-}(a_{OH^-})^2)/(K_D^{OH^-} + a_{OH^-}) \quad (17)$$

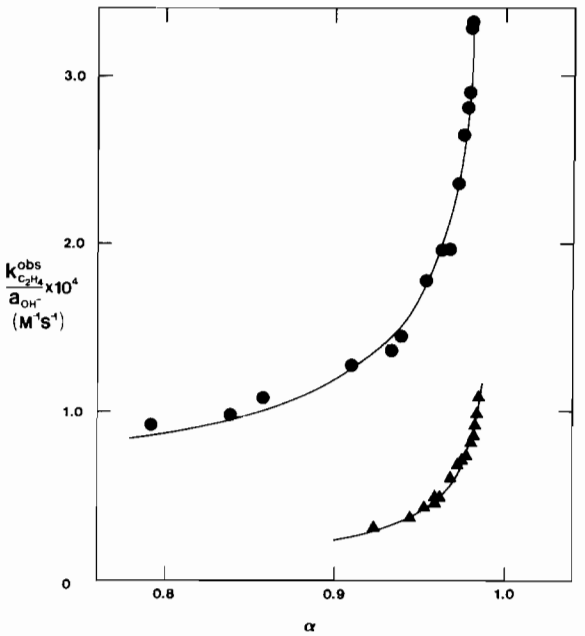


Fig. 3. Plots of $k_{C_2H_4}^{obs}/a_{OH^-}$ *vs.* α 25.0 ± 0.1 °C, ionic strength 1.0 M (KCl) for (•), $CH_3OCH_2CH_2Co(D_2H_2)OH_2$ (**Ic**) and (▲), $CH_3CH_2OCH_2CH_2Co(D_2H_2)OH_2$ (**Id**). The solid lines were calculated from eqn. (17) and the relevant rate constants listed in Table II.

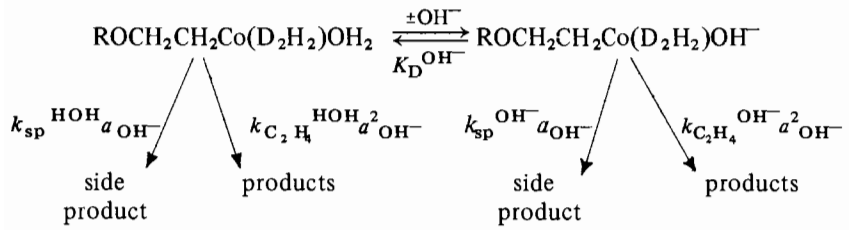
$(a_{OH^-})^2$ *versus* α (not shown), based on the rearranged eqn. (18) (*i.e.*, analogous to eqn. (13)) were linear,

$$k_{C_2H_4}^{obs}/(a_{OH^-})^2 = k_{C_2H_4}^{HOH} + (k_{C_2H_4}^{OH^-} - k_{C_2H_4}^{HOH})\alpha \quad (18)$$

it is statistically preferable to use the rearranged form of eqn. (19) for determination of $k_{C_2H_4}^{HOH}$ and

$$k_{C_2H_4}^{obs}/\alpha a_{OH^-} = k_{C_2H_4}^{OH^-}a_{OH^-} + K_D^{OH^-}k_{C_2H_4}^{HOH} \quad (19)$$

$k_{C_2H_4}^{OH^-}$ due to the limited range of α values over which data could be collected. Plots of $k_{C_2H_4}^{obs}/\alpha a_{OH^-}$ *versus* a_{OH^-} are shown in Fig. 4 for **Ic** **Id** and **Ie**. The linearity of these plots confirms the second order dependence of the reaction on hydroxide ion The values of the specific third order rate constants for ethylene formation from these complexes obtained from the slopes and intercepts of least squares fits of the data sets to eqn. (19), are collected in Table II.



Scheme 3 (**Ic** **d** or **e**)

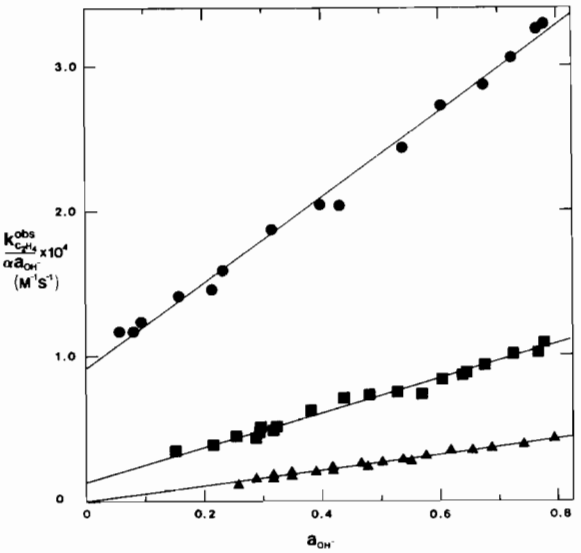


Fig. 4. Plots of $k_{C_2H_4}^{obs}/\alpha a_{OH^-}$ *vs.* a_{OH^-} for $ROCH_2CH_2$-$Co(D_2H_2)OH_2$ decomposition at 25.0 ± 0.1 °C, ionic strength 1.0 M (KCl). The solid lines are least squares fits to eqn. (19). (•), $CH_3OCH_2CH_2Co(D_2H_2)OH_2$ (**Ic**), slope = 2.95 ± 0.08 $\times 10^{-4}$ M^{-2} s^{-1}, intercept 9.11 ± 0.36 $\times 10^{-5}$ M^{-1} s^{-1}; (■), $CH_3CH_2OCH_2CH_2Co(D_2H_2)OH_2$ (**Id**), slope = 1.18 ± 0.04 $\times$ 10^{-4} M^{-2} s^{-1}, intercept = 1.36 ± 0.20 $\times 10^{-5}$ M^{-1} s^{-1}; (▲), $(CH_3)_2CHOCH_2CH_2Co(D_2H_2)$ (**Ie**), slope = 5 28 ± 0 18 $\times 10^{-5}$ M^{-2} s^{-1}, intercept = 3.04 ± 9.44 $\times 10^{-7}$ M^{-1} s^{-1}.

Because of the limited range of pH values over which data could be obtained the values of $k_{C_2H_4}^{HOH}$ are more poorly determined than those of $k_{C_2H_4}^{OH^-}$. In the extreme case for **Ie**, where the lowest pH at which data could be collected was 13.41 ($\alpha = 0.957$, $T_{1/2}$ = 24 h, yield = 36.4%), the calculated value of $k_{C_2H_4}^{HOH}$ is not significantly different from zero, although it seems likely that the aquo species of **Ie** is, in fact reactive. Despite these uncertainties it again appears that the sensitivity of the reaction of the aquo complexes to leaving group basicity is significantly higher than that of the hydroxo complexes as was the case for **Ia** and **Ib**.

The dependence of the side reaction of **Ic–Ie** on hydroxide ion, however, appears to be first-order, as plots of k_{sp}^{obs}/a_{OH^-} *versus* α (not shown) were linear. Again, it is statistically preferable to treat these data according to eqn. (20) due to the limited range of α values over which data could be obtained.

$$k_{sp}^{obs}/\alpha = k_{sp}^{OH^-} a_{OH^-} + k_{sp}^{HOH} K_D^{OH^-} \qquad (20)$$

Representative plots are shown in Fig. 5 and the linearity of the plots supports the idea that the side reaction is first-order in hydroxide ion. The values for the second-order rate constants for side product formation from **Ic–Ie** obtained from the slopes and intercepts of least squares fits of these data to eqn.

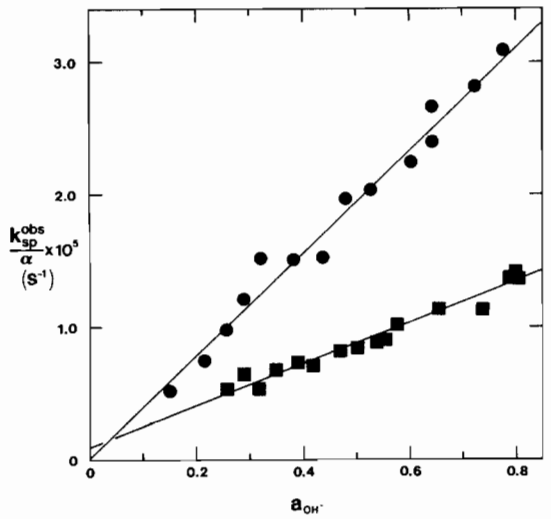


Fig. 5. Plots of k_{sp}^{obs}/α *vs.* a_{OH^-}, 25.0 ± 0.1 °C, ionic strength 1.0 M (KCl). The solid lines are least squares fits to eqn. (20). (•), $CH_3CH_2OCH_2CH_2Co(D_2H_2)OH_2$ (**Id**), slope = 3.87 ± 0.18 $\times$ 10^{-5} M^{-1} s^{-1}, intercept = 5.92 ± 87.3 $\times$ 10^{-8} s^{-1}; (■), $(CH_3)_2CHOCH_2CH_2Co(D_2H_2)OH_2$ (**Ie**), slope = 1.57 ± 0.08 $\times 10^{-5}$ M^{-1} s^{-1}, intercept = 9.76 ± 4.70 $\times$ 10^{-7} s^{-1}.

(20) are listed in Table II. Again, there is considerably more uncertainty in k_{sp}^{HOH} values than in the $k_{sp}^{OH^-}$ values and the value of k_{sp}^{HOH} for **Id** is not significantly different from zero. These values show a rather small dependence on leaving group basicity and are comparable to the values previously obtained for side product formation from the aquo and hydroxo species of methylcobaloxime [2] (taking the difference in temperature between the two studies into consideration). These observations are both consistent with the side reaction being formation of the alkoxyethyl derivatives of **II**, a question to which we shall return shortly.

The alkali-induced decomposition of CH_3CH_2-$OCH_2CH_2Co(D_2H_2)OH_2$, **Id**, has also been investigated by ^1H NMR spectroscopy as shown in Fig. 6. The initial spectrum (Fig. 6a, *ca.* 0.1 M **Id** in D_2O/methanol-d_4, 3:1 *v/v*) is characterized by a singlet at 2.251 ppm for the equatorial methyls, triplets at 1.530 ppm and 2.910 ppm for the α- and β-methylene groups, respectively, a quartet at 3.385 ppm for the ethoxy methylene group and a triplet at 1.062 ppm for the ethoxy methyl. Immediately after addition of 50 μl of 40% NaOD/D_2O (Fig. 6b, $[OD^-]_{tot}$ *ca.* 1.0 M, *ca.* 98% conversion to the hydroxo complex) the α- and β-methylene resonances shift in opposite directions (as was the case for **Ib**), in this case the α-methylene resonance moving to 1.107 ppm (where it partially overlaps with the ethoxy methyl group triplet) and the β-methylene moving to 3.037 ppm. As a function of time (*e.g.* Fig. 6c, 2 h after NaOD addition, $T_{1/2}$ *ca.* 105 min) an ethylene resonance

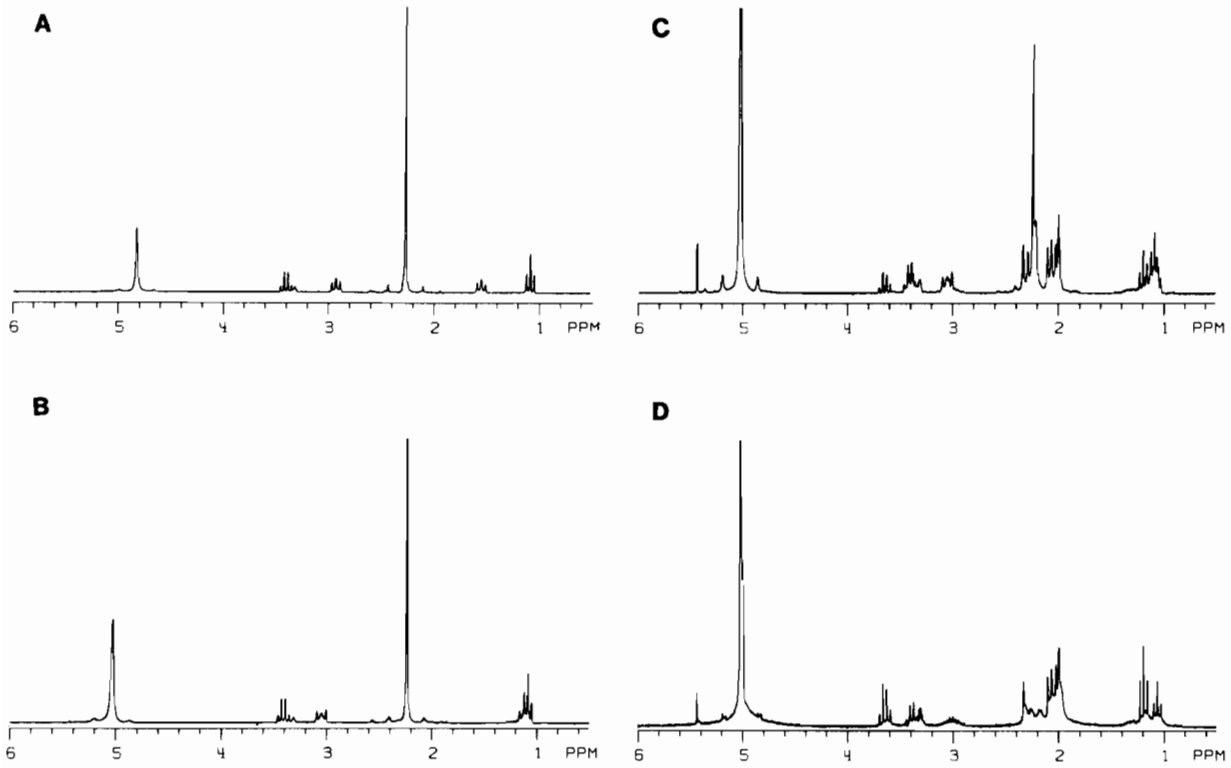
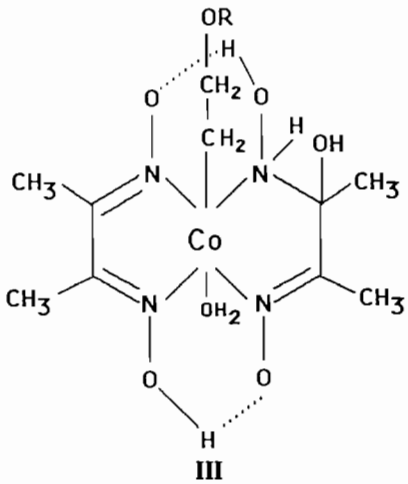


Fig. 6. (a) 200 MHz ^{1}H NMR spectrum of $CH_3CH_2OCH_2CH_2Co(D_2H_2)OH_2$ (**Id**), *ca.* 0.1 M in D_2O/methanol-d_4 (*ca.* 3:1 *v*/*v*). (b) Spectrum of the sample of A, immediately after addition of 50 μl of 40% NaOD/D_2O (final $[OD^-]_{tot}$ *ca.* 1.0 M, approximately 98% conversion of **Id** to the hydroxo complex). (c) Same, but 2 h after NaOD addition. (d) Same, but 23 h 35 min after NaOD addition.

appears at 5.415 ppm, a new triplet and a new quartet appear at 1.187 ppm and 3.643 ppm, respectively (the proper positions for ethanol) and the equatorial methyl resonance again fragments into a multiplet indicative of a cobalt chelate product in which the equatorial methyls are non-equivalent. Figure 6d shows the completion of these spectral changes after approximately 13.5 half-times. In addition to indicating that the decomposition of the complex is again initiated by attack of hydroxide ion on the equatorial ligand these spectra contain valuable information about the nature of the side product. The lack of appearance of any resonances for ethyl vinyl ether (particularly the vinyl protons at 3.931 ppm (d), 4.148 ppm (d) and 6.433 (d of d)) as well as the persistence, even after 13.5 half times, of resonances near the positions of the resonances of the organic ligand of starting material (as the hydroxo complex, *i.e.*, Fig. 6b) strongly suggest that the side product is the organocobalt derivative of **II** (*i.e.*, **III**, R = CH_3CH_2). In order to prove that this is the case we looked carefully for ethyl vinyl ether among the decomposition products of **Id**. When samples of **Id** were incubated in 0.5 M KOH at 25 °C for 48 h (9.3 half-times) and then extracted with heptane, no ethyl vinyl ether could be detected in the extracts



III

by GC/MS analysis, despite the fact that control samples in which ethyl vinyl ether was incubated and assayed under the same conditions showed that ethyl vinyl ether survived the incubation and was readily detectable in heptane extracts. In order to substantiate the presence of **III** in such reaction mixtures we took advantage of its anticipated photolability. When neutral samples of **Id** were photolyzed anaerobically and extracted with heptane, the

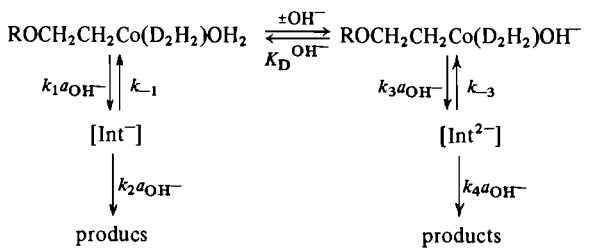
extracts contained readily detectable amounts of ethyl vinyl ether (again by GC/MS) as anticipated [36, 37]. Similarly, when reaction mixtures containing **Id** in 0.5 M KOH were photolyzed after 9.3 half times at 25 °C in the dark, ethyl vinyl ether was readily detectable in the heptane extracts. We conclude that the base-induced decomposition of **Ic–Ie** proceeds via attack of hydroxide ion on the equatorial ligand to produce mixtures of ethylene (plus leaving group alcohol) and **III**. The absence of any significant side reactions to form **III** in the base-induced decomposition of **Ia** and **Ib** is evidently due to the much better leaving ability of the alkoxide leaving groups of these complexes so that base-catalyzed formation of **III** is unable to compete successfully with ethylene formation.

The mechanistic interpretations presented above differ significantly from conclusions drawn by Mock and Bieniarz [13] regarding the base-induced decomposition of 2-alkoxyethylcobaloximes. Although these authors synthesized a number of such complexes (as the pyridine derivatives) the hydroxide ion dependence of the decomposition of only one (tetrahydrofurfuryl(pyridine)cobaloxime) was studied. As the data presented above show that kinetic patterns in the decomposition of 2-alkoxyethylcobaloximes are strongly dependent on the nature of the leaving alkoxide group conclusions drawn from study of a single compound may not be valid in general. Mock and Bieniarz [13] found the spectrophotometric kinetics of tetrahydrofurfuryl(pyridine)cobaloxime decomposition to be first-order in hydroxide ion at $[OH^-] \geqslant 0.5$ M (although only three data points are shown in this range) but of mixed order at lower $[OH^-]$, the observed rate constant apparently tending to zero at very low hydroxide ion concentration. However, these authors also showed that the reaction was strongly inhibited by added pyridine at a constant hydroxide ion concentration. Consequently the use of the pyridine complex in kinetic studies of the influence of hydroxide ion concentration represents a serious complication since it is not clear if pyridine dissociates rapidly enough to insure that decomposition of only the aquo (or hydroxo) species is being observed. Mock and Bieniarz [13] also present some NMR data on the decomposition of this compound but unfortunately show no NMR spectra and give no details on the concentrations of reagents employed. They report only that the chemical shift of the equatorial methyls of tetrahydrofurfuryl(pyridine)cobaloxime in DMSO-d_6 (2.05 ppm) is shifted upfield to 1.93 ppm upon addition of 2 equivalents of 40% NaOD in H_2O. No mention is made of the effect of decomposition on the equatorial methyl resonance. However, when decomposition was immediately halted by addition of an unspecified excess of pyridine, two resonances of equal intensity separated by 0.13 ppm (1.93 and 1.80 ppm) are observed. This is interpreted to be due to formation of the alkyl(pyridine)cobaloxime anion in which one (of two) equatorial oxime bridged hydrogens has dissociated leading to non-equivalent equatorial methyls. However, although measured rates of dissociation of these equatorial hydrogens [38] show that they are considerably slower than the diffusion controlled limit, they are clearly much too fast to permit independent observation of non-equivalent methyl resonances on the NMR time scale (see discussion below). In addition, since the pK_a for this dissociation of a 2-alkoxyethyl(pyridine)cobaloxime would be expected to be about 13.4 [9] a very high deuteroxide concentration would be required for complete dissociation. It seems much more likely that addition of excess pyridine creates a solution in which both the alkyl(hydroxo)cobaloxime (δ = 1.93 ppm) and the alkyl(pyridine)cobaloxime (partially equatorially ionized, δ = 1.80 ppm) are present although it is impossible to be certain without knowing the exact deuteroxide and pyridine concentrations. In all, four potential axial ligands (pyridine, DMSO-d_6, OD^- and D_2O) are present in this solution, significantly complicating interpretation of the results.

At any rate, from these observations, Mock and Bieniarz [13] conclude that it is the hydroxo species of tetrahydrofurfurylcobaloxime which decomposes spontaneously and that this decomposition is aided by removal of one of the equatorial oxime bridged hydrogens. The latter conclusion seems extremely unlikely on electronic grounds (as discussed below) and the former conclusion is clearly not correct in general, as adequately shown in the decomposition of **Ia** and **Ib** (above, and Fig. 1). Most importantly of the conclusion that 'coordination of hydroxide anion to the exchangeable ligand position of the metal induces carbon-cobalt bond cleavage' [13] gives the false impression that such coordination provides the driving force for organocobalt complex decomposition. This is not the case for any known base-induced organocobalt cleavage reaction, nor, apparently in the present case in which attack of hydroxide ion on the equatorial ligand provides the driving force for reaction. Evidently tetrahydrofurfurylcobaloxime is similar to **Ia** in terms of base-induced decomposition, *i.e.*, it characterized by kinetics which are first-order in hydroxide ion, the deviations at low hydroxide ion concentration being due to formation of the aquo complex which is evidently more reactive than the hydroxo species. This can be seen by replotting the data given in Mock and Bieniarz's Table II [13] as $k_{obs}/[OH^-]$ *versus* $[OH^-]$. The resulting plot (not shown) is a rectangular hyperbola with Y-intercept 0.24 M^{-1} s^{-1} and asymptote 0.056 M^{-1} s^{-1} and is exactly fit by the appropriate rearranged form of our eqn.

(11) based on Scheme 1 to give $K_D^{OH^-} = 0.118$ M, $k_{C_2H_4} = 0.056$ M^{-1} s^{-1} and $k_{C_2H_4}^{HOH} = 0.24$ M^{-1} s^{-1}. Hence the kinetics of tetrahydrofurfurylcobaloxime decomposition are adequately explained by attributing reactivity to both the aquo and hydroxo species without the necessity of invoking equatorial proton dissociation [13].

The second-order dependence of the ethylene forming reaction of **Ic–Ie** on hydroxide ion is not completely understood. It is a simple matter to write a kinetic scheme which will account for the order of the ethylene forming reaction on hydroxide ion for all five complexes. Such a scheme (Scheme 4) envi-



Scheme 4. (Ia–Ie)

sions deprotonation of the equatorial ligand of starting material to form an anionic (from the aquo complex) or dianonic intermediate (from the hydroxo complex) which is subsequently attacked equatorially by hydroxide ion to form ethylene. ROH and **II**. Application of the steady state approximation to the two anionic intermediates readily leads to the rate law of eqn. (21). The kinetic behavior of the two

$$k_{obs} = k_3k_4(a_{OH^-})^3]/(k_{-3} + k_4a_{OH^-})(K_D^{OH^-} + a_{OH^-}) + k_1k_2K_D^{OH^-}(a_{OH^-})^2/(k_{-1} + k_2a_{OH^-})(K_D^{OH^-} + a_{OH^-}) \quad (21)$$

groups of complexes described in this work is obtained from the appropriate limit behavior of eqn. (21). Hence if $k_{-1} \ll k_2a_{OH^-}$ and $k_{-3} \ll k_4a_{OH^-}$ then formation of the anionic intermediates is rate-determining and eqn. (21) simplifies to eqn. (22) which is identical in form to eqn. (11) and describes the first-

$$k_{obs} = (k_3(a_{OH^-})^2 + k_1K_D^{OH^-}a_{OH^-})/(K_D^{OH^-} + a_{OH^-}) \quad (22)$$

order dependence on hydroxide ion typical of **Ia** and **Ib**. On the other hand, if $k_{-1} \gg k_2a_{OH^-}$ and $k_{-3} \gg k_4a_{OH^-}$ attack of hydroxide ion on the anionic intermediates is rate-determining and eqn. (21) reduces to eqn. (23), which is identical in form to eqn. (17)

$$k_{obs} = [(k_3k_4/k_{-3})(a_{OH^-})^3 + (k_1k_2/k_{-1})K_D^{OH^-}(a_{OH^-})^2]/(K_D^{OH^-} + a_{OH^-}) \quad (23)$$

and describes the second-order dependence on hydroxide ion characteristic of **Ic–Ie**. There are, however, several problems with this idea. Although organocobaloximes can be deprotonated both at the oxime bridged hydrogens [9] and at the equatorial methyl groups [2, 3, 39] it is difficult to see how such ionization would increase the rate of hydroxide ion attack on the equatorial ligand. Although it is, of course, possible that the wave function for the anionic species formed via one or the other of these deprotonation reactions could conceivably show a decreased electron density at the equatorial quarternary carbons (relative to the unionized complexes), this seems quite unlikely. A second problem involves the rate of such proton transfer reactions. Not only must the rate of reprotonation of the anionic intermediates for **Ia** and **Ib** be slower than the rate of attack of hydroxide ion on the anionic intermediates (to explain the first-order dependence on hydroxide ion for **Ia** and **Ib**) but the rate of deprotonation must be slow enough to account directly for the observed rates of **Ia** and **Ib** decomposition. While it is true that proton transfer reactions involving hydrogen bonded protons are retarded relative to those which are not hydrogen bonded [40], existing data on the rates of proton transfers from cobaloxime equatorial oxime bridges [38] suggest that proton transfers from this equatorial site are probably too fast. Birk *et al.* [38] have studied the rate of proton transfers from the oxime bridged protons of cobaloximes of the type $Co(D_2H_2)XY^-$ (eqn. (24)), X, Y = CN^-, NO_2^-, Br^-) by temperature-jump

$$Co(D_2H_2)XY^- + OH^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} Co(D_2H)XY^{2-} + H_2O \quad (24)$$

spectroscopy at 15 °C. pK_a values for these deprotonations varied from 11.82 to 12.22 and while the rate constant for deprotonation showed little variation with pK_a (average $k_f = 1.4 \times 10^5$ M^{-1} s^{-1}), k_r varied from 0.8×10^3 s^{-1} to 2.0×10^3 s^{-1}, increasing monotonically with pK_a. These anionic cobaloximes are probably good models for such proton transfer from anionic organo(hydroxo)cobaloximes although the pK_a values for oxime bridged proton dissociation from the latter are clearly considerably higher [9]. In earlier work we found the pK_a for oxime bridged proton dissociation from organo(hydroxo)cobaloximes low enough to measure in water only for those derivatives with extremely electron withdrawing organic ligands. For instance, for cyanomethyl(hydroxo)cobaloxime the pK_a was 14.16, while cyanomethyl(pyridine)cobaloxime had a pK_a of 11.78 [9]. Assuming a constant difference in this pK_a for the hydroxo and pyridine derivatives we can estimate a pK_a of about 15.8 for the alkoxyethyl(hydroxo)cobaloximes from the interpolated value of about 13.4 for $CH_3OCH_2CH_2Co(D_2H_2)py$. We can consequently estimate values of k_f (eqn. (24))

of 1.4×10^5 M^{-1} s^{-1} and k_r of 8.8×10^6 s^{-1} for the alkoxyethyl(hydroxo)cobaloximes (*i.e.*, equivalent to k_3 and k_{-3}, respectively, in Scheme 4). It seems extremely unlikely that the rate of hydroxide ion attack on the dianionic intermediate (*i.e.*, $k_4 a_{OH^-}$ in Scheme 4) could ever exceed 8.8×10^6 s^{-1} at any pH, as required for the limiting form of eqn. (22) relevant to **Ia** and **Ib** decomposition. Furthermore, the rate of deprotonation ($k_f a_{OH^-}$) even at pH values as low as 11 would still be much too fast ($k_f a_{OH^-} = 1.4 \times 10^2$ s^{-1}) to account for **Ia** and **Ib** decomposition (even for **Ia**, k_{obs} at pH 11 is 2.2×10^{-3} s^{-1}). Furthermore, it is hard to see how the rate constants for rate-limiting deprotonation of the aquo complexes of **Ia** and **Ib** could depend so strongly on R (as required by the observed values of $k_{C_2H_4}^{HOH}$ for these two complexes (Table II)) given its remoteness from the equatorial oxime oxygens.

Much less information is available on the rates of equatorial methyl deprotonation of organocobaloximes and no pK_a values have been measured. We have however, previously measured the rate of exchange of solvent deuterons with the equatorial methyl protons of ethyl(hydroxo)cobaloxime by NMR spectroscopy In 1.0 M NaOD (in D_2O/methanol-d_4, 50% *v/v*) at 37 °C the exchange rate constant was only $9.57 \pm 0.22 \times 10^{-5}$ s^{-1} [3]. Similarly, Cartaño and Ingraham [39, 41] studied this exchange for methyl(aquo)cobaloxime in DMSO-d_6/D_2O (10:1 *v/v*) at 35 °C and varying concentrations of OD^- and obtained second-order rate constants of about 3.5×10^{-4} M^{-1} s^{-1} for the hydroxo species and 5.3×10^{-4} M^{-1} s^{-1} for the aquo species. It is not known if the exchange reaction is rate limited by deprotonation or reprotonation. However, if deprotonation is rate limiting, then proton transfer from the equatorial methyl groups is clearly too slow to be rate limiting for **Ia** and **Ib** decomposition. In addition, the failure to observe deuterium incorporation into the equatorial methyls of **Id** by NMR spectroscopy during its decomposition (Fig. 6) also implies that reprotonation at the equatorial methyls is not faster than hydroxide ion attack on the supposed anionic intermediates as required to generate eqn. (23) for the second-order dependence of ethylene formation on hydroxide ion for **Ic**–**Ie**. Consequently, we cannot currently explain the observed second order dependence of the rate of ethylene formation on hydroxide ion for the alkoxyethylcobaloximes with poor alkoxide leaving groups. Experiments are in progress in a closely related system to try to understand this phenomenon.

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