Kinetics Studies of the Cleavage and Rearrangement Reactions of (β-Hydroxyalkyl)cobaloximes in Acid Solution[1]
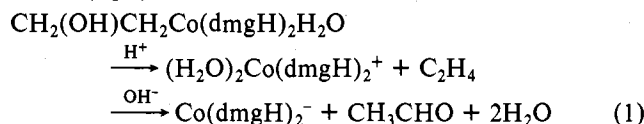
JAMES H. ESPENSON* and DIANA M. WANG
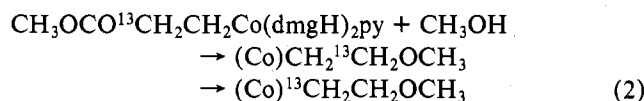
Kinetics studies have been carried out on the title reactions. β-Hydroxyethyl derivatives evolve ethylene, whereas β-hydroxy-*n*-propyl and β-hydroxyisopropyl derivatives undergo reversible isomerization prior to olefin release. The kinetic data are analyzed in terms of a mechanism involving an intermediate in which the olefin is π bonded to the cobalt complex. Based on this analysis it is possible to evaluate (1) rate constants for the conversion of each of the parent compounds to the π intermediate and (2) values for return of the π complex to the parent alkyl(s) compared to those for product formation. The cleavage reactions of the BF₂-substituted macrocycle are much slower than for the bis(dimethylglyoximato) compounds, indicating the sensitivity of the reaction rate to electron-attracting substituents. Chloride ion causes modest rate accelerations, presumably because of its nucleophilicity when present in the complex trans to the cobalt–carbon bond.

(Hydroxyalkyl)cobaloximes are obtained similarly to alkylcobaloximes[2] and have rather similar characteristics. But whereas the latter are remarkably stable in both acidic and basic solutions, it is well established[2] that (β-hydroxyethyl)cobaloxime undergoes ready decomposition in both media (eq 1).

$$CH_2(OH)CH_2Co(dmgH)_2H_2O$$

$$\xrightarrow{H^+} (H_2O)_2Co(dmgH)_2^+ + C_2H_4$$

$$\xrightarrow{OH^-} Co(dmgH)_2^- + CH_3CHO + 2H_2O \qquad (1)$$

Schrauzer[2] was quick to note the relevance of these processes to the role of coenzyme B_{12} in the action of dioldehydrase. Brown and Ingraham[3] showed that, prior to cobalt–alkyl cleavage, there occurred an acid-catalyzed rearrangement of the β-OH-*i*-Pr compound (i) to β-OH-*n*-PrCo(dmgH)₂B (n). Following Golding et al.,[4] who postulated a π-complex intermediate in the reaction of (2-acetoxyethyl)cobaloxime and ethanol to form (2-ethoxyethyl)cobaloxime, these authors invoked an olefin–cobalt(III) π complex as a reaction intermediate. Dolphin[5] noted that three extreme electronic forms of such an intermediate could be envisaged, but in view of the scrambling of ¹³C observed to occur during methanolysis, the symmetrical π-olefin intermediate was deemed the most likely (eq 2).

$$CH_3OCO^{13}CH_2CH_2Co(dmgH)_2py + CH_3OH$$

$$\rightarrow (Co)CH_2{}^{13}CH_2OCH_3$$

$$\rightarrow (Co)^{13}CH_2CH_2OCH_3 \qquad (2)$$

In view of the importance of these reactions, both in B_{12} chemistry and in homogeneous catalysis, we undertook an examination of the mechanism by which cleavage and rearrangement occur in strongly acidic aqueous solution. We report here on such reactions of the β-hydroxyalkyl derivatives e, f, i, and n. At the outset it should be noted that we discount the possibility that reaction 1 (and its analogues) occurs in a single step in which olefin release accompanies protonation and loss of H_2O from the β-OH group. Were this the case, then none of the rearrangements[4,5] referred to would be possible. Indeed, these results, as well as the kinetic data we have obtained, point clearly to the key role played by an intermediate which can be rehydrated (to either of two products, in the case of the propyl derivatives) or can lose olefin. On the basis of the scrambling shown in eq 2, this conclusion can be drawn equally[3b] soundly, even for those compounds which give a symmetrical olefin intermediate (compounds which, by virtue of that symmetry, are not subject to conversion into different products); this includes the β-hydroxyethyl complex e and the 2-acetoxyethyl derivative.[4]

β-OH-EtCo(DMGH)₂B (E)   β-OH-*n*-PrCo(DMGBF₂)₂B (F)

β-OH-*i*-PrCo(DMGH)₂B (I)   β-OH-*n*-PrCo(DMGH)₂B (N)
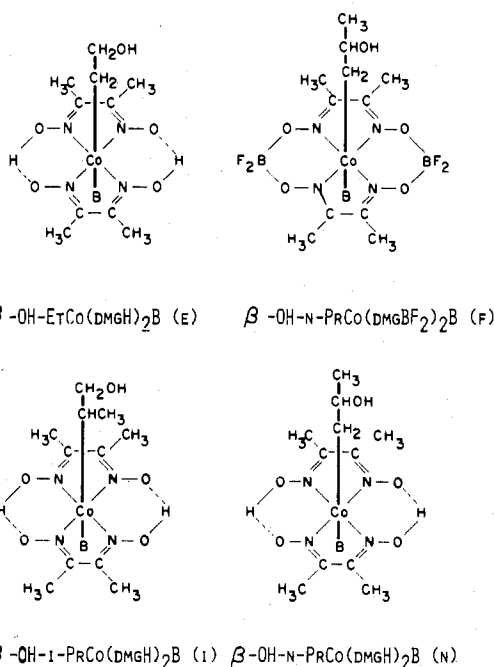
Experimental Section

The alkylcobaloximes with an axial pyridine base were prepared by adaptations[1b] of standard methods.[2,3] These compounds gave good elemental analyses and NMR spectra,[1b] and all had absorption maxima[1b] typical of alkylcobaloximes at 440–455 and 375–380 nm. The aquo derivatives of e and n were prepared[3] from the pyridine derivatives by treatment with Dowex-50 cation-exchange resin in the H^+ form. Similar treatment of i (B = py) gave a mixture of n and i (B = H_2O), as shown by the proton NMR spectrum.[3] We were unable to resolve the mixture chromatographically, albeit repeated attempts were not made.

Kinetic determinations were carried out spectrophotometrically, following the absorbance (D) with time at a constant wavelength, using Cary Model 14 and 219 spectrophotometers. For those reactions which followed pseudo-first-order kinetics, plots were constructed of log ($D_t - D_\infty$) vs. time.

Much of the kinetic data did not follow a simple first-order kinetic expression, for reasons to be considered subsequently. In these instances the data could be resolved into a sequence of two exponentials. In these runs the kinetic data followed an expression of the form of eq 3, where D represents the absorbance of a solution in a cell of optical path length l and $[Co]_0$ is the initial cobalt concentration.

$$(D_t - D_\infty)/l[Co]_0 = \phi_f \exp(\lambda_f t) - \phi_s \exp(\lambda_s t) \qquad (3)$$

These kinetic data were resolved by standard methods;[6] at sufficiently long times a plot of ln ($D_t - D_\infty$) vs. time provides a value
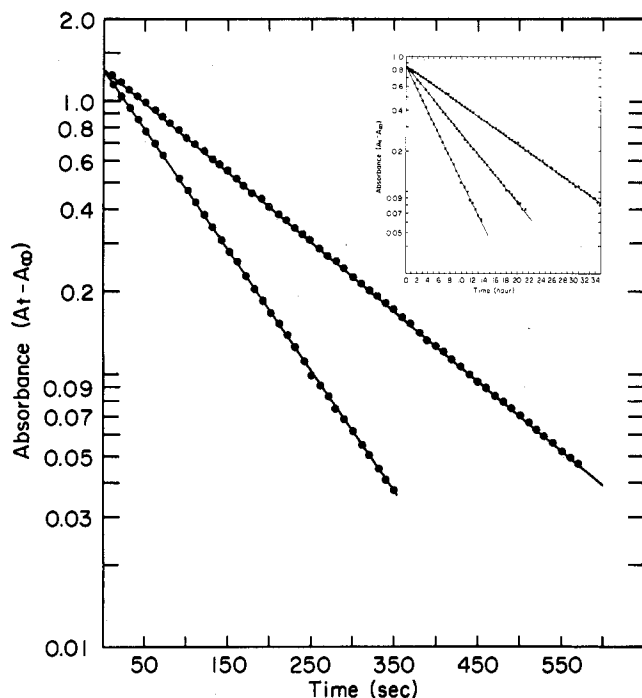
Figure 1. Pseudo-first-order kinetic plots for reaction of CH_2-$(OH)CH_2Co(dmgH)_2H_2O$ (e) with H^+. The runs shown here have $[H^+] = 0.100$ M (upper line) and $[H^+] = 0.200$ M (lower line) at 30.0 °C and $\mu = 0.20$ M. Inset: Similar data for $CH_3CH(OH)$-$CH_2Co(dmgBF_2)_2H_2O$ (f) at 0.0450, 0.100, and 0.200 M H^+ at 25.3 °C and $\mu = 0.20$ M.

Table I. Kinetic Data for Reaction of (β-Hydroxyethyl)cobaloxime (e) with Perchloric Acid at $T = 25.1 \pm 0.1$ °C and $\mu = 0.20$ M ($LiClO_4$)

	$10^3 k/s^{-1}$			
	obsd			
$[H^+]$/M	B = py	B = H_2O	calcd[a]
0.0500	1.45, 1.51	1.47	1.47
0.100	2.72, 2.79	2.68, 2.77	2.79
0.200	5.11, 5.10	5.34, 5.07	5.08

[a] Calculated from eq 6 with $k_a = 3.09 \times 10^{-2}$ M^{-1} s^{-1} and $K_H = 1.09$ M^{-1}.

of λ_s from its slope and (by extrapolation to zero time) of ϕ_s from its intercept. Values of λ_f and ϕ_f are then obtained from a plot of $\ln [(D_t - D_\infty)/l[Co]_0 - \phi_s \exp(\lambda_s t)]$ vs. time. The quantities of λ_f and λ_s have dimensions corresponding to the negative of a first-order rate constant. The relationship of these parameters to more conventional kinetic parameters will be considered in the analysis of the results.

The runs were carried out by dissolving the cobaloxime in the desired solvent containing all components other than perchloric acid. Reaction was initiated by injecting the desired quantity of perchloric acid solution into the carefully thermostated cobaloxime solution.

Results

β-OHEtCo(dmgH)$_2$B, e. Treatment of e (B = py or H_2O) with dilute aqueous perchloric acid leads to slow evolution of ethylene and formation of the well-known cobalt(III) complex $(H_2O)_2Co(dmgH)_2^+$, p. The kinetics were studied at λ 446 nm at 25.1 ± 0.1 °C and ionic strength 0.200 M (maintained with lithium perchlorate). The pseudo-first-order kinetic traces are linear to 4 half-lives, as shown in Figure 1. The rate constants were determined as a function of $[H^+]$, 0.0500–0.200 M (Table I). Loss of pyridine from the axial position occurs rapidly and, in these strongly acidic solutions, is essentially irreversible.[7] Thus the effective starting complex is really the aquo derivative of e. Directly prepared samples of the latter

Table II. Kinetic Data for Reaction of the β-Hydroxy-n-propyl Derivative of $Co(dmgBF_2)_2$ with Perchloric Acid at 25.3 ± 0.1 °C

		$10^5 k/s^{-1}$	
$[H^+]$/M	μ/M	obsd	calcd[a]
0.0450	0.200	1.85, 1.85	1.87
0.100	0.200	3.24, 3.25	3.20
0.150	0.200	4.46, 4.45	4.40
0.200	0.200	5.51, 5.50	5.61
0.200	0.330	6.70, 6.65	
0.200	0.460	7.50, 7.29	

[a] From eq 7, using the values $k_0 = 7.8 \times 10^{-6}$ s^{-1} and $k_a = 2.41 \times 10^{-4}$ dm^3 mol^{-1} s^{-1} at $\mu = 0.200$ M.

gave identical rate constants as shown in Table I.

Protonation of oxime oxygens in alkylcobaloximes is a well-recognized equilibrium. These equilibria are represented by general reaction 4. The value of K_H for e has not been

$$RCo(dmgH)_2H_2O + H^+ \xrightleftharpoons{K_H} RCo(dmg_2H_3)H_2O^+ \quad (4)$$
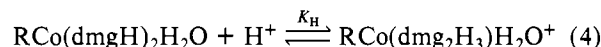
independently evaluated, although it is likely in the range 1.0–4.2 M^{-1}, the range of values typical of these equilibria.[6b,8] In this case a value was determined from the kinetic data. To do this, and to formulate a valid kinetic dependence of k_{obsd} on $[H^+]$, we imagine that three possible pathways may operate simultaneously. These three consist of reaction of e with H_2O (k_0), of e with H^+ (k_a), and of e·H^+ with H_2O (k_0'). With this formulation the observed rate constant would vary with $[H^+]$ according to eq 5.

$$k_{obsd} = \frac{k_0 + k_a[H^+] + k_0'K_H[H^+]}{1 + K_H[H^+]} \quad (5)$$

The pathways which make a significant contribution to the rate are determined as follows. A plot of k_{obsd} vs. $[H^+]$ has a zero intercept, indicating that the k_0 pathway is unimportant. It was then postulated that the k_0' pathway contributes negligibly compared to that represented for k_a; the basis for this is that a very dramatic lowering of rate was found upon substitution of the much more strongly electron-withdrawing chelate $(dmgBF_2)_2$ for $(dmgH)_2$. That is to say that since the $dmgBF_2$ chelate f reacts much more slowly than either n or e and since it is related to the latter by addition of electron-attracting BF_2, it is reasonable to make the tentative assignment that the protonated species e·H^+ is much less reactive than e. This can be tested from the data obtained; with this *assumption* that only the k_a pathway contributes to the reactivity of compound e, the rate law simplifies to

$$k_{obsd} = k_a[H^+]/(1 + K_H[H^+]) \quad (6)$$

The test of this model and of these assumptions is whether the kinetic data can be satisfactorily fit to this expression and, if so, whether the parameters are reasonable ones. A least-squares fit of the data from Table I to eq 6 gives the values $k_a = (3.09 \pm 0.06) \times 10^{-2}$ dm^3 mol^{-1} s^{-1} and $K_H = 1.09 \pm 0.17$ dm^3 mol^{-1}. These parameters reproduce the experimental data with an average error of 1.3% and a maximum error of 3.0%. This fit, along with a value of K_H typical of values found for other alkylcobaloximes,[8] is used as a justification for the simplified treatment.

Experiments at other temperatures were also fit well by eq 6 and gave $k_a = 0.143$ (35.0 °C), 0.0686 (30.0 °C), and 0.0126 (20.0 °C) dm^3 mol^{-1} s^{-1}. Correlation by the Eyring equation of activated complex theory gives $\Delta H_a^{\ddagger} = 119 \pm 2$ kJ mol^{-1} and $\Delta S_a^{\ddagger} = 125 \pm 5$ J mol^{-1} K^{-1}.

β-OH-n-PrCo(dmgBF$_2$)$_2$B, f. Kinetic data for this reaction were obtained only with the pyridine derivative of f, and we

Table III. Kinetic Data for Reaction of (β-Hydroxy-n-propyl)cobaloxime with Perchloric Acid at 25.1 °C and μ = 0.200 M (LiClO$_4$) (λ 366 nm)

[H$^+$]/M	$-10^3\lambda_f/s^{-1}$	$-10^3\lambda_s/s^{-1}$	$\phi_f = \phi_s/M^{-1}$ cm^{-1}	t_{max}/s obsd (±10%)	calcd[a]	$[(D_{max}-D_\infty)/l[n]_0]/$ M^{-1} cm^{-1}
0.010	5.49	0.99	194	400	380	107
0.050	28.9	4.04	156	85	72.8	96
0.050	30.1	4.22	145	85	72.8	89
0.050	34.8	4.05	150	80	72.8	95
0.050	30.0	5.38	161	70	72.8	88
0.050	30.2	5.07	157	75	72.8	92
0.100	56.5	7.64	145	42.5	41.5	91
0.100	55.8	7.33	145	42.5	41.5	89
0.100	51.9	8.49	145	45	41.5	89
			av 155 ± 16			av 93 ± 6

[a] From eq 30, using average values of λ_s and λ_f.
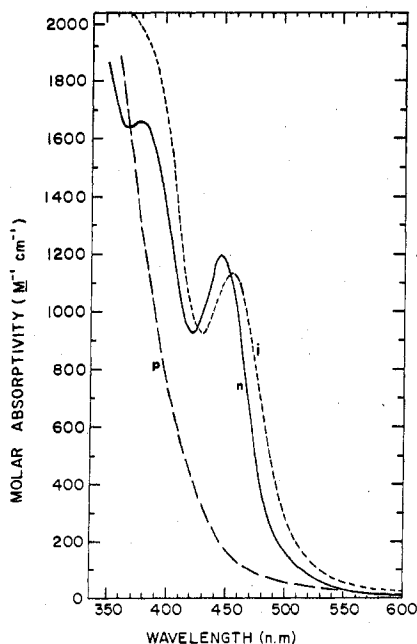
Figure 2. UV–visible absorption spectra for CH$_3$CH(OH)CH$_2$(Co)H$_2$O (n), CH$_2$(OH)CH(CH$_3$)(Co)H$_2$O (i), and (H$_2$O)$_2$(Co)$^+$ (p).

assume as justified previously that complete conversion to the aquo complex occurs very rapidly and prior to the reaction of interest. The reaction followed pseudo-first-order kinetics exactly (see inset in Figure 1). The rate constants for this reaction are given in Table II as a function of [H$^+$] at μ = 0.20 M and at 0.200 M H$^+$ as a function of μ (0.20–0.46 M). For this complex no protonation equilibrium analogous to eq 4 need be considered, and the dependence of k_{obsd} upon [H$^+$] is simply that given by eq 7. The values at 25.0 °C and μ

$$k_{obsd} = k_0 + k_a[\text{H}^+] \tag{7}$$

= 0.200 M are k_0 = (7.8 ± 0.3) × 10^{-6} s^{-1} and k_a = (2.41 ± 0.04) × 10^{-4} M^{-1} s^{-1}.

The ionic strength dependence of k_{obsd} is seen from the data tabulated to be real but slight, consistent with there being no ionic charge on the starting organocobalt derivative.

β-OH-n-PrCo(dmgH)$_2$B, n. The kinetic data for this complex conform to eq 3. The wavelength 366 nm is an isosbestic point for n and p in the spectra of n, i, and p, at which i absorbs most intensely (ϵ_i > ϵ_n = ϵ_p); see Figure 2. The absorbance first rises and later returns to its starting value, as in Figure 3. This is consistent with i being an intermediate in this reaction.

The resolution of the data into two exponentials is also depicted in Figure 3. Values of the apparent rate constant
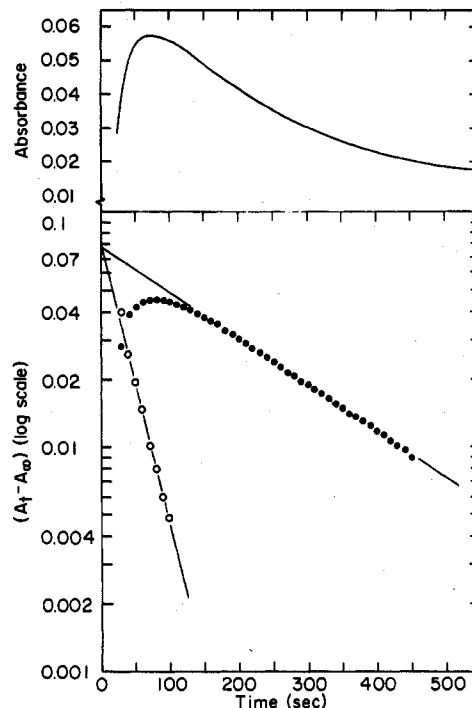

Figure 3. Reaction of CH$_3$CH(OH)CH$_2$(Co)H$_2$O (n) with H$^+$ at 0.050 M H$^+$ followed at the 366-nm isosbestic point, showing partial conversion to i: Upper portion, absorbance–time profile; lower portion, resolution of the kinetic data into its two component exponentials.

composites, λ_f and λ_s of eq 3, were evaluated at different concentrations of the cobalt complex and at different [H$^+$]. These values are summarized in Table III along with values of the intercepts ϕ_f and ϕ_s (which, because 366 nm is an isosbestic point for n and p, are equal).

Consider along with these data a similar set of experiments at 450–454 nm, an isosbestic point for n and i (ϵ_n = ϵ_i > ϵ_p). The absorbance now steadily decreases, but the pseudo-first-order kinetic plots are nonlinear and again resolve into two stages as shown in Figure 4. These data are summarized in Table IV and illustrate that the same kinetic results are found for B = py and B = H$_2$O, again suggesting rapid conversion of the pyridine complex to the aquo complex.

The data in Tables III and IV show that the values of λ_f and λ_s are identical within experimental error from the determinations at the two isosbestic wavelengths. These parameters are the negatives of apparent rate constants consisting of complicated composites, and further interpretation of these values and of the intercepts ϕ_f and ϕ_s is left to a later section. We do note, however, that the dependence of both λ_f and λ_s upon [H$^+$] takes the same form as that of k_a in eq 6. As a consequence, these parameters can be converted to [H$^+$]-

Table IV. Kinetic Data[a] for Reaction of (β-Hydroxy-*n*-propyl)cobaloxime with Perchloric Acid at 25.1 ± 0.1 °C and $\mu = 0.200$ M (LiClO₄) at 450 or 454 nm

[H⁺]/M	$-10^3\lambda_f/s^{-1}$	$-10^3\lambda_s/s^{-1}$	ϕ_f/dm^3 mol^{-1} cm^{-1}	ϕ_s/dm^3 mol^{-1} cm^{-1}
0.010	5.77	1.01	925	76.6
0.050	26.2	4.88	968	68.8
0.050	24.2	4.89	895	66.8
0.050		4.18		66.8
0.050		4.83		66.8
0.050		5.42		74.8
0.050	27.5	4.19	1004	58.2
0.050	31.0	4.99	984	51.2
0.050	26.9	4.38	964	58.6
0.050	25.2			
0.050	25.3			
0.050	25.1[b]			
0.050	25.5[b]			
0.100	46.9	8.34	948	65.4
0.100	48.2	9.14	935	66.1
0.100	49.3	8.83	981	66.8
0.100		8.54		68.8
0.100		8.04		67.4
0.100		8.30		67.4
0.100	44.8			
0.100	45.5			
0.100	43.8[b]			
0.100	41.4[b]			
0.200		17.5		68.1
0.200		17.3		66.8
0.200		16.8		67.4
0.200	73.7			
0.200	78.6			
0.200	73.7[b]			
0.200	74.0[b]			

[a] According to eq 3; runs had [β-OH-*n*-PrCo]₀ in the range $(4.0-7.5) \times 10^{-4}$ M. [b] β-OH-*n*-PrCo(dmgH)₂H₂O used directly as reactant; the other runs employed the pyridine complex, although it is presumed to be rapidly converted to the aquo complex.

independent rate constant composites by the relationships in eq 8 and 9, with $K_H = 2.4$ M⁻¹.

$$k_f = -\lambda_f(1 + K_H[H^+])/[H^+] \quad (8)$$

$$k_s = -\lambda_s(1 + K_H[H^+])/[H^+] \quad (9)$$

The average values of λ_f, λ_s, k_f, and k_s are summarized in Table V for all [H⁺]. Also included are data from runs in which i is the starting complex, as described in the next section.

β-OH-*i*-PrCo(dmgH)₂B, i. Only studies starting with B = py were successfully done. The sequence of events is com-
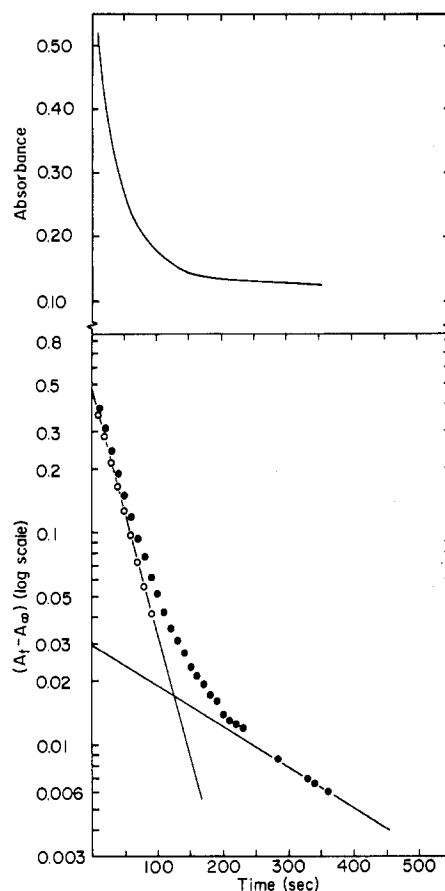

Figure 4. Same reaction and conditions as those of Figure 3 followed at the 454-nm isosbestic point, again showing a kinetic pattern corresponding to a summation of two exponentials.

plicated by a partial isomerization accompanying the loss of pyridine which is just slow enough[9] that an initial large decrease in absorption at 366 nm occurs. Thus at the end of this rapid first step there is present in solution a nonequilibrium mixture of the two aquo complexes of n and i. The former predominates strongly, n being favored by axial pyridine. The subsequent events are similar to those in experiments starting with n; the absorbance rises with partial isomerization to i (B = H₂O) and then falls as p is formed. The rate constants λ_f and λ_s obtained in the usual fashion from determinations starting with i at 450 nm are summarized in Table VI along with intercepts ϕ_f and ϕ_s. It should be noted that these values

Table V. Average Values of λ_f and λ_s and of k_f and k_s for Reactions of n and i with Various Concentrations of [H⁺] (25 °C, $\mu = 0.200$ M)

(A) Average Values of λ_f and λ_s

[H⁺]/M	$-10^3\lambda_f/s^{-1}$			$-10^3\lambda_s/s^{-1}$		
	n_{366}[a]	n_{450}[a]	i_{450}[b]	n_{366}[a]	n_{450}[a]	i_{450}[b]
0.010	5.49	5.77		0.99	1.01	
0.050	30.8 ± 2.3	26.3 ± 2.0	23.4 ± 0.5	4.6 ± 0.6	4.7 ± 0.4	3.8 ± 0.1
0.100	54.7 ± 2.5	45.7 ± 2.7	45.0 ± 2.3	7.8 ± 0.6	8.5 ± 0.4	7.0 ± 0.3
0.200		75.0 ± 2.4	81.4 ± 1.9		17.2 ± 1.0	12.3 ± 0.6

(B) Average Values of k_f, k_s, and ϕ

	[H⁺]/M	k_f[c]/M⁻¹ s⁻¹			k_s[c]/M⁻¹ s⁻¹		
		n_{366}	n_{450}	i_{450}	n_{366}	n_{450}	i_{450}
	0.010	0.56	0.59		0.10	0.103	
	0.050	0.69	0.59	0.52	0.103	0.105	0.085
	0.100	0.68	0.57	0.56	0.097	0.105	0.087
	0.200		0.56	0.60		0.127	0.091
			av 0.60 ± 0.05			av 0.102 ± 0.013	
ϕ/M⁻¹ cm⁻¹		155 ± 16	956 ± 34	950 ± 48	155 ± 16	66.3 ± 5.7	62.1 ± 4.2

[a] From Table IV. [b] From Table VI. [c] From eq 8 and 9 with $K_H = 2.4$ M⁻¹.

Table VI. Kinetic Data for Reaction of β-OH-i-PrCo(dmgH)$_2$B with Perchloric Acid at 25.1 °C and μ = 0.200 M (LiClO$_4$) (λ 450 nm)

[H$^+$]/M	$-10^3\lambda_f$/s^{-1}	$-10^3\lambda_s$/s^{-1}	ϕ_f/dm^3 mol^{-1} s^{-1}	ϕ_s/dm^3 mol^{-1} s^{-1}
0.050	23.9	3.73	899	59.3
0.050	23.4	3.76	899	59.3
0.050	22.8	3.74	906	56.5
0.100	42.5	7.17	906	64.7
0.100	46.9	6.60	1008	61.3
0.100	45.6	7.02	967	59.3
0.200	83.5	11.7	1001	62.0
0.200	79.9	12.8	954	68.1
0.200	80.8	12.5	1008	68.8

Table VII. Kinetic Data for the Effect of Chloride Ions on the Reaction of β-OHEtCo(dmgH)$_2$B with Perchloric Acid at 25 °C and μ = 0.200 M (LiClO$_4$)

[H$^+$]/M	[Cl$^-$]/M	$10^3 k_{obsd}$/ s^{-1}	$10^3 k_{calcd}{}^a$/ s^{-1}
0.050	0.200	1.83	1.82
0.100	0.020	2.76	2.85
0.100	0.060	3.01	2.99
0.100	0.080	3.09	3.05
0.100	0.100	3.22	3.12
0.100	0.140	3.26	3.25
0.100	0.200	3.40	3.45
0.200	0.200	6.22	6.29

^{a} From eq 10 with k_a = 3.04 × 10^{-2} s^{-1}, K_H = 1.09 M^{-1}, and $k_{Cl}K_{Cl}$ = 3.7 × 10^{-2} M^{-1} s^{-1}.
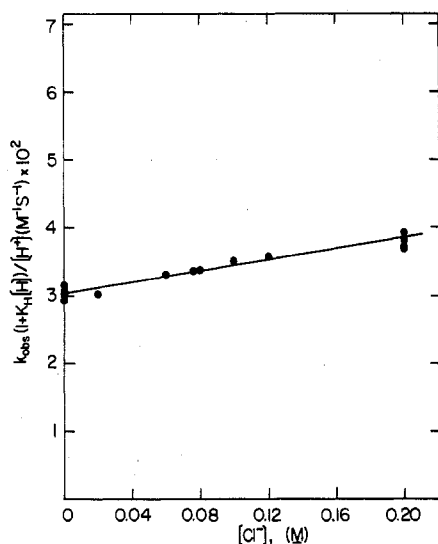

Figure 5. Plot according to eq 10, correlating the effect of added Cl$^-$ on the rate of reaction of CH$_2$(OH)CH$_2$Co(dmgH)$_2$H$_2$O (e) with H$^+$.

are within experimental error of those obtained in runs starting with n. With this in mind, these runs too have been included in the summary in Table V.

β **Elimination in the Presence of Cl$^-$.** The reaction in the presence of Cl$^-$ was studied for the β-hydroxyethyl complex e. The rate is higher in the presence of Cl$^-$, but at a given [H$^+$] the rate is only some 25% higher at 0.20 M Cl$^-$ than it is with [Cl$^-$] = 0.0.[10] The rate constant follows a rate law in which the rate enhancement due to the addition of Cl$^-$ is directly proportional to [Cl$^-$] (eq 10). The data are given in Table
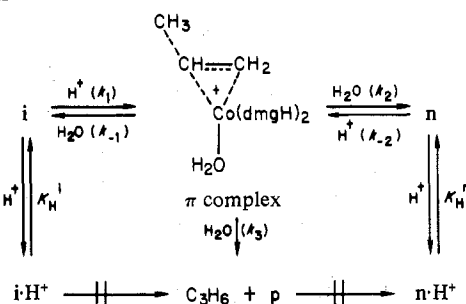
$$k_{obsd} = \frac{k_a[H^+] + k_{Cl}K_{Cl}[Cl^-][H^+]}{1 + K_H[H^+]} \quad (10)$$

VII and a linearized plot suggested by eq 10 is shown in Figure 5. The value of $k_{Cl}K_{Cl}$[11] so calculated is (3.7 ± 0.2) × 10^{-2} M^{-2} s^{-1}.

Scheme I
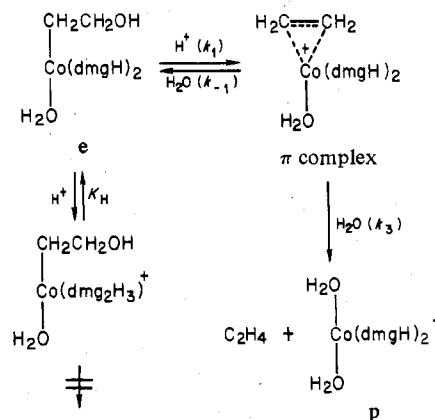
Scheme II

Interpretation and Discussion

Reactions Showing Uniphasic Kinetics. The mechanism proposed for the β-hydroxyethyl compound e is shown in Scheme I. This scheme, with the steady-state approximation made for the concentration of the π intermediate, gives k_a of eq 6 as a composite value (eq 11).

$$k_a = k_1 k_3 / (k_{-1} + k_3) \quad (11)$$

The rate law does not answer whether formation of the π complex or its release of olefin is rate-limiting; that is, it does not distinguish the case $k_3 \gg k_{-1}$ ($k_a \simeq k_1$) from $k_3 \ll k_{-1}$ ($k_a \simeq k_1 k_3 / k_{-1}$). For reasons presented in the final paragraphs of this paper, we find the first alternative more likely for this particular derivative, although this is not a general conclusion. With this interpretation, k_1 (25 °C) = (3.09 ± 0.06) × 10^{-2} dm^3 mol^{-1} s^{-1}, $\Delta H_1{}^{\ddagger}$ = 119 ± 2 kJ mol^{-1}, and $\Delta S_1{}^{\ddagger}$ = 125 ± 5 J mol^{-1} K^{-1}.

Reactions Showing Biphasic Kinetics. Following earlier workers,[3,5] we interpret the kinetic data for n and i by the mechanism shown in Scheme II. The basis for this has been summarized in the introduction. In this instance one π complex is common to both isomers, and it is again assumed that the steady-state approximation can be made for [π complex].

It is convenient in considering this mechanism to simplify the notation which describes the dependence upon [H$^+$]. We do this by defining quantities k_1' and k_2' which incorporate the first-order [H$^+$] dependence as well as the nonproductive protonation equilibrium:

$$k_1' = k_1[H^+]/(1 + K_H{}^i[H^+]) \quad (12)$$

$$k_{-2}' = k_{-2}[H^+]/(1 + K_H{}^n[H^+]) \quad (13)$$

When this notation is used, the differential equations take the form

$$\frac{d[i]}{dt} = \frac{-k_1'(k_2 + k_3)}{k_{-1} + k_2 + k_3}[i] + \frac{k_{-1}k_{-2}'}{k_{-1} + k_2 + k_3}[n] \quad (14a)$$

$$\frac{d[n]}{dt} = \frac{k_1'k_2[i]}{k_{-1} + k_2 + k_3} + \frac{-k_{-2}'(k_{-1} + k_3)[n]}{k_{-1} + k_2 + k_3} \quad (15a)$$

These equations can be written more simply by representing the rate constant composites of eq 14a and 15a as a' and b' and c' and d', respectively (the primes denoting terms containing $[H^+]$ dependences in eq 12 and 13).

$$d[i]/dt = a'[i] + b'[n] \quad (14b)$$

$$d[n]/dt = c'[i] + d'[n] \quad (15b)$$

The general solution[12] of this system of linear differential equations yields[13] expressions 16 and 17 [i] and [n], where

$$[i] = \phi_f' \exp(\lambda_f t) + \phi_s' \exp(\lambda_s t) \quad (16)$$

$$[n] = \left(\frac{\lambda_f - a'}{b'}\right)\phi_f' \exp(\lambda_f t) + \left(\frac{\lambda_s - a'}{b'}\right)\phi_s' \exp(\lambda_s t) \quad (17)$$

λ_f and λ_s are the two roots of the determinental equation

$$\begin{vmatrix} a' - \lambda & b' \\ c' & d' - \lambda \end{vmatrix} = 0 \quad (18)$$

$$\lambda = \frac{(a' + d') \pm [(a' + d')^2 - 4(a'd' - b'c')]^{1/2}}{2} \quad (19)$$

The quantities ϕ_f' and ϕ_s' have dimensions of concentration (compared to ϕ_f and ϕ_s of eq 3 which have dimensions of molar absorptivity). The relationships for ϕ_f' and ϕ_s' depend on the boundary conditions of the experiment. Thus when n is the starting complex and $[i]_0 = 0$, eq 20 applies, whereas in runs starting with i and having $[n]_0 = 0$, eq 21 applies.

$$\phi_f' = \frac{b'[n]_0}{\lambda_f - \lambda_s} \text{ and } \phi_s' = \frac{-b'[n]_0}{\lambda_f - \lambda_s} \quad (20)$$

$$\phi_f' = \frac{-(\lambda_s - a')[i]_0}{\lambda_f - \lambda_s} \text{ and } \phi_s = \frac{(\lambda_f - a')[i]_0}{\lambda_f - \lambda_s} \quad (21)$$

It is now necessary to relate these solutions to the form in which the experimental data are expressed. This requires substitution in terms of absorbance values, as well as specification of the appropriate boundary conditions (i.e., initial concentration and ϵ values) of a given experiment. We consider the following experiments:

(a) At λ 366 nm ($\epsilon_i > \epsilon_n = \epsilon_p$), starting with $[n]_0$ at $t = 0$ and $[i]_0 = 0$

$$\phi_f = \phi_s = b(e_i - \epsilon_p)/(k_f - k_s) \quad (22)$$

(b) At λ 450 nm ($\epsilon_i = \epsilon_n > \epsilon_p$), also starting with n only

$$\phi_f = \frac{(\epsilon_n - \epsilon_p)(k_f - b + a)}{k_f - k_s} \quad (23a)$$

$$\phi_s = \frac{-(\epsilon_n - \epsilon_p)(k_s - b + a)}{k_f - k_s} \quad (23b)$$

(c) At λ 450 nm, starting only with i

$$\phi_f = \frac{(\epsilon_n - \epsilon_p)(k_f - b + a)(a + k_s)}{(k_f - k_s)b} \quad (24a)$$

$$\phi_s = \frac{(\epsilon_n - \epsilon_p)(k_s - b + a)(a + k_f)}{(k_f - k_s)b} \quad (24b)$$

Analysis of the results based on these equations and on the data summary given in Table V proceeds as follows:

(1) The quantity $b - a$ can be calculated from runs at 450 nm by using either eq 23a ($b - a = 0.11 \pm 0.12$ M^{-1} s^{-1}) or

eq 23b ($b - a = 0.13 \pm 0.01$ M^{-1} s^{-1}). The values agree well, and we adopt the latter since it is more precise.

(2) The quantity $b(\epsilon_i - \epsilon_p)^{366}$, obtained from eq 22, has the value 78 ± 8 M^{-2} cm^{-1} s^{-1}.

(3) Limits on a can be set by the requirements $k_f > -a > k_s$ and by the value of $b - a$ from eq 23b, since a must be negative and b positive. Moreover, eq 14 and 15 require $-a > c$. These provisions give a in the range -0.102 to -0.105 M^{-1} s^{-1}.

(4) When this value of a is used, b is between 0.028 and 0.025 M^{-1} s^{-1} and $(\epsilon_i - \epsilon_p)^{366} = (2.9 \pm 0.3) \times 10^3$ M^{-1} cm^{-1}.

(5) Equation 19 affords the relationship $d = -(k_f + k_s + a)$; with the values given, $d = -0.60 \pm 0.06$ M^{-1} s^{-1}. The requirements $-d < k_f$ and $-a > k_s$ narrow the range of permissible values, and we assign $d = -0.59_5$ to -0.59_6 M^{-1} s^{-1}.

(6) The value of c is given by either of the expressions in eq 25, both of which involve small differences. As a consequence, c is known only approximately from the data and the

$$c = (k_f + a)(k_f + d)/b \quad (25a)$$

$$c = (k_s + a)(k_s + d)/b \quad (25b)$$

mathematical requirements, coupled with suitable values of a, b, and d. The range of values of c between 0.017 and 0.099 M^{-1} s^{-1} satisfies the data.

(7) The rate constant k_1 is obtained by relationship 26 and has the value 0.10_5 M^{-1} s^{-1}.

$$k_1 = -\lambda_f\lambda_s/(b + d) \quad (26)$$

(8) The value of k_{-2} is not accurately determined because of the uncertainty in c; the value of k_{-2} from eq 27 is between 0.71 and 10 M^{-1} s^{-1}.

$$k_{-2} = -\lambda_f\lambda_s/(a + c) \quad (27)$$

(9) The three rate constants for the reaction of the steady-state intermediate, the π complex, cannot, of course, be determined directly. Ratios of the values can be determined by relations 28 and 29. The value (range) of k_{-1}/k_3 is between

$$k_{-1}/k_3 = -b/(b + d) \quad (28)$$

$$k_2/k_3 = -c(a + c) \quad (29)$$

0.051 and 0.044 and that of k_2/k_3 is between 0.20 and 17 (the latter ratio shows a wide range of values because it depends upon the poorly known c).

(10) Runs starting with n at 366 nm show a maximum in the absorbance–time curves. The observed values of t_{max}, somewhat imprecise because the maximum is a flat one, are given in Table III. For comparison, values of t_{max} calculated from eq 30 are also shown; the values agree satisfactorily.

$$t_{max} = [\ln(\lambda_f/\lambda_s)]/(\lambda_s - \lambda_f) \quad (30)$$

The values of $D_{max} - D_\infty$ are related to other kinetic parameters by expression 31 which can be used to calculate an

$$\frac{D_{max} - D_\infty}{l[n]_0} = \frac{b'(\epsilon_i - \epsilon_p)^{366}}{\lambda_f - \lambda_s}(e^{\lambda_f t_{max}} - e^{\lambda_s t_{max}}) \quad (31)$$

independent value of $b(\epsilon_i - \epsilon_p)^{366}$. The value thus calculated is $b(\epsilon_i - \epsilon_p)^{366} = 76 \pm 5$ M^{-2} cm^{-1} s^{-1}, using also the expression $b = b'[H^+]/(1 + K_H[H^+])$ with $K_H = 2.4$ M^{-1}. This value is in good agreement with that presented in (2).

Comparisons and Conclusions

Comparisons involving compounds e and f establish that substitution of electron-withdrawing groups on the oxime oxygens greatly lowers the rate of reaction. Considering the electronic structure of the transition state and that the mechanism involves electrophilic attack of H^+ at the β-OH

group, this is quite reasonable. We thus find for e, $k_a \gg k_0$ and $k_a \gg k_0'$. Also, for f, the acid-dependent pathway is by far the more important.

Similarly, reasonable values are found for k_1 and (perhaps) k_{-2}. Consider that i is related to e by substitution of a CH_3 group, electron donating relative to H, on the α carbon; consider also that the mechanism of σ-alkyl to π-olefin conversion involves electrophilic attack of H^+ at the β-OH group, a process presumably favored by increased electron density. On this basis the value of $k_1 = 0.10_5$ M^{-1} s^{-1} for i is reasonable given $k_a = 0.031$ M^{-1} s^{-1} for e. Now n is related to i by substitution of the CH_3 group on the β rather than the α carbon, and with the electron donating group nearer the β-OH group being attacked, a value of $k_{-2} > k_1$ is to be expected. Although any value of k_{-2} within the range 0.71–10 M^{-1} s^{-1} is permissible, the effect is not likely to be enormous, and a value near the lower end of the range seems more reasonable.

If one takes $k_{-2} = 0.7$ M^{-1} s^{-1}, the rate ratios then have these values: $k_{-1}/k_3 = 0.075$, $k_2/k_3 = 0.22$, and $k_{-1}/k_2 = 0.34$. These three ratios describe the relative rates of reaction of the π intermediate of Scheme II. Expressed in a different fashion, the π intermediate reacts to form n with 6% probability, i with 17% probability, and p with 77% probability. The preference for i over n, roughly 3:1, suggests that the reactivity follows Markownikoff's rule and that the steric hindrance of the methyl group is not a determining factor.

We return now to the question of which step is rate limiting in formation of the π intermediate. (Refer to Scheme I and the discussion following it.) For Scheme II we have found $k_{-1}/k_3 = 0.075$ and $k_2/k_3 = 0.22$. In these cases the favored reaction is seen to be loss of olefin and not return to the β-OH complex. Thus in Scheme I it also seems likely that $k_3 \gg k_{-1}$, in which case $k_a \simeq k_1$.

Addition of Cl^- produces a quite mild rate enhancement. The effect can be attributed to a small but more reactive species containing axial chloride. Schrauzer[2] has made note of such nucleophilic rate enhancements, particularly for stronger nucleophiles more tightly coordinated to cobalt, such as cyanide ion. The quantitative rate effect of chloride cannot be separated from its binding constant in this instance, because the latter is so small. The conservative estimate $K_{Cl} \leq 0.2$ M^{-1} gives $k_{Cl} \geq 5k_a$.

The isomerization of n to i and its reverse proceed through a common intermediate, proposed to be the π complex shown in Scheme II. There now exists ample precedent for such intermediates,[4] but the present work shows that they remain at only very low concentrations throughout an experiment

performed under the conditions of this work. The presence of the intermediate does, however, manifest itself in the chemistry of these reactions, particularly in the occurrence of this isomerization. The clear similarity of this transformation to biological processes requiring the B_{12} coenzyme have been noted,[2-4] and further elaboration of this relationship is not needed.

References and Notes

(1) (a) This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division. (b) Based on the M.S. thesis of Diana M. Wang, 1978; experimental details of spectra and kinetics are given in this thesis.
(2) Schrauzer, G. N.; Windgassen, R. J. *J. Am. Chem. Soc.* **1967**, *89*, 143.
(3) Brown, K. L.; Ingraham, L. L. *J. Am. Chem. Soc.* **1974**, *96*, 7681.
(4) Golding, B. T.; Holland, H. L.; Horn, U.; Sakrikar, S. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 1959.
(5) (a) Silverman, R. B.; Dolphin, D. *J. Am. Chem. Soc.* **1972**, *94*, 4028. (b) Abeles, R. H.; Dolphin, D. *Acc. Chem. Res.* **1976**, *9*, 114. See also: Babior, B. M. *Ibid.* **1975**, *8*, 376.
(6) (a) Wilkins, R. G. "The Study of Kinetics and Mechanisms of Reactions of Transition Metal Complexes"; Allyn and Bacon: Boston, Mass., 1974; pp 20–5. (b) Espenson, J. H.; Chao, T.-H. *Inorg. Chem.* **1977**, *16*, 2553.
(7) Brown, K. L.; Lyles, D.; Pencovic M.; Kallen, G. *J. Am. Chem. Soc.* **1975**, *97*, 7338.
(8) (a) Adin, A.; Espenson, J. H. *Chem. Commun.* **1971**, 653. (b) Abley, P.; Dockal, E. R.; Halpern, J. *J. Am. Chem. Soc.* **1973**, *95*, 3166.
(9) This rapid step varies with $[H^+]$ (molar concentrations in parentheses): k_{obsd} = 0.026 (0.01), 0.053 (0.02), 0.085 (0.03), 0.13 (0.04), and 0.39 (0.20) s^{-1} at 25 °C and μ = 0.2 M.
(10) We emphasize the magnitude of the rate enhancement of chloride ions because one might infer a considerably larger enhancement from previous qualitative observations[2] [("...(β-hydroxyalkyl)cobaloximes are readily decomposed in 0.1–0.3 N aqueous hydrochloric acid at room temperature.... In the acid-cleavage reaction of the (hydroxyalkyl)cobaloximes the nucleophilicity of the acid anion and of the base component B are of special significance. Thus, solutions of (β-hydroxyethyl)cobaloxime in 0.5 N H_2SO_4 or $HClO_4$ evolve ethylene at a hardly perceptible rate...")].
(11) Were the extent of axial ligation of e by Cl^- appreciable, such that $K_{Cl}[Cl^-]$ were not very small compared to 1, then eq 10 would contain an added denominator term $K_{Cl}[Cl^-]$. Inclusion of this term in eq 10 gives a value $K_{Cl} = 0.01 \pm 0.07$ M^{-1}, justifying its omission. This conclusion is supported by data of Crumbliss (Crumbliss, A. L.; Wilmarth, W. K. *J. Am. Chem. Soc.* **1970**, *92*, 2593), showing minimal complexation of CH_3Co-$(dmgH)_2H_2O$ by Cl^-.
(12) Ritger, P. D.; Rose, N. J. "Differential Equations with Applications"; McGraw-Hill: New York, 1968; pp 247–50.
(13) The detailed method of solution is given in the thesis cited.[1b]