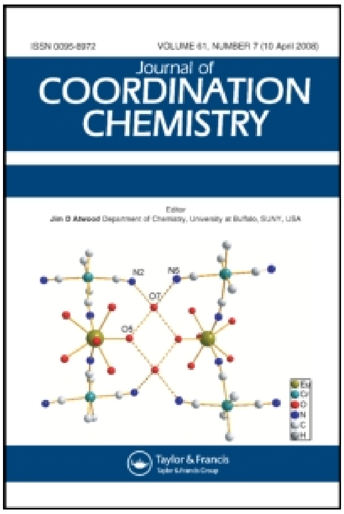

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KINETICS OF ACID DISSOCIATION OF MALONATO-AND SUCCINATOBIS (ETHYLENEDIAMINE)COBALT(III)

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Acid-catalysed dissociation of malonato- and succinatobis(ethylenediamine) cobalt(III) has been studied kinetically in aqueous acidic media (0.05-1.0 mol dm^{-3}) over a temperature range of 40-80°C. The variation of observed pseudo-first-order rate constants on [acid] suggests the operation of two concurrent paths with $k_{obs} = k_0 + k_{H^+}[H^+]$, where k_0 and k_{H^+} are the appropriate rate constants for spontaneous and acid-catalysed pathways respectively. The influence of basicity and chelate ring size of the carboxylato chelate on the rate and activation parameters for the acid-catalysed path has been discussed. Analysis of the rate data corresponding to k_{H^+} suggests a dissociative mechanism involving the protonated complex.

Keywords: cobalt, kinetics, carboxylates, acid-catalysis, dissociation

INTRODUCTION

Kinetic studies on the aquation of a variety of *cis*- and *trans*-$[Co^{III}(en)_2XY]^{n+}$ complexes have been the subject of several investigations,[1-3] where electronic and steric effects of the non-leaving group, X, on the release of Y (usually a halogen) have been examined. In contrast to the extensive studies on the aquation of unidentate ligands, the dissociation of a bidentate carboxylato chelate, L-L, from the $[Co^{III}(en)_2L\text{-}L]^{n+}$ species has been sparingly studied.[4,5] This is mainly because bidentate chelates derived from dicarboxylic acids like oxalic is bound very strongly to the metal ion. Preliminary investigations of $[Co(en)_2ox]^+$ ion showed that acid hydrolysis even in 10 mol dm^{-3} perchloric acid at 90°C is very slow. Basolo[4] reported on approximate value of $k_d \sim 10^{-10}$ sec^{-1}. Since aquation of octahedral cobalt(III) complexes is believed to proceed by a dissociative (D or Id) mechanism, the variation of factors influencing metal-ligand strength would be likely to alter reaction rates appreciably. With this in mind, the acid-catalysed dissociations of $[Co(en)_2mal]^+$ and $[Co(en)_2suc]^+$ ions have been studied kinetically. The effects of basicity and ring size of the carboxylate chelate on the dissocation rate have been examined and a plausible mechanism consistent with the experimental results is discussed.

EXPERIMENTAL

Materials and reagents

$[Co(en)_2CO_3]Cl$ and $[Co(en)_2mal]ClO_4$ were prepared according to standard procedures[6,7] and purified by recrystallisation. Chemical analysis confirmed purify, as did a comparison with the published visible[5,8] and ^{1}H nmr[7] spectra. Succinatobis(ethylenediamine)cobalt(III) perchlorate, $[Co(en)_2suc]ClO_4$, was prepared by a modified method to that described by Duff.[9] 1.6 gm of succinic anhydride was added in small batches to a boiling solution of 5 gm of $[Co(en)_2CO_3]Cl$ in 100 cm^3

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of water. After complete addition of the succinic anhydride the solution was boiled for 20 minutes followed by evaporation of the reaction mixture over a steam bath to one fourth of its original volume. The solution was cooled in ice and solid $NaClO_4$ was added to obtain a red precipitate of the succinato complex as the perchlorate salt. This was washed thoroughly with warm water and then with absolute ethanol, and finally dried *in vacuo*. The purity of the complex was checked by elemental analysis. Anal; Found: C, 24.54, H, 4.85, N, 14.30%. Calculated for $[Co(en)_2suc]ClO_4$; C, 24.33, H, 5.07, N, 14.20%. The positions and intensities of the ligand field bands of the complex in KNO_3 (2 mol dm^{-3}) solution (λ_{max}: 530, 363 nm, ε: (M^{-1} cm^{-1}), 82.0 and 83.5 respectively) agreed well with reported values.[8] All other chemicals used for the study were of reagent grade purity.

Measurements

A Varian Superscan-3 spectrophotometer with quartz cell of suitable pathlength was employed for the absorbance measurements. The extent of aquation was monitored by following the change in absorbance at 500 nm for the malonato complex and at 492 nm for the succinato complex. The reaction of the malonato complex has been studied in aqueous perchloric acid media (0.2-1.0 mol dm^{-3}) at an ionic strength of 2.2 mol dm^{-3} adjusted with sodium perchlorate. The corresponding reaction of the succinato complex however, has been investigated in nitrate (HNO_3-KNO_3) medium as the $[Co(en)_2suc]^+$ ion was found to be sparingly soluble in $HClO_4$-$NaClO_4$ solution. The rate studies were carried out using a batch sampling technique[10] with the temperature controlled to ±0.1°C. All experiments were carried out in excess acid so that the pseudo-first-order rate law was applicable and the pseudo-first-order rate constants, k_{obs}, were computed from the gradients of the linear plots of $\ln(A_t-A_\infty)$ *versus* time by means of a least-squares analysis. The spectram of experimental solutions of both complexes after digesting for several half lives (six and higher) agreed well with that of the *cis*-$[Co(en)_2(OH_2)_2]^{3+}$ ion, indicating the absence of any complication due to reverse anation. The k_{obs} value for the aquation of the malonato complex at 60°C in HNO_3-KNO_3 solution agreed within 5% of that in perchlorate ($HClO_4$-$NaClO_4$) medium, thus confirming the absence of any catalytic effect due to the nitrate ion.

RESULTS AND DISCUSSION

The spectrophotometrically determined pseudo-first-order rate constants, k_{obs}, for the dissociation of the title complexes have been evaluated under different sets of experimental conditions, *viz* acid concentration, temperature and ionic strength of the medium. The variations of k_{obs} with acid concentration at different temperatures are illustrated in Figures 1 and 2. The value of k_{obs} increases linearly with $[H^+]$ and fits the relationship (*1*)

$$k_{obs} = k_o + k_{H^+}[H^+] \qquad (1)$$

Apparently the dissociations of both complexes proceed *via* two pathways, a spontaneous (k_o) and an acid-catalysed (k_{H^+}) one. Their values at different temperatures, as obtained from the intercepts and slopes of the plots as shown in Figures 1 and 2, using a linear regression analysis, are listed in Table I. Activation

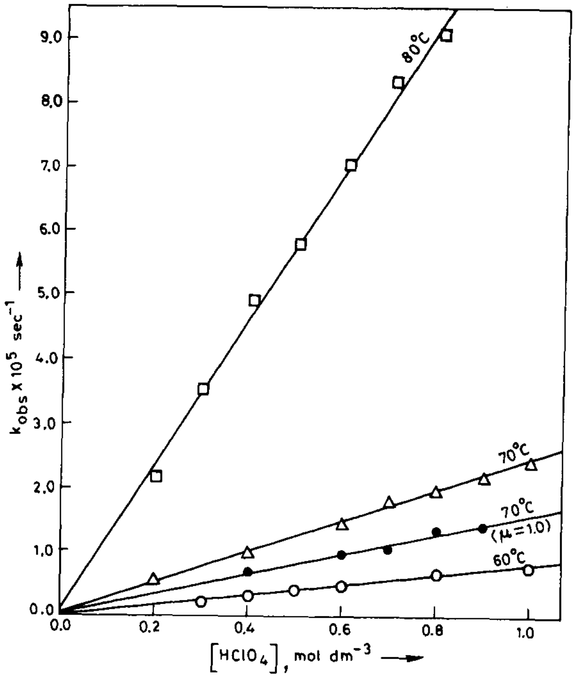


FIGURE 1 Effect of acid concentration on k_{obs} at different temperatures. $[Co(en)_2mal]^+ = 0.004$ mol dm^{-3}, $\mu = 2.2$ mol dm^{-3}.

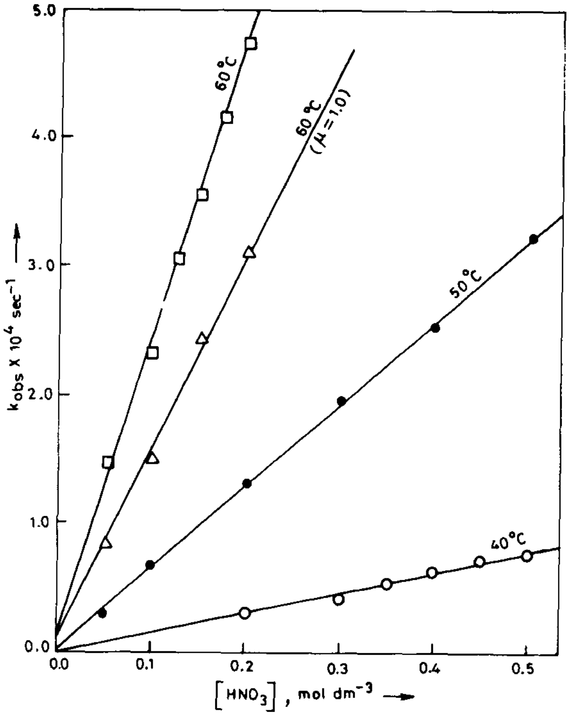


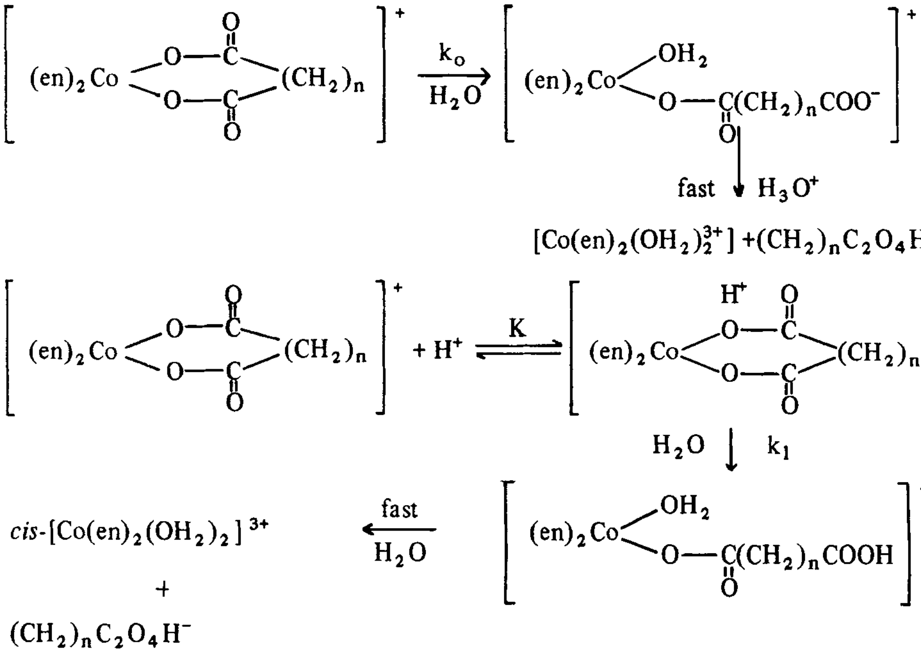
FIGURE 2 Effect of acid concentration on k_{obs} at different temperatures. $[Co(en)_2suc]^+ = 0.004$ mol dm^{-3}, $\mu = 2.2$ mol dm^{-3}.

TABLE I

Rates and activation parameters for the dissociation of malonato- and succinatobis(ethylenediamine) cobalt(III) ion.

		$[Co(en)_2mal]^+ = 0.004$ mol dm^{-3}	
Temp. (°C)	μ (mol dm^{-3})	10^6k_o (sec^{-1})	$10^5k_{H^+}$ (mol^{-1} dm^3 sec^{-1})
60.0 ± 0.1	2.2	~0	0.73 ± 0.05
70.0 ± 0.1	2.2	0.3 ± 0.1	2.45 ± 0.1
70.0 ± 0.1	1.0	0.2 ± 0.1	1.55 ± 0.15
80.0 ± 0.1	2.2	1.0 ± 0.2	11.5 ± 0.15
$\Delta H^\ddagger$ (kJ mol^{-1})			137.5 ± 5.0
$\Delta S^\ddagger$ (J K^{-1} mol^{-1})			76.0 ± 9.2
		$[Co(en)_2suc]^+ = 0.004$ mol dm^{-3}	
Temp. (°C)	μ (mol dm^{-3})	10^5k_o (sec^{-1})	$10^4k_{H^+}$ (mol^{-1} dm^3 sec^{-1})
40.0 ± 0.05	2.2	~0	1.2 ± 0.05
50.0 ± 0.1	2.2	0.4 ± 0.1	6.33 ± 0.1
60.0 ± 0.1	1.0	1.3 ± 0.3	14.9 ± 0.3
60.0 ± 0.1	2.0	1.5 ± 0.2	21.6 ± 0.3
$\Delta H^\ddagger$ (kJ mol^{-1})			126.2 ± 4.2
$\Delta S^\ddagger$ (J K^{-1} mol^{-1})			81.5 ± 8.5

parameters for the acid-catalysed path computed from the usual transition state equation, are included in Table I. A sequence of changes consistent with the kinetic results are depicted below.



Here n = 1 for the malonato- and n = 2 for the succinato-complex respectively. The first step refers to the uncatalysed path and the acid catalysed path involves the dissociation of the conjugate acid formed by the protonation of the substrate complex in a rapid preequilibrium step. Both rate-determining dissociations for spontaneous and acid catalysed path are thus believed to involve a one ended dissociation of the carboxylato chelate ring with the simultaneous entry of a molecule of water into the coordination sphere of Co(III), followed by the rupture of second Co-O bond of the unidentate. This is a much faster process with a simultaneous insertion of a molecule of water leading to the *cis*-$[Co(en)_2(OH_2)_2]^{3+}$ product. The catalytic rate constant k_{H^+} is related to K and k_1 by the relation (*2*).

$$k_{H^+} = Kk_1/1 + K[H^+] \qquad (2)$$

Under the present experimental conditions $K[H^+] \ll 1$ as is evident from the linearity of the plots of k_{obs} *versus* $[H^+]$ even at the highest acid concentration. Hence (*2*) reduces to $k_{H^+} = Kk_1$. The activation parameters thus involve both rate and equilibrium constants. Comparison of k_0 and k_{H^+} values indicates that the protonated species is much more labile than the unprotonated one. This can be ascribed to the fact that acid catalysis is suggested to involve the protonation of the carboxylato chelate leading to a formal positive charge on the carbonyl oxygen atom of the ligand. Strong bonding between oxygen atom of the ligand and H^+ in the protonated form of the complex leads to electron withdrawal from one of the Co-O bonds and thus facilitates its fission thus providing easy entry for a water molecule from the solvation sheath to form the aquohydrogen carboxylate complex ion. Experimental evidence for the protonation of a carbonyl oxygen in metal carboxylato chelates has been reported in the literature.[11]

The influence of ionic strength on the aquation rate has been examined. The k_{H^+} values are found to increase with increase in ionic strength and are listed in Table I. The equilibrium constant, K, between cations such as that shown in the scheme above generally increases with an increase in ionic strength. Hence, the increase in k_{H^+} can be explained as being due to an increase in the value of the equilibrium constant K. The second order H^+ ion-dependent rate constant, k_{H^+}, for the dissociation of the malonate complex at 60°C is observed to be 7.3×10^{-6} mol^{-1} dm^3 sec^{-1} whereas that of the succinato-complex is to 21.6×10^{-4} mol^{-1} dm^3 sec^{-1}, a rate increase by some 295 times which is accompanied by a lowering of the $\Delta H^{\ddagger}$ value. The rate of dissociation of the oxalato-complex is much slower than that of the malonato-complex. There are two effects to be considered in explaining the observed reactivity sequence. In the absence of resonance stabilisation, both from steric and entropy considerations,[12] the five-membered ring is expected to form the most stable chelate followed by six- and seven-membered ring structures. Malonate and succinate form six- and seven-membered rings; oxalate dianion gives rise to a five-membered chelate ring. Since the dissociation of carboxylato chelates of Co(III) is proposed to proceed by the rate determining rupture of a Co-O bond, the stability of the chelate would influence its rate in a major way. Crawford,[8] from an examination of the width of visible and ultra-violet bands, predicted an increase in strain and distortion with increase in chelate ring size of the carboxylato chelate. The sequence parallels the observed reactivity order. The other important effect seem to arise from the basicity of the carboxylic acid. Acid-catalysed aquation rate constants of carboxylatopentamminecobalt(III) were found to increase with an increase in pK of the carboxylic acid and are almost independent of steric effects.[13] For instance, a thirty fold increase in rate was reported for a change in pK by 4 units (at 70°C, k_{H^+} for $[Co(NH_3)_5CH_3COO]^{2+} = 9.3 \times 10^{-4}$ mol^{-1} dm^3 sec^{-1}; k_{H^+} for $[Co(NH_3)_5CF_3COO]^{2+} = 3 \times 10^{-5}$ mol^{-1} dm^3 sec^{-1}). In comparison, *ca* a three hundred-fold rate enhancement is observed from $[Co(en)_2mal]^+$ to $[Co(en)_2suc]^+$ for a difference in pK of only 1.5 units (pK_1, succinic acid = 4.21, malonic acid = 2.7). It is thus evident that effects of both chelate ring size and basicity of the leaving group play a significant role with respect to the reactivity sequence. Hence, it can be concluded that the greater lability of the succinato- compared with the malonato-complex may possibly be due to the higher basicity of the succinate ion, which increasingly favours the formation of its conjugate acid with the simultaneous dissociation of one of the chelate rings. This too is favoured by the lower thermodynamic stability of the succinato-complex.

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