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Preliminary communication

KINETICS AND MECHANISM OF ACID-INDUCED HOMOLYSIS OF THE METAL—CARBON BOND IN ORGANOCOBALT(III) CHELATES WITH A TRIDENTATE LIGAND*

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Summary

Kinetics of acid-induced decomposition of the complexes [RCo(7-Me-salen)(en)]$^{+}$** (I), where R = Me, Et and n-Bu, and related equilibria involving protons have been studied. The complexes lose reversibly the diamine ligand at pH of ca. 5—6 to give [RCo(7-Me-salen)$(H_2O)_2$]$^+$ (II). At much lower pH the latter species undergo fast reversible protonation at the phenolate oxygen to afford [RCo(7-Me-salenH)$(H_2O)_2$]$^{2+}$ (III). Both the organometallic intermediates II and III decompose homolytically, the latter being by a factor of 8—400 as reactive as the former. Kinetic data suggest the splitting of the Co—C bond to be a rate-limiting step.

The homolytic cleavage of organocobalt(III) complexes received growing attention in connection with disputed functioning of coenzyme B_{12} and elucidating factors which affect the stability of transition metal—carbon σ-bonds [1]. In most cases studied so far the homolysis is induced thermally or by light, and is complicated by side reactions. On the other hand, it has been recently found [2,3] that octahedral alkylcobalt(III) complexes containing a mixed tridentate ligand, such as 7-Me-salen, undergo homolysis readily and smoothly under the action of acids. We report here preliminary results of a mechanistic study.

Equilibria. It has been shown [3] that the interaction of [RCo(7-Me-salen)-

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*Dedicated to Prof. Oleg A. Reutov on the occasion of his 65th birthday on September 5th, 1985.

**7-Me-salen denotes the meridional tridentate ligand, o-$^{-}OC_6H_4C(Me){=}N(CH_2)_2NH_2$.

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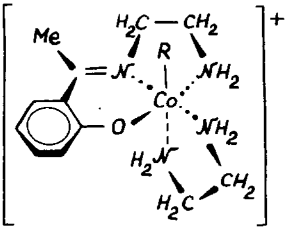
(en)]$^+$ (I) with acids is reversible at low H^+ concentrations and results in releasing the diamine ligand to give the corresponding diaquo complexes [RCo(7-Me-salen)$(H_2O)_2$]$^+$ (II) (Scheme 1, eq. 1). Though the process is slow on the NMR time scale, the equilibration occurs within a few minutes at ambient temperature. Determination of the equilibrium constant $K_1 = [I][H^+]^2/[II][enH_2{}^{2+}]$ is complicated by subsequent processes. Nevertheless, in the case of the least labile methylcobalt complex, we have been able to measure the K_1 value of (6.7 ± 1.3) × 10^{-9} *M* (R = Me, in H_2O, 25°C, without supporting electrolyte) at low acid to complex molar ratios ($HClO_4$/I = 0.5—1) by pH measurements.



[RCo(7-Me-salen)(en)]$^+$

(I)

Furthermore, ^1H NMR data (Table 1), viz. the observed dependencies of chemical shifts of II (R = Me) on the concentration of free $HClO_4$, have revealed that process 1 is followed by another reversible reaction involving protons which is fast on the NMR time scale. This reaction could possibly be protonation of donor atoms of the tridentate ligand or its protolysis. Protonation of the "Schiff" nitrogen can be ruled out since (a) azomethines are much weaker bases than amines or phenolate ions, and (b) it would result in breaking of both stable chelate cycles. To choose among the remaining possibilities, experiments with a mixture of diastereomeric complexes methylated at the amino group of the tridentate ligand, [MeCo(7-Me-salen-*N*-Me)(*c*-NH_3)(*t*-H_2O)]$^+$* [3], were performed using the ^1H NMR technique. It has been shown that one equivalent of $HClO_4$ converts the mixture into a pair of diaqua complexes, [MeCo(7-Me-salen-*N*-Me)$(H_2O)_2$]$^+$ (Table 1).
Upon further addition of acid, the doublet is retained without broadening

TABLE 1

SELECTED ^1H NMR DATA FOR THE METHYLCOBALT COMPLEXES IN D_2O

Complex	δ (ppm)		
	Co—CH_3	Tridentate ligand	
		N—CH_3	C—CH_3
[MeCo(7-Me-salen)$(H_2O)_2$]$^+$	2.99 s	—	2.48 s
[MeCo(7-Me-salen-*N*-Me)$(H_2O)_2$]$^{+\,a}$	3.04 s;	1.89 s ^{b};	2.48 s;
	3.06 s	2.12 s ^{b}	2.50 s
[MeCo(7-Me-salenH)$(H_2O)_2$]$^{2+\,c}$	3.70	—	2.64

^{a} Mixture of diastereomers. ^{b} Doublet in H_2O, with *J* 6.1 Hz. ^{c} Calculated spectrum (extrapolation to $[H^+] = \infty$).

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*Symbols *c* and *t* denote *cis*- and *trans*-position with respect to R groups, respectively.

while the position is shifted similarly to that of related resonances in the case of the non-methylated complex II (R = Me). Thus, despite a fast proton transfer, diastereomeric forms still exist and do not interconvert (on the NMR time scale). Such a pattern is inconsistent with protonation of the amino group which could be either direct or result from protolysis of the tridentate ligand. In either case the "amine' nitrogen would decoordinate and hence lose its chiral character so that rapid interconversion of the diastereomers should occur. Thus, the reaction under consideration evidently is a process involving protonation of the phenolate oxygen. The experimental $\delta = f[H^+]$ relationships obtained for II (R = Me) support 1/1 stoichiometry and allow the constant for this simple acid—base equilibrium (Scheme 1, eq. 2) to be calculated: $K_2 = [II][H^+]/[III] = 0.21 \pm 0.02\ M$ (R = Me, in D_2O, 25°C, ionic strength 0.8 *M*). It is noteworthy that a similar protonation mode was observed [4] for organocobalt chelates with tetradentate Schiff bases in a similar pH range.

Kinetics. Upon acidification of aqueous methanol solutions of I (R = Me, Et and n-Bu) a fast change of their UV-visible spectra (220—450 nm) occurs followed by much slower changes. The final spectra are practically identical with that of o-HOC_6H_4COMe at a given pH. The fast process can be ascribed to the conversion of I into II, while the subsequent slower process should correspond to total degradation of the organocobalt species involving homolysis of Co—C bonds.

The slow reaction was followed by spectrophotometry recording the disappearance of organocobalt species in H_2O/MeOH ((3—7)/1 v/v) solutions under argon at 370 nm. At a given pH the kinetics obeyed a simple first-order rate law at least up to ca. 5 half-lives. From these kinetic curves pseudo-first-order rate constants, k_{obs}, were obtained. In the air kinetic curves remained the same up to one half-life. The interdependent relationship of k_{obs} on pH is shown in Fig. 1. At pH > 6 the reaction rate tends to zero, then it increases

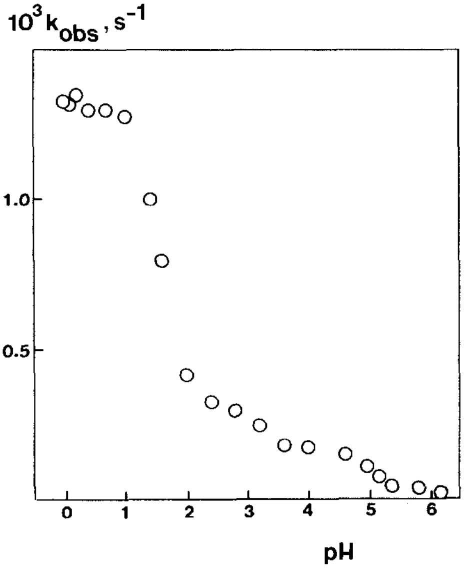
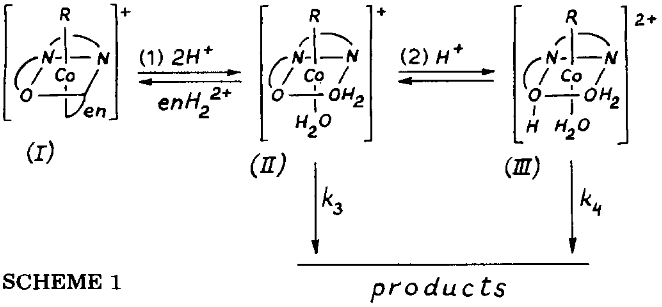


Fig. 1. The k_{obs} vs. pH profile for decomposition of the ethylcobalt complex at 25°C and 1.0 *M* ionic strength.

with lowering of pH, and at pH 4.5—3.5 becomes nearly pH independent. The second and much sharper rise of k_{obs} occurs at far lower pH and apparently is followed by another plateau. Such a profile of the plots obtained for all three complexes suggests the existence of two decomposition routes. Thus, taking into account the results of equilibrium studies, an overall reaction mechanism can be proposed as shown in Scheme 1.



SCHEME 1

Computer fitting of the experimental data in these terms gave numerical values for k_3, k_4 and K_2 while only order-of-magnitude estimates could be obtained for K_1 (Table 2). Considering equilibrium constants first, one can note that the series of K_2 values (R = Me > Et ≈ n-Bu) is in accord with the inductive effect of alkyl ligands. In the case of methylcobalt complex the constants K_1 and K_2 can be compared with more reliable values obtained from the equilibrium study. The agreement seems to be satisfactory if one takes into account (a) the primary deuterium isotopic effect which should increase the "thermodynamic" value of K_2 (0.21 M) by a factor of ca. 3 established for OH acids [5], and (b) low accuracy of "kinetic" estimates of K_1 and probably strong temperature dependence of the latter constant. Thus, the comparison can be considered as conclusive evidence in favour of Scheme 1.

The rate constants in Table 2 are consistent with the assumption that the homolysis of Co—C bonds is a rate-limiting step for the decomposition of II as well as of III. It is established [1] that the dissociation of a Co^{III}—R bond will proceed more readily, if the products of this step are more stable, viz. (a) the Co^{II} complex (with the remaining ligand environment) and (b) the free radical R$^•$. In accord with this, (a) the reactivity series I < II < III, for any given R (Me, Et, n-Bu), corresponds to overall lowering of the donor strength of the ligands which should result in relative destabilization of the

TABLE 2

RATE AND EQUILIBRIUM CONSTANTS OF THE DECOMPOSITION OF THE ALKYLCOBALT COMPLEXES (Scheme 1) AT 25°C AND 1.0 M $NaClO_4$

R	10^7 K_1 [a] (M)	10^2 K_2 (M)	10^5 k_3 (s^{-1})	10^5 k_4 (s^{-1})
Me	~2 [b]	68 [b]	0.17 ± 0.06	64 ± 9
Et	~1	2.9	18 ± 1	140 ± 20
n-Bu	—	2.9	26 ± 1	250 ± 10

[a] Rough estimates. [b] At 50°C.

Co^{III} state*, and (b) the series for various R groups in both II and III Me << Et < n-Bu apparently reflects a growing stability of free alkyl radicals. It should be pointed out that rates of homolytic decomposition of organocobalt chelates with α-dioximes or tetradentate Schiff bases generally depend on processes following the reversible dissociation of a Co^{III}—C bond and therefore increase if an effective acceptor (e.g. O_2) of its paramagnetic products is present [1]. Hence, the essential insensitivity of the decompositions under consideration to the presence of O_2 is probably a further indication for the homolysis being here a rate-determining step. In this case a striking difference in reactivity between the complexes being discussed and those with tetradentate Schiff bases or α-dioximes may be partially due to extreme lability of Co^{II} complexes with a single tridentate Schiff base ligand in protolytic media or to their rapid transition into the high-spin state.

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*The acceleration of homolysis on passing from II to III can be compared with a similar effect observed by Gjerde and Espenson [6] due to protonation of the bis(dimethylglyoximate) ligand in the case of (α-phenylethyl)aquocobaloxime.