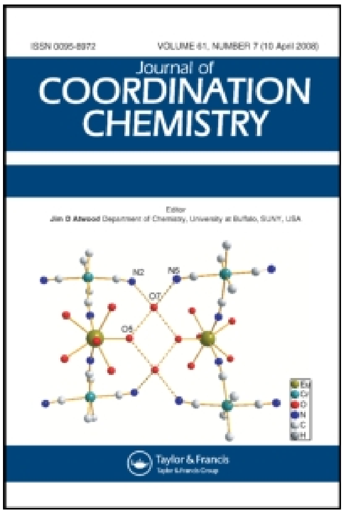

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Chatterjee, C. and Das, S.(1986) 'KINETICS OF DISSOCIATION OF THE MALONATOBISTRIMETHYLENEDIAMINE COBALT(III) COMPLEX IN ACIDIC MEDIA', Journal of Coordination Chemistry, 15: 2, 147 — 152

To link to this Article: DOI: 10.1080/00958978608079779

URL: http://dx.doi.org/10.1080/00958978608079779

J. Coord. Chem. 1986, Vol. 15, p. 147–152
0095-8972/86/1502-0147 $18.50/0

KINETICS OF DISSOCIATION OF THE MALONATOBISTRIMETHYLENEDIAMINE COBALT(III) COMPLEX IN ACIDIC MEDIA

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(Received January 20, 1986)

The kinetics of dissociation of malonate from the malonatobistrimethylenediaminecobalt(III) complex have been investigated in aqueous perchloric acid media (0.1–1.0 mol dm^{-3}) over a temperature range of 50–70°C at an ionic strength of 2.2 mol dm^{-3} adjusted with sodium perchlorate. The variation of observed pseudo-first-order rates on [acid] suggests the operation of two concurrent paths with $k_{obs} = k_o + k_{H^+}[H^+]$, where k_0 and k_{H^+} are the rate constants for uncatalysed and acid-catalysed pathways respectively. Under identical conditions the malonato complex was found to dissociate 10^3 times faster rate than that of corresponding oxalato complex. The influence of basicity and chelate ring size of the carboxylate and diamine groups on the aquation rate has been discussed. Analysis of rate data corresponding to k_{H^+} suggests a dissociative mechanism involving the protonated complex.

Key words: Cobalt' aquation; kinetics; 1,3-diaminopropane; carboxylates

INTRODUCTION

Aquation of bistrimethylenediaminecobalt(III) octahedral complexes are intriguing. It has been noted that there is a rate enhancement of acid hydrolysis by 1500 times in going from ethylenediamine to trimethylenediamine complexes in the case of *trans*-$[Co(en)_2X_2]^+$ and *trans*-$[Co(tmd)_2X_2]^+$, where X stands for halide ion.[1] For the corresponding "en" and "tmd" complexes of Cr(III) on the other hand, the rates of acid hydrolysis are comparable and are therefore not very dependent on the ring size. The greater relative reactivity between "tmd" and "en" in case of cobalt(III) is due to greater conformation flexibility of the chelate rings and enhanced stability of the twist mode conformer in which there is severe steric interaction with the leaving group. The lack of strong dependence of hydrolysis rate on ring size for chromium(III) has been suggested to be due to the greater stability of the chair conformer for both "tmd" and "en" ligands. Similar but somewhat smaller rate enhancement has been observed in case of the carbonatobistrimethylenediaminecobalt(III) ion compared to the carbonatobis-ethylenediaminecobalt(III) ion. Barraclough and Murray[2] suggested from observation of molecular models that amine protons are appreciably closer to the carbonate ion. In order to gain further insight into the mechanism of dissociation of cobalt(III) chelates, the kinetics of the acid catalysed aquation of $[Co(tmd)_2ox]^+$ and $[Co(tmd)_2mal]^+$ ions have been studied and the results compared with analogous ethylenediamine complexes.

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EXPERIMENTAL

Materials and reagents

Trans-$[Co(tmd)_2Cl_2]Cl \cdot 3.5H_2O$ and $[Co(tmd)_2ox]ClO_4$ were prepared by following methods described in the literature.[3] The purity of the samples were checked by elemental and spectral analysis.[4]

$[Co(tmd)_2mal]ClO_4 \cdot 2H_2O$

6.3 g of *trans*-$[Co(tmd)_2Cl_2]Cl \cdot 3.5H_2O$ (0.017 mol) and 2.52 g of sodium hydrogen malonate (0.02 mol) were dissolved in 50 cm^3 of hot water. The reaction mixture was digested on a steam bath for one hour, whereupon the green solution changed to a purple colour, and then this solution was cooled in ice. To this, 3 cm^3 of 60% perchloric acid was added and the whole was kept overnight at 5°C for crystallization. The crimson-red crystals of the malonato complex which separated were filtered off and washed successively with cold water and ethanol and dried *in vacuo.* The purity of the complex was ascertained by elemental analysis. [Anal.: Found : C, 24.6; H, 5.5; N, 12.45%. Calculated for $[Co(tmd)_2mal]ClO_4 \cdot 2H_2O$: C, 24.3; H, 5.85; N, 12.6%].

The positions and intensities of the d-d bands of the complex (λ_{max}, 510, 360 nm; ε, 89.5, 107.5 M^{-1} cm^{-1}) correspond to ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$ transitions respectively. Proton magnetic resonance spectra revealed broad bands due to amine hydrogens at $\delta = 4.68, 4.54$ and 4.02 ppm with intensity ratio of 1:1:2, respectively. Two downfield signals intensity four are ascribed to amine hydrogens *cis* to the carboxylate oxygen whereas the upfield band is identified as due to hydrogens *trans* to the carboxylate oxygen. The methylene hydrogens of the malonate appeared as a sharp singlet at $\delta = 3.1$ ppm. The signals at δ 2.35 and 1.64 ppm are assigned to hydrogens on the C_1, C_3 and C_2 carbons of 1,3-propanediamine, respectively. All other chemicals used were of reagent grade purity.

Measurements

Pmr spectra were recorded on a Varian-XL 100 spectrometer operating at 100 MHz. The spectra were run in perdeuteriodimethylsulphoxide (Me_2SO-d_6, Aldrich, 99.9 atom % D minimum) with TMS as an internal reference. A Varian Superscan-3 spectrophotometer was employed for absorbance measurements. The extent of the aquation was monitored by following the change in absorbance at 505 nm for both malonato and oxalato complexes. The reaction has been studied in aqueous perchloric acid media (0.1-1.0 mol dm^{-3}) at an ionic strength of 2.2 mol dm^{-3} adjusted with sodium perchlorate in the temperature range 50–70°C. The rate studies were made by a batch sampling technique[5] with the temperature controlled to ±0.1°C. All experiments were carried out in the presence of perchloric acid 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 (t) by means of a least-squares program. The absorbance of the experimental solution after digesting for several half-lives (six and higher) agreed well with that of the *cis*-$[Co(tmd)_2(OH_2)_2]^{3+}$ ion, indicating the absence of any complication due to reverse anation.

Results and Discussion

The pseudo-first-order rate constants, k_{obs}, for the dissociation of malonato complex have been evaluated at different acid concentrations, temperatures and ionic strengths. The

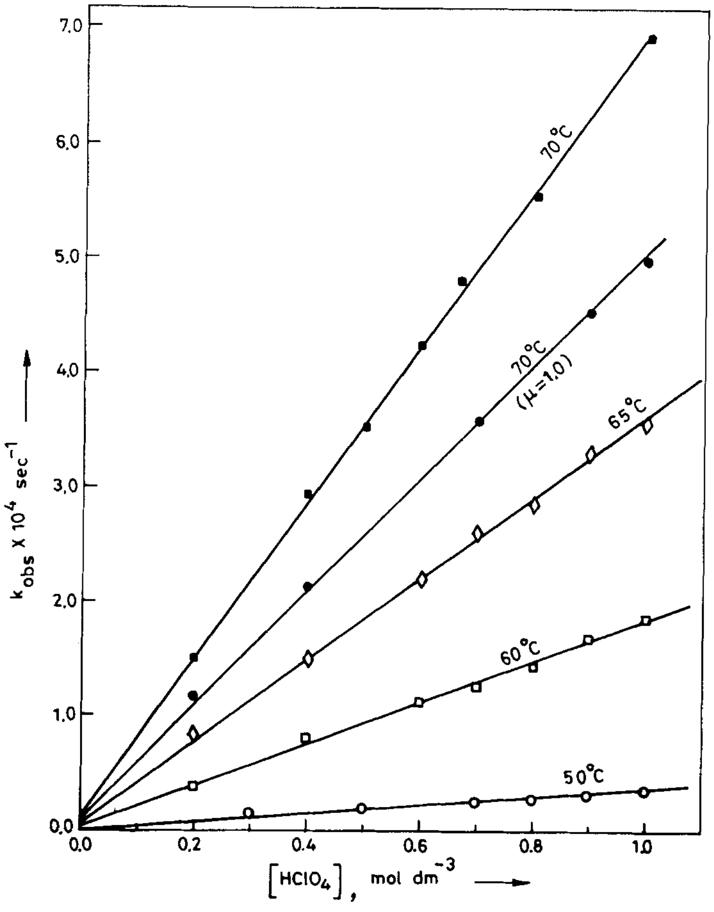


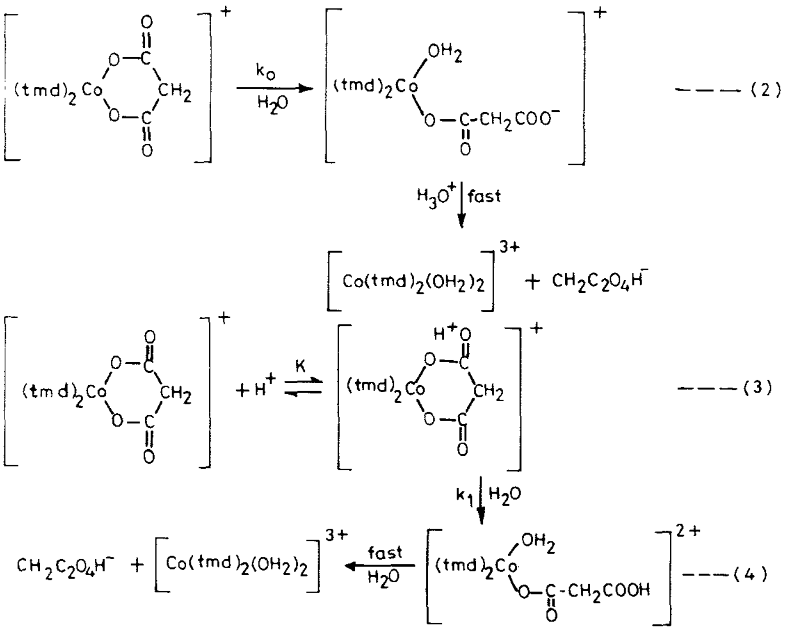
FIGURE 1 Effect of acid concentration on k_{obs} at different temperatures. [Co(tmd)$_2$mal]$^+$ = 0.004 mol·dm^{-3}, μ = 2.2 mol·dm^{-3}.

variation of k_{obs} on acid concentration at different temperatures is illustrated in Figure 1 and the results suggest the operation of two concurrent paths as shown in (*1*)

$$k_{obs} = k_o + k_{H^+}[H^+] \tag{1}$$

where k_o is the first-order rate constant for spontaneous aquation and k_{H^+} is the second-order rate constant describing the acid catalysed pathway, respectively. Their values at different temperatures, as obtained from the intercepts and slopes of the plots of Figure 1, using a linear regression analysis, are summarised in Table I along with the activation parameters, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values corresponding to the acid-catalysed path were computed using the transition state equation, $k = (RT/Nh)\exp(-\Delta H^{\ddagger}/RT + \Delta S^{\ddagger}/R)$. Reactions consistent with the kinetic results are shown in the scheme.

The reaction (*2*) corresponds to the uncatalysed path involving attack of a solvent molecule in the rate-determining step, while acid catalysis (*4*) involves dissociation of the conjugate acid formed by the protonation of the substrate complex in a rapid



Scheme . 1

preequilibrium step (*3*). Both rate-determining dissociations for spontaneous and acid-catalysed paths are thus believed to involve a one-ended dissociation of the carboxylate 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 ligand. A much faster process involving the entry of a molecule of water leads to *cis*-$[Co(tmd)_2(OH_2)_2]^{3+}$ as the final product. The catalytic rate constant, k_{H^+}, is related to K and k_1 by the relation (*5*)

$$k_{H^+} = Kk_1/1 + K[H^+] \qquad (5)$$

The absence of any deviation from linearity for the k_{obs} *vs* $[H^+]$ plot even at the highest acid concentration indicates that $K[H^+] < 1$, and hence (*5*) reduces to $k_{H^+} = Kk_1$. The activation parameters thus involve both rate and equilibrium constants. In conformity with the proposed scheme, the protonated species is found to be much more labile than the unprotonated one (Table I). This can be rationalised by considering that acid catalysis involves protonation of the carboxylato chelate. Strong bonding between oxygen atom of the ligand and H^+ leads to electron withdrawal from one of the Co–O bonds, thereby facilitating its cleavage and providing a means for the facile entry of a water molecule from the solvation sheath to form the aquo hydrogen carboxylate complex ion. Protonation of a carbonyl oxygen in octahedral cobalt(III) carboxylates has been reported by several workers.[6,7]

The effect of ionic strength on the aquation rate has been studied at 70°C. The acid dependent rate constant, k_{H^+}, is observed to increase with an increase in ionic strength (see Table I). The equilibrium constant, K, generally increases with increasing ionic strength and hence the observed increase in k_{H^+} can thus be attributed to the increase in this parameter.

TABLE I
Rates and activation parameters for the dissociation of the malonatobistrimethylenediamine cobalt(III) ion.

	$[Co(tmd)_2mal]^+ = 0.04$ mol dm^{-3}		
T (°C)	μ(mol dm^{-3})	10^5k_0 sec^{-1}	$10^5k_{H^+}$ mol^{-1} dm^3 sec^{-1}
50.0 ± 0.1	2.2	0	3.5 ± 0.05
60.0 ± 0.1	2.2	0.25 ± 0.1	18.0 ± 0.2
65.0 ± 0.1	2.2	0.60 ± 0.2	35.5 ± 0.4
70.0 ± 0.1	1.0	0.90 ± 0.3	49.7 ± 0.4
70.0 ± 0.1	2.2	1.1 ± 0.2	68.7 ± 0.3
$\Delta H^\ddagger$ (kJ mol^{-1})			131.7 ± 5.0
$\Delta S^\dagger$ (J K^{-1} mol^{-1})			75.8 ± 8.5

In order to examine the influence of electronic and structural variations of the carboxylato chelate on the aquation rate, the kinetics of dissociation of oxalate from $[Co(tmd)_2ox]^+$ ion in acidic media has also been investigated. Unlike the malonato complex, $[Co(tmd)_2ox]^+$ underwent dissociation at an extremely slow rate. The second order rate constant, k_{H^+}, at 70°C is 2.8×10^{-7} mol^{-1} dm^3 sec^{-1} whereas that of the malonato complex is 6.9×10^{-4} mol^{-1} dm^3 sec^{-1}, a rate increase by more than three orders of magnitude. There are two effects which need to be considered in explaining the difference in reactivity. In the absence of aromaticity, both from entropy and steric considerations,[8] the five membered ring is expected to form the most stable chelate. Malonate forms a six-membered ring, and oxalate ion gives rise to a five-membered chelate ring. Since the dissociation of the carboxylato chelate is proposed to involve the rate-determining rupture of a Co–O bond, the stability of the chelate would influence its reactivity in a major way. Crawford,[9] from an examination of the width of ultraviolet and visible bands, predicted an increase in strain and distortion with increase in the chelate ring size of the carboxylato chelate. The sequence parallels the observed reactivity order. The other important effect contributing to the reactivity sequence seem to arise from the basicity of the carboxylic acid. Hence, the greater lability of the malonato complex compared with the oxalato system may possibly be due to the higher basicity of the malonate ion. This favours the formation of its conjugate acid with the simultaneous dissociation of one of the chelate rings, this again being favoured by the lower thermodynamic stability of the malonato complex.

In order to examine the influence of chelate ring size of the diamine on the ease of dissociation of the carboxylato chelate, the results of the present investigation have been compared with those of the ethylenediamine analogue. Comparison of k_{H^+} indicates that trimethylenediamine complex reacts nearly thirty times faster than the corresponding ethylenediamine analogue[10] (k_{H^+} at 70°C: $(Co(en)_2mal^+)$, 2.45×10^{-5} mol^{-1} dm^3 sec^{-1}; $(Co(tmd)_2mal^+)$, 6.9×10^{-4} mol^{-1} dm^3 sec^{-1}, respectively). This is accompanied by a lower $\Delta H^\ddagger$ value for the former. The results could possibly be explained by the fact that the formation of the five-coordinate intermediate in the transition state is more favourable in the case of the 1,3-diaminopropane complex compared to its 1,2-diaminoethane counterpart. Six-membered ring formation with a cobalt(III) centre by trimethylenediamine in its twist-boat conformation is known[11,12] to result in considerable steric interaction with the leaving carboxylate, which is relieved by expansion of the bite angle at the metal centre on formation of a five-coordinate intermediate, thus accounting for its higher reactivity.

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