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SYNTHESIS, CHARACTERIZATION AND DECOMPOSITION OF 2-ARYL-2-HYDROXYETHYLCOBALOXIMES

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Summary

2-Phenyl-2-hydroxyethyl(aquo)cobaloxime (Ia) and the *p*-methyl (Ib) and *p*-cyano (Ic) derivatives have been synthesized and characterized. The parent compound and the *p*-methyl derivative decompose spontaneously both in the solid state and in methanol to give mixtures of the appropriate styrenes and acetophenones. Kinetics and product ratios of the decomposition of Ia and Ib in methanol have been studied as a function of temperature. Evidence is presented that both reaction pathways are ionic in nature and that an intermediate (presumed to be a phenethylcobaloxime carbonium ion) is involved in the styrene forming pathway. Acetophenones are apparently formed via a 1,2-hydride shift mechanism with solvent acting as a general base. Both reaction pathways show a large substituent effect with electron donating substituents increasing reactivity. Ic proved to be extraordinarily stable in methanol but decomposed readily in aqueous sulfuric acid to produce primarily *p*-cyanoacetophenone. Kinetic evidence for formation of a cationic intermediate is presented.

Introduction

2-Hydroxyalkylcobalt complexes are well known to decompose in aqueous base (and in one case, spontaneously in methanol [1]) to ketones or aldehydes and cobalt(I) complexes (eq. 1 [2,3]). These complexes are also known to decompose in

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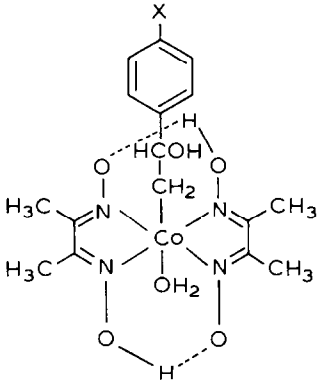
acid to olefins and cobalt(III) complexes (eq. 2 [2,4–7]).

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

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

Because of our continuing interest in the mechanism of carbon–cobalt bond cleavage reactions [4,6–13] we became interested in the preparation of a series of substituted 2-phenyl-2-hydroxyethyl(aquo)cobaloximes (I). These intriguing complexes offered the possibility of bimodal cleavage with the rates of individual cleavage pathways (and microscopic steps within each pathway) being controllable via changes in the substituent, X.



(Ia, X = H ;
Ib, X = CH_3;
Ic, X = CN)

The mechanism of acid-induced olefin formation from 2-hydroxyalkylcobaloximes is now reasonably well understood [7]. Dissociation of water from hydroxyl protonated starting material leads to formation of an intermediate which has been characterized for 2-hydroxyethylcobaloxime as a σ-bonded ethylcobaloxime carbonium ion, probably significantly stabilized by hyperconjugation [7]. However, except in the single case of 1-phenyl-2-hydroxyethylcobaloxime [1] which decomposes spontaneously in methanol via concerted elimination of hydridocobaloxime to form enol acetophenone, the mechanisms of carbonyl compound formation from 2-hydroxyalkylcobaloximes is poorly understood. We have consequently undertaken a study of the synthesis, characterization and decomposition of several substituted 2-phenyl-2-hydroxyethylcobaloximes which is the subject of this report.

Experimental

The 2-aryl-2-hydroxyalkyl(aquo)cobaloximes (I) were obtained by the standard reductive alkylation procedure [10,14] in which the appropriate substituted styrene bromohydrins were used to alkylate hydrido(aquo)cobaloxime. The only modification, due to the instability of Ia and Ib in methanol (see below), was the necessity to work the organocobalt products up to solids as rapidly as possible. In agreement

with our kinetic study in methanol (see below), the yield of Ia and Ib was significantly improved if the alkylation was performed at −20 rather than 0°C.

$C_6H_5CHOHCH_2Co(D_2H_2)OH_2$ (Ia). Elemental anal. Found: C, 44.62; H, 6.03; N, 13.01. $C_{16}H_{25}CoN_4O_6$ calcd.: C, 44.86; H, 5.88; N, 13.08%.

$CH_3C_6H_4CHOHCH_2Co(D_2H_2)OH_2$ (Ib). Elemental anal. Found: C, 46.37; H, 6.12; N, 12.33. $C_{17}H_{27}CoN_4O_6$ calcd.: C, 46.15; H, 6.16; N, 12.67%.

$NCC_6H_4CHOHCH_2Co(D_2H_2)OH_2$ (Ic). Elemental anal. Found: C, 44.36; H, 5.69; N, 15.05. $C_{17}H_{24}CoN_5O_6 \cdot \frac{1}{2}H_2O$ calcd.: C, 44.16; H, 5.45; N, 15.15%.

The styrene bromohydrins were prepared by aluminum isopropoxide reduction of the appropriate α-bromo-*p*-substituted acetophenones in dry isopropanol [15–17]. α-Bromoacetophenone and α-bromo-*p*-methylacetophenone were from Aldrich while α-bromo-*p*-cyanoacetophenone was prepared by bromination of *p*-cyanoacetophenone in dry acetic acid [18]. *p*-Cyanoacetophenone was prepared by reaction of *p*-bromoacetophenone with copper cyanide in pyridine [19].

Spectrophotometric kinetic measurements were made on a Cary 219 spectrophotometer whose cell compartment was thermostatted at the desired temperature ±0.1°C by means of a circulating water bath. First-order rate constants were obtained from the slopes of plots of $\ln|A_\infty - A_t|$ vs. time at appropriate wavelengths determined from scanning experiments. Rate constants from biphasic traces were obtained by plotting $\ln|A_\infty - A_t|$ vs. time, the slope of the linear portions of such plots (i.e., at times such that $t > 5 \times T_{\frac{1}{2}}$ of the faster phase) were taken as the first-order rate constants for the slower phase, k_2. The linear portion was then extrapolated to time zero and a replot of the natural log of the absolute value of the difference between the extrapolated absorbance and the absorbance at time t (i.e., $\ln|A_{ext} - A_t|$) vs. time yielded a second straight line whose slope was taken as the first-order rate constant for the faster phase, k_1. All such biphasic kinetic samples were ran in at least triplicate and the average values of k_1 and k_2 were taken as the best estimates.

Acidities of kinetic samples in H_2SO_4/H_2O were determined by titration of duplicate aliquots (100–500 μl) with standard KOH to a phenolphthalein endpoint. All such duplicate titrations agreed to within ±1%. Values of the Hammett acidity function [20] were obtained from the determined sulfuric acid molarities from literature data [21,22], interpolating between literature data points, when necessary.

Gas chromatographic analysis of organic products from the decomposition of I were performed on a Hewlett-Packard F&M5750 Gas Chromatograph equipped with a 6 ft. × 1/8 in. 5% Carbowax on Anachrom ABX column. After injection, the column was maintained at 80°C for 5 min, then programmed to 140°C at 60°C/min, then held at 140°C for 6 min. At a carrier flow rate of 25 ml min^{-1}, the retention times were styrene, 3.4 min, *p*-methylstyrene, 3.7 min, acetophenone, 10.4 min, and *p*-methylacetophenone, 11.3 min. Molar ratios of styrenes to acetophenones were determined from the ratios of the areas of the GC peaks by comparison to those obtained from standards of known molar ratio. Triplicate samples were analyzed at each reaction temperature and at least triplicate injections were made from each sample, the average values being used. Standards containing molar ratios of styrenes to acetophenones close to that expected from each sample were run before and after samples daily. As Ia and Ib decomposed even in the solid state and appropriate experiments showed that the ratio of styrenes to acetophenones from solid state decomposition were substantially larger than those from decomposition in solution,

it was necessary to wash the organic products from the solids immediately prior to their decomposition to determine product ratios. This was achieved by suspending the solids in cyclohexane, centrifuging, and then removing the cyclohexane supernatant. This procedure was repeated three times and the washed solids were dried in a stream of argon. Such prewashing of Ia and Ib was shown, however, not to effect the kinetics of decomposition.

Isotopic composition of styrene and acetophenone obtained from decomposition of Ia in CH_3OD was determined from mass spectra of these products obtained on a Finnigan 3200 GC/MS instrument equipped with a Sadar Nearmag Data system and a 50 meter capillary OV101 50QC2 column. At a column temperature of 150°C, the retention times were methanol, 3.21 min, styrene, 3.52 min, acetophenone, 4.30 min. Control samples of Ia in CH_3OH and acetophenone in CH_3OD were analyzed similarly.

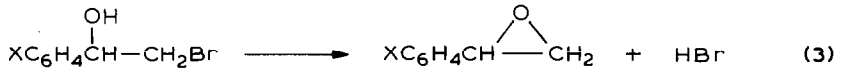
Results and discussion

Synthesis and characterization of the 2-aryl-2-hydroxyethylcobaloximes

Despite the relative instability of the unsubstituted (Ia) and *p*-methyl-substituted (Ib) compounds, the 2-aryl-2-hydroxyethyl(aquo)cobaloximes are readily prepared from the appropriate styrene bromohydrin alkylating agents via standard reductive alkylation techniques [10,14] provided that work-up of the solid products is performed as rapidly as possible. As suggested by the relatively large dependence of the kinetics of Ia and Ib decomposition on temperature (see below) yields may be substantially improved by carrying out the alkylation at −20 rather than 0°C. Thus, the yield of the *p*-methyl compound (Ib) is improved from 20% at 0°C to 45% at −20°C.

The unsubstituted (Ia) and *p*-methyl derivative (Ib) are quite unstable even in the solid state when stored at −20°C in the dark, as reliably determined by the strong odor of acetophenone and *p*-methylacetophenone on the stored solids. Anaerobic pyrolysis of Ia gave a much higher ratio of styrene to acetophenone ($R_m = 7.24$) than did solution decomposition (see below). It was consequently necessary to carefully remove organic decomposition products from solid samples (by washing with cyclohexane, see Experimental) prior to determination of product ratios for decomposition in solution. However, decomposition kinetics were found to be unaffected by washing of solid starting materials, suggesting that the decomposition reactions are irreversible.

The instability of Ia and Ib precludes their characterization by NMR spectroscopy. However, several lines of evidence suggest that relatively pure materials of the anticipated structures have been obtained. First, excellent elemental analysis [23] has been obtained for all three compounds (Experimental) confirming their empirical formulas. However, it is important to eliminate the possibility of contamination with the isomeric 1-phenyl-2-hydroxyethylcobaloximes due to the lability of the styrene bromohydrins toward epoxide formation (eq. 3) and the fact that styrene



(3)

oxide is known to add to both hydridocobaloxime and cobaloxime(I) to give exclusively the 1-phenyl-2-hydroxyethyl derivative [1]. Careful analysis of the organic

products of both anaerobic pyrolysis and solution decomposition of Ia and Ib in both methanol and chloroform by GC and GC/MS was unable to detect any phenylacetaldehydes (i.e., only styrenes and acetophenones were formed). Since 1-phenyl-2-hydroxyethylcobaloxime is known to decompose in methanol to phenylacetaldehyde [1], we conclude that our compounds are free of these isomeric contaminants.

The much greater stability of the *p*-cyano complex (Ic) does, however, permit its characterization by ^{1}H NMR spectroscopy, which was performed on the pyridine derivative in $CDCl_3$. The aromatic region shows a 9 proton multiplet between 9.60 and 7.20 ppm representing the aryl group of the organic ligand and the axial pyridine. As anticipated, the four equatorial methyl groups are diastereotopic due to the presence of an asymmetric center in the organic ligand [24–26] and appear as two closely-spaced lines of equal intensity at 2.189 and 2.151 ppm. The β-proton of the organic ligand appears as a broadened doublet (J 9.4 Hz) suggesting that it is coupled only very weakly to one of the two diastereotopic α-hydrogens. As a result, the α-methylene group appears as a five line pattern, apparently the superposition of a symmetrical triplet (δ 1.170 ppm, J 9.9 Hz) and a doublet (δ 1.167 ppm, J 9.0 Hz). Hence, the two diastereotopic α-methylene protons have nearly identical chemical shifts, but one (H_A) is coupled very strongly to the β-proton (H_C, J_{AC} 9.4 Hz) while the other (H_B) is coupled very weakly ($J_{BC} \sim 0$ Hz). Since these two protons are strongly coupled to each other with a coupling constant (J_{AB} ca. 9.5 Hz) nearly identical to J_{AC}, H_A appears as a symmetrical triplet, while H_B appears as a doublet.

Kinetics and mechanism of decomposition of Ia and Ib

Ia was found to decompose readily in methanol with strictly first-order kinetics at temperatures of 15°C or less (Fig. 1). However, at temperatures of 25°C or above, the decomposition was clearly biphasic, consisting of two sequential exponentials (Fig. 1). Biphasic kinetic traces were resolved into two first-order rate constants (k_1 and k_2) as described in the Experimental section and these rate constants are listed in Table 1, along with values for the molar ratio (R_m) of styrene to acetophenone. Activation energy analysis (see below) shows that the single phase at low temperature is analogous to the more rapid kinetic process at higher temperatures. Inspection of the product ratios shows that both styrene and acetophenone forming pathways occur at all temperatures and that the ratio of styrene to acetophenone increases monotonically with temperature.

A similar situation occurs for the *p*-methyl compound (Ib) except that the reaction is monophasic above 25°C but biphasic below 25°C (Fig. 2, Table 2). In this case, it is the slower phase at low temperature that is analogous to the single phase at higher temperature, and again, the molar ratio of *p*-methylstyrene to *p*-methylacetophenone increases with increasing temperature. Activation energy plots (as $\ln(kh/k_bT)$ vs. $1/T$ where h is Planck's constant and k_b is Boltzmann's constant) are shown for both processes for Ia in Fig. 3a and for Ib in Fig. 3b. Clearly, these decomposition reactions are characterized by two types of kinetic processes, one of which is characterized by a high enthalpy of activation ($+25.6 \pm 0.5$ kcal mol^{-1} for Ia and $+23.6 \pm 0.4$ kcal mol^{-1} for Ib) and a positive entropy of activation (18.3 ± 1.8 e.u. for Ia and 11.6 ± 1.3 e.u. for Ib) while the other is characterized by a low enthalpy of activation (5.5 ± 0.5 kcal mol^{-1} for Ia and

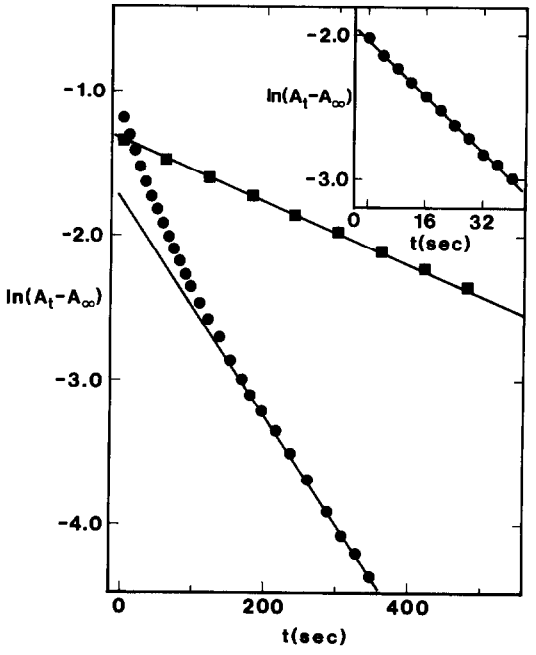


Fig. 1. Plots on $\ln(A_t - A_\infty)$ at λ 480 nm vs. time for the decomposition of Ia (5.0×10^{-4} M) in methanol. (■), 15.0±0.1°C, the solid line is a least-squares fit, slope -2.15×10^{-3} s^{-1}, intercept −1.34. (●), 30.0±0.1°C, the solid line is a least-squares fit to the data at $t > 160$ s, slope $(-k_2)$ -7.56×10^{-3} s^{-1}, intercept −1.75. *Inset*: Replot of the first phase data at 30.0±0.1°C as $\ln(A_t - A_{ext})$ vs. time, where A_{ext} is the extrapolated absorbance from the least-squares fit to the second phase. The solid line is a least-squares fit, slope $(-k_1)$ -2.42×10^{-2} s^{-1}, intercept −2.04.

2.6 ± 0.6 kcal mol^{-1} for Ib) and a negative entropy of activation (−50.2 ± 1.6 e.u. for Ia and −58.5 ± 2.0 e.u. for Ib). It must be stressed that these kinetic phenomena are not due to the availability of two reaction pathways (i.e., to styrenes and to acetophenones), as parallel first-order kinetic systems give strictly first-order decomposition kinetics [27]. Instead, these kinetics imply that one of the two reaction

TABLE 1

RATE CONSTANTS AND PRODUCT RATIOS FOR THE DECOMPOSITION OF Ia IN METHANOL

T (°C)	R_m [a]	k_1 (k_{s_2}) ($\times10^{-3}$) (s^{-1})	k_2 ($\times10^{-3}$) (s^{-1})	k_{s_1} ($\times10^{-3}$) (s^{-1})	k_A ($\times10^{-3}$) (s^{-1})
5	0.133	0.431	–	–	–
10	0.138	1.14	–	–	–
15	0.158	2.11	–	–	–
25	0.210	12.5	6.33	1.10	5.23
30	0.268	23.5	7.80	1.65	6.15
35	0.375	43.5	9.16	2.50	6.66
40	0.476	86.9	10.3	3.32	6.96

[a] Molar ratio of styrene to acetophenone.

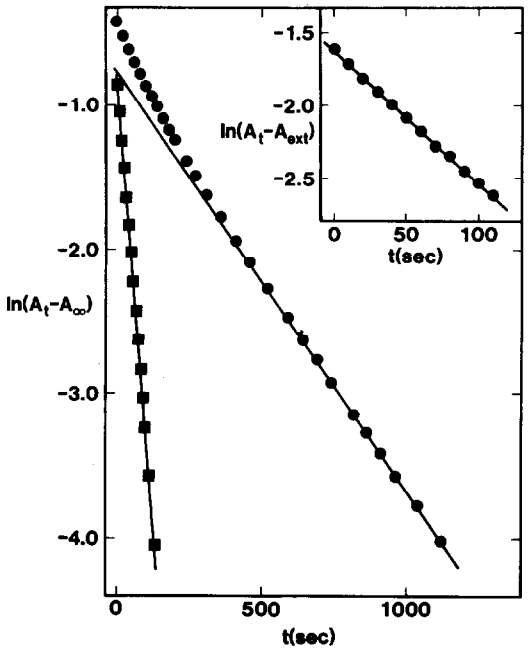


Fig. 2. Plots of $\ln(A_t - A_\infty)$ at λ 480 nm vs. time for the decomposition of Ib (1.0×10^{-3} M) in methanol. (■), 30.0 ± 0.1°C, the solid line is a least-squares fit, slope -2.30×10^{-2} s^{-1}, intercept -0.846. (●), 15.0 ± 0.1°C, the solid line is a least-squares fit to the data at $t > 600$ s, slope $(-k_2)$ -2.90×10^{-3} s^{-1}, intercept -0.804. *Inset*: Replot of the first phase data at 15.0 ± 0.1°C as $\ln(A_t - A_{ext})$ vs. time, where A_{ext} is the extrapolated absorbance from the least-squares fit to the second phase. The solid line is a least-squares fit, slope $(-k_1)$ -9.40×10^{-3} s^{-1}, intercept -1.622.

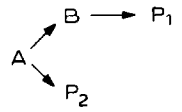
pathways contains a spectrophotometrically detectable intermediate, i.e., that a reaction scheme of the type shown in Scheme 1 is operative. In order to determine in which reaction pathway (i.e., the styrene or acetophenone pathway) the intermediate occurs, it is necessary to consider what is currently known about the mechanisms of reactions of the type shown in eqs. 1 and 2.

TABLE 2

RATE CONSTANTS AND PRODUCT RATIOS FOR THE DECOMPOSITION OF Ib IN METHANOL

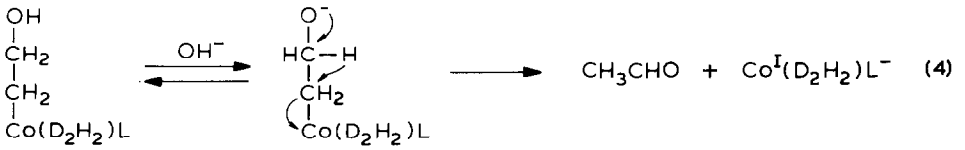
T (°C)	R_m [a]	k_1 ($\times10^{-3}$) (s^{-1})	k_2 (k_{s_2}) ($\times10^{-3}$) (s^{-1})	k_{s_1} ($\times10^{-3}$) (s^{-1})	k_A ($\times10^{-3}$) (s^{-1})
0	0.302	7.37	0.256	1.71	5.66
5	0.277	8.82	0.530	2.24	6.58
10	0.313	9.40	1.20	2.24	7.16
15	0.334	9.90	2.60	2.48	7.42
20	0.475	11.4	4.90	3.67	7.73
30	0.717	–	23.3	–	–
35	0.855	–	42.0	–	–
40	0.903	–	65.0	–	–

[a] Molar ratio of *p*-methylstyrene to *p*-methylacetophenone.

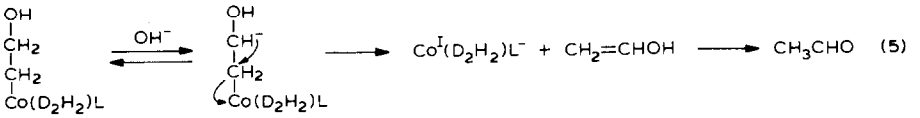


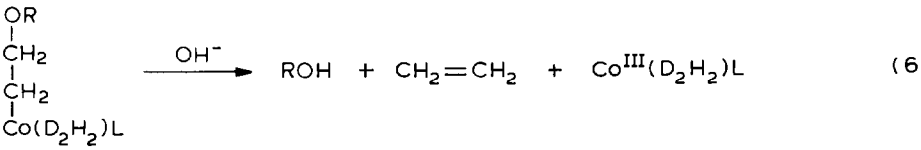
SCHEME 1

Schrauzer and Sibert [3] originally proposed a 1,2-hydride shift mechanism for the base-induced formation of acetaldehyde from 2-hydroxyethylcobaloximes (eq. 4).



Although detailed kinetic studies are lacking, formation of an accumulating intermediate in a kinetically slow step for this mechanism is impossible. The major competing mechanism for this reaction is base-induced β-elimination (eq. 5). However, it has recently been demonstrated [28,29] that 2-alkoxyethylcobaloximes decompose in aqueous base to give ethylene (eq. 6) and do not undergo detectable β-elimination.





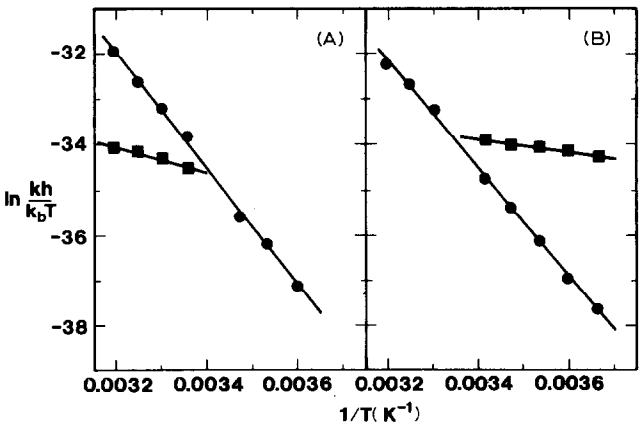
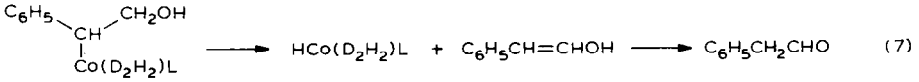


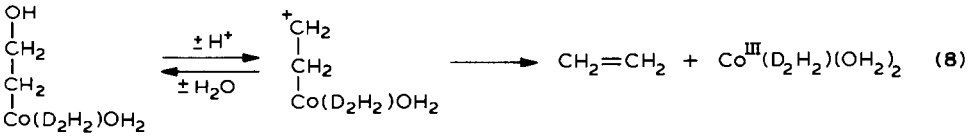
Fig. 3. Plots of $\ln(kh/k_bT)$ vs. $1/T$ for k_1 and k_2 for decomposition of Ia and Ib in methanol. The solid lines are least-squares fits. (A) Ia, X = H, (●), k_1, slope $-1.29\pm0.03\times10^4$ K, intercept 9.22 ± 0.91; (■), k_2, slope $-2.75\pm0.24\times10^3$ K, intercept -25.3 ± 0.8. (B) Ib, X = CH_3, (●), k_2, slope $-1.19\pm0.02\times10^4$ K, intercept 5.85 ± 0.65; (■), k_1, slope $-1.31\pm0.28\times10^3$ K, intercept -29.4 ± 1.0.

This makes it unlikely that 2-hydroxyalkylcobaloximes decompose via a base-induced β-elimination mechanism. Since the only other known reaction in which carbonyl compounds are formed from 2-hydroxyalkylcobaloximes is the concerted elimination of hydridocobaloxime from 1-phenyl-2-hydroxyethylcobaloxime (eq. 7) [1], it seems extremely unlikely that the intermediate formed in the decomposition of Ia and Ib occurs in the acetophenone pathway.



(7)

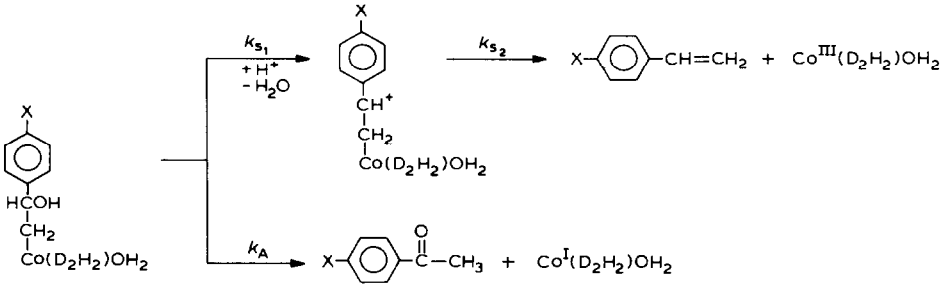
Olefin formation from 2-hydroxyalkylcobaloximes, however, is known to occur via an acid-induced pathway in which an intermediate is formed [7]. In the case of 2-hydroxyethylcobaloxime, we have shown the intermediate, which accumulates in strong acid, to be a σ-bonded ethyl carbonium ion (eq. 8) which is probably stabilized by $\sigma-\pi$ hyperconjugation [7].



(8)

Importantly, studies of the temperature-dependence of the decomposition of the intermediate in strong acid (where it occurs as the trication due to protonation of the equatorial ligand) gave values of 24.7 ± 0.3 kcal mol^{-1} and 8.6 ± 1.1 e.u. for the enthalpy and entropy of activation, respectively. As these values are very similar to those now obtained for the high enthalpy process in the decomposition of Ia and Ib, we must conclude that it is the styrene-forming pathway which contains the intermediate and that the high enthalpy process represents the decomposition of the intermediate. Consequently, the operative kinetic scheme must be that shown in Scheme 2, and k_1 for Ia decomposition and k_2 for Ib decomposition may be equated with k_{s_2} (Scheme 2).

The lower enthalpy process in the decomposition of Ia and Ib must then represent the step in which starting material is committed to either the styrene or acetophenone reaction pathway. Since the observed rate constant must be equal to the sum of k_{s_1} and k_A and the product ratio, R_m, must be equal to the ratio of these rate constants [27], the values of the rate constants for the lower enthalpy process may be resolved into values of k_{s_1} and k_A as is done in Tables 1 and 2. Activation energy plots for



SCHEME 2

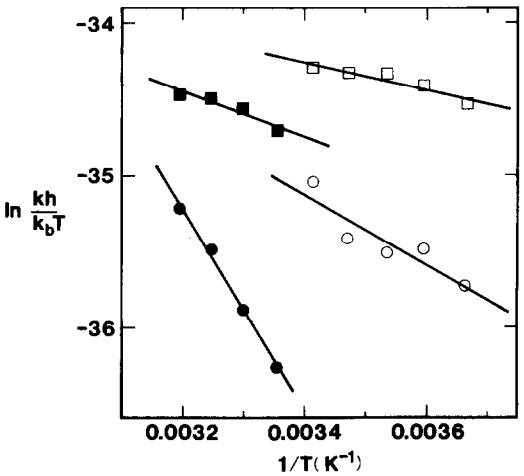


Fig. 4. Plots of $\ln(kh/k_bT)$ vs. $1/T$ for k_{s_1} and k_A (Scheme 2) for Ia and Ib decomposition in methanol. The solid lines are least-squares fits. (●), k_{s_1} for Ia, X = H, slope $-6.63\pm0.33\times10^3$ K, intercept -14.0 ± 1.1; (■), k_A for Ia, X = H, slope $-1.48\pm0.20\times10^3$ K, intercept -29.7 ± 0.6; (○), k_{s_1} for Ib, X = CH_3, slope $-2.31\pm0.61\times10^3$ K, intercept -27.3 ± 2.2; (□), k_A for Ib, X = CH_3, slope $-9.02\pm1.74\times10^2$ K, intercept -31.2 ± 0.6.

these rate constants are shown in Fig. 4, and the resultant values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are listed in Table 3. The formation of the intermediate in the styrene pathway (k_{s_1}) is characterized by moderate enthalpies of activation and rather strongly negative entropies of activation both of which depend strongly on the substituent, X. Thus, the reaction is subject to a large substituent effect and is activated by electron-donating substituents. This is the expected direction of the substituent effect if, as implied in Scheme 2, protonation of the β-hydroxyl group is required prior to formation of the intermediate. The large, negative entropies of activation imply either that a molecule of solvent is involved in the transition state (as a general acid) or that a large reorganization of the solvent shell accompanies formation of the transition state (due to substantial separation of charge) or both.

The acetophenone pathway (k_A) is characterized by very small enthalpies of activation but large, negative entropies of activation (Table 3). Again, the substituent effect appears to be very large and in the same direction as that for the styrene pathway, i.e., electron-donating substituents accelerate the reaction. As described above, there are only two reasonable possibilities for the mechanism of this reaction,

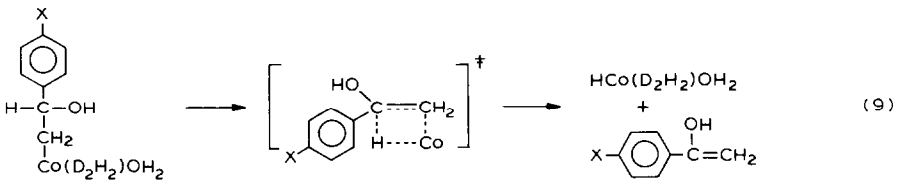
TABLE 3

ACTIVATION ENTHALPIES AND ENTROPIES FOR THE DECOMPOSITION OF Ia AND Ib IN METHANOL

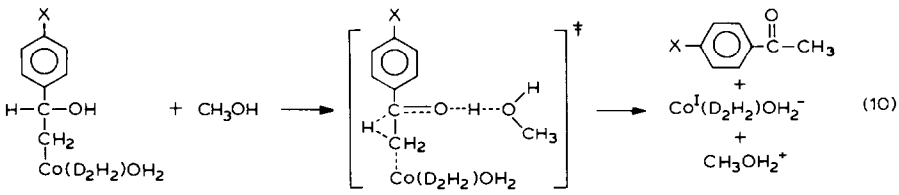
X	k_{s_1}		k_{s_2}		k_A	
	$\Delta H^{\ddagger}$ [a]	$\Delta S^{\ddagger}$ [b]	$\Delta H^{\ddagger}$ [a]	$\Delta S^{\ddagger}$ [b]	$\Delta H^{\ddagger}$ [a]	$\Delta S^{\ddagger}$ [b]
H	13.2 ±0.7	−27.8±2.2	25.6±0.5	18.3±1.8	2.94±0.39	−59.0±1.3
CH_3	4.59±1.21	−54.2±4.3	23.6±0.4	11.6±1.3	1.79±0.35	−62.0±1.2

[a] In kcal mol^{-1}. [b] In e.u.

concerted elimination of hydridocobaloxime to form the enol acetophenone (eq. 9) and the base-induced 1,2-hydride shift mechanism (eq. 10), base-induced β-elimination being ruled out by the failure of the 2-alkoxyethylcobaloximes to decompose via this route [28,29]. Although the elimination process (eq. 9) has been depicted as



(9)



(10)

going through a four-center transition state, reactions analogous to the reverse process, such as the addition of hydridopentacyanocobaltate to olefins [30], have been suggested to proceed via transition states with considerable biradical character. However, Gaudemer and coworkers [31] have provided excellent evidence for *cis*-addition of hydridocobaloximes to olefins which implies either a concerted addition via a four-center transition state or that the biradical character of the transition state is so slight as to prevent rotation about the carbon–carbon bond. At any rate, the low enthalpy of activation associated with acetophenone formation is probably quite consistent with the concerted elimination process (eq. 9) since the enthalpies associated with bond-forming and bond-breaking processes in such a transition state are likely to be very nearly equal. However, it is much harder to reconcile the large, negative entropies of activation with such a mechanism. Although a small decrease in entropy might be expected to be associated with formation of the four-center transition state, major reorganization of the solvation shell seems unlikely as very little separation of charge is anticipated for such a transition state. On the other hand, it is difficult to predict the enthalpy of activation for the base-assisted hydride shift mechanism (eq. 10). If this mechanism is correct, the low enthalpy of activation may indicate that the transition state is quite early. However, this mechanism is consistent with a large, negative entropy of activation both because of its bimolecular nature (with solvent acting as a general base) and its anticipated ionic character which should be accompanied by significant solvation changes as the transition state is approached.

In order to attempt to distinguish experimentally between these two mechanisms, we took advantage of the fact that the concerted elimination mechanism must produce the enol of acetophenone while the hydride shift mechanism produces the ketone directly. Since the enol will undergo a solvent-assisted ketonization [1], labile deuterides from the solvent must be incorporated into the methyl group of the ketone. Ia (washed free of organic products as described) was consequently allowed to decompose in methanol-d_1 for 6 h at room temperature and the isotopic composition of the acetophenone product was determined by mass spectrometry to

be 18.1 ± 2.5 atom% D. A control sample in which acetophenone was incubated in methanol-d_1 for the same period of time was only 0.81 ± 0.12 atom% D. We conclude that although the hydridocobaloxime elimination pathway (eq. 9) may contribute to a small extent to the total reactivity toward acetophenone, the predominant mechanism for acetophenone formation is the base-assisted 1,2-hydride shift (eq. 10). In this light, it is of interest to consider the apparently substantial substituent effect on the acetophenone-forming pathway (Fig. 4, Table 3). As electron-donating substituents must necessarily decrease the acidity of the β-hydroxyl group, the apparent acceleration of hydride ion migration away from the β-carbon due to increased electron density on the β-carbon must be a much more important effect.

In retrospect, it is interesting to note that prior to collecting and interpreting the detailed kinetic data for Ia and Ib in methanol, we anticipated that both reaction pathways (i.e., to acetophenones and to styrenes) would involve concerted reaction mechanisms and be unassisted by solvent. This expectation was based on our preliminary observations that both products were formed in the solid state and in non-hydroxylic solvents (such as $CHCl_3$) as well as in methanol and took into consideration the relatively weak acidity [32] and basicity [33] of methanol. In fact, both reaction pathways are ionic and solvent assisted in methanol, suggesting that despite the poor acidity and basicity of the solvent the concerted pathways are of considerable higher energy. This is in direct contrast to 1-phenyl-2-hydroxyethylcobaloxime [1] which forms only the carbonyl product (phenylacetaldehyde) in methanol via a concerted, *cis*-elimination of hydridocobaloxime. Apparently, the presence of a bulky phenyl substituent on the α-carbon is sufficient to reverse the relative energetics of the stepwise vs. concerted pathways providing evidence of the importance of steric effects in organocobalt decomposition reactions.

Decomposition of Ic in aqueous sulfuric acid

To our great surprise, the *p*-cyano derivative of I (i.e., Ic) proved to be completely stable in methanol (and, apparently in the solid state). Incubation of Ic at 45°C in methanol for 24 h, produced no detectable change in its UV-VIS spectrum. This negative result provides further perspective on the magnitude of the substituent effect on the decomposition of I.

Ic did, however, readily decompose in aqueous sulfuric acid. The principal organic product was *p*-cyanostyrene, although small amounts of *p*-cyanoacetophenone were also found. Kinetics of this decomposition reaction were measured spectrophotometrically at 15 ± 0.1°C and were found to be distinctly biphasic at all sulfuric acid concentrations employed (Fig. 5). Rate constants for the two exponential phases (k_1 and k_2) were resolved as described above and are plotted (as $\log k_1$ and $\log k_2$) against the Hammett acidity function, H_0 [20–22] in Fig. 6. The logarithm of k_1 is evidently a linear function of H_0, the least-squares slope of -0.974 ± 0.017 implying both that k_1 represents a specific-acid catalyzed process and that H_0 is an appropriate acidity function for this compound. The average value of $k_{H^+} = k_1/a_{H^+}$ over the acidity range studied is $2.05 \pm 0.16\ M^{-1}\ s^{-1}$. k_2, on the other hand, is independent of acidity in this range, the average value being $1.35 \pm 0.06 \times 10^{-3}\ s^{-1}$. These results suggest that an intermediate is formed in an acid-catalyzed step (k_1) followed by first-order decomposition of the intermediate in an acid-independent step (k_2) as shown in Scheme 3, where the intermediate is

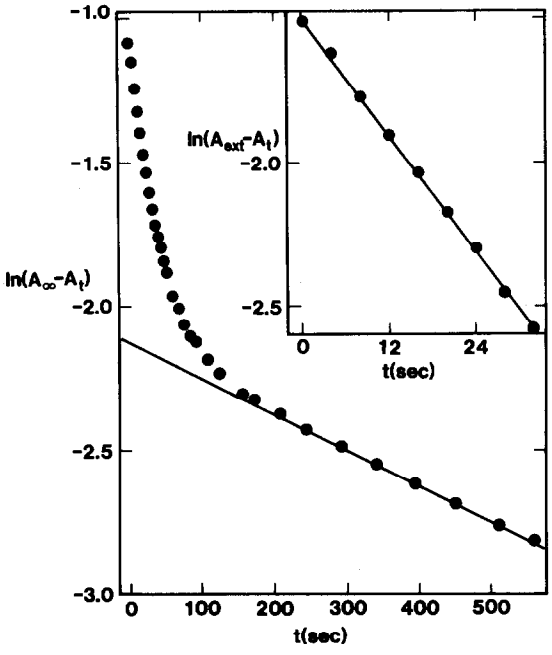


Fig. 5. Plots of $\ln(A_\infty - A_t)$ at λ 256 nm vs. time for the decomposition of Ic, 5.0×10^{-5} M, in 0.0107 M aqueous sulfuric acid ($H_0 = 1.77$), 15.0 ± 0.1°C. The solid line is a least-squares fit to the second phase data at $t > 270$ s, slope $(-k_2)$ -1.24×10^{-3} s^{-1}, intercept -2.13. *Inset*: Replot of the first phase data as $\ln(A_{ext} - A_t)$ vs. time, where A_{ext} is the extrapolated absorbance of the second phase. The solid line is a least-squares fit, slope $(-k_1)$ -3.37×10^{-2} s^{-1}, intercept -1.50.

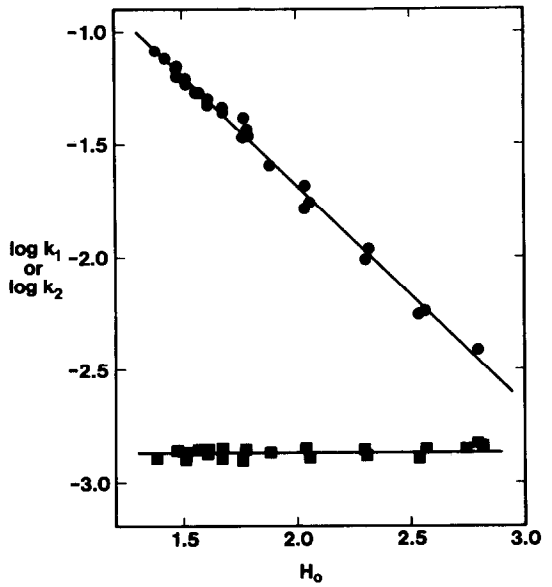
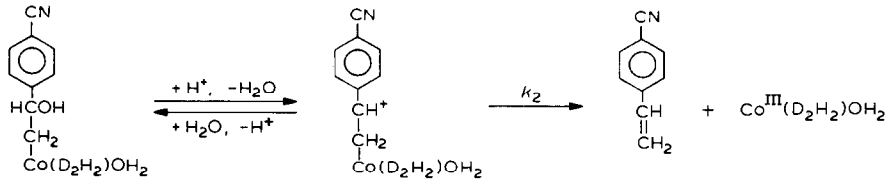


Fig. 6. Plots of $\log k_1$ (●) and $\log k_2$ (■) vs. H_0, the Hammett acidity function, for the decomposition of Ic in aqueous sulfuric acid at 15.0 ± 0.1°C. For k_1 (●) the solid line is a least-squares fit, slope -0.974 ± 0.017, intercept 0.265 ± 0.031. For k_2 (■) the solid line is the log of the average value of k_2 at all acidities ($1.35\pm0.06\times10^{-3}$ s^{-1}).



SCHEME 3

assumed to be a σ-bonded phenethyl carbonium ion based on our recent conclusions regarding the acid-induced decomposition of 2-hydroxyethylcobaloxime [7]. It should be noted that in general, as depicted in Scheme 3, formation of the intermediate from hydroxyl protonated Ic must be assumed to be reversible, particularly in weakly acidic media where the activity of water is close to unity. However, under the current conditions, since the intermediate accumulates, its rate of decomposition must exceed its rate of rehydration significantly.

We note that over the acidity range studied, there is no evidence of a downward inflection in the dependence of $\log k_1$ on H_0 or a decrease in k_2 with increasing acidity. This indicates that the equatorial ligands of Ic and the intermediate (Scheme 3) have not been significantly protonated at the highest acidity studied. This is not surprising since the pK_a for the first equatorial protonation of the cationic intermediate formed in the acid-induced decomposition of 2-hydroxyethylcobaloxime is -0.16 and that of 2-hydroxyethylcobaloxime itself is less than 0.5 [7].

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