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THE HYDROLYSIS OF SOME CARBOXYLATO-BIS(ETHYLENEDIAMINE)-COBALT(III) COMPLEXES

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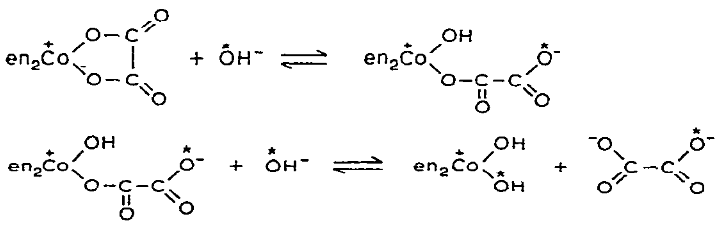
When a cobalt(III) complex contains a ligand linked by a carboxylato group, the possibility exists that hydrolysis can take place without rupture of the metal–ligand bond It is possible for either the cobalt–oxygen or the carbon–oxygen bond to be cleaved. The position of cleavage can be determined by the use of ^{18}O-labelled water. Using this technique, Caglioti and Illuminati[1] have shown that in the series *cis*- and *trans*-$[Co(en)_2(OCOC_6H_4R)_2]^+$ cobalt–oxygen fission is involved in base hydrolysis.

Taube[2] has further found that for unidentate carboxylate ligands, a two-term rate law operates, viz.

$$\text{Rate} = \{k_1[OH^-] + k_2[OH^-]^2\}\,[\text{complex}] \qquad (1)$$

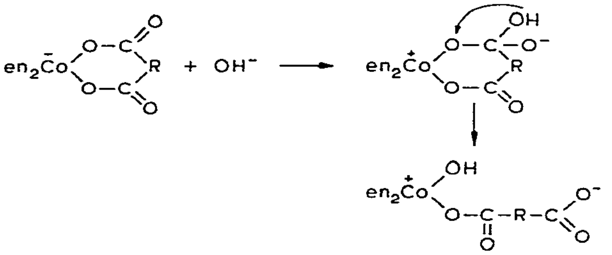
The k_1 pathway involves cobalt–oxygen fission, and the possibility of steric change, whereas the path second-order in hydroxide proceeds via carbon–oxygen fission. This latter reaction takes place with complete retention of configuration about the cobalt atom. When the concentration of base is high, therefore, the kinetics may be complicated by this reaction.

If the ligand is a chelate, and contains two carboxylate donors, the mechanism is yet further complicated. The reaction may take place in two stages dechelation, followed by complete loss of ligand. The question of the position of bond rupture applies to each step in the reaction This two-stage mechanism has already been demonstrated for the base hydrolyses of the $[Co(NH_3)_4CO_3]^+$ ion[3], and the $[Co(en)_2CO_3]^+$ ion[4]. It was postulated in the base hydrolysis of the oxalato ion[5], $[Co(en)_2C_2O_4]^+$, and subsequently confirmed in this system[6]. ^{18}O-exchange studies on this last ion suggest that the oxalato–chelate ring is ruptured by OH^- attack on the carbon, i e with carbon–oxygen fission[7].



(2)

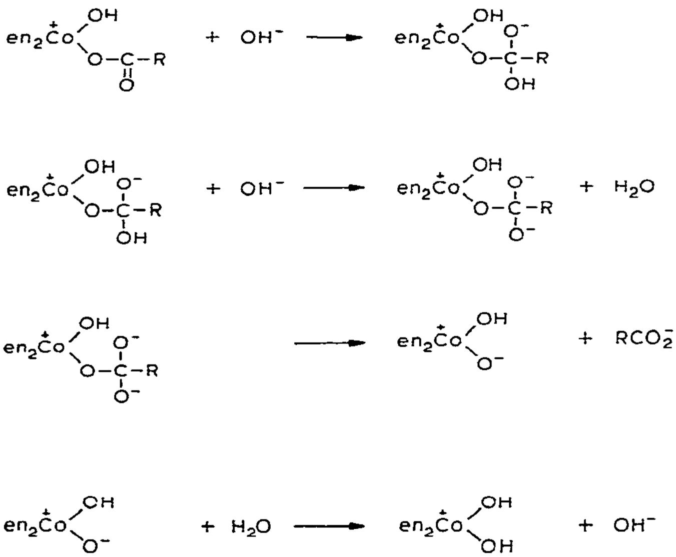
We can now consider, in general terms, the mechanisms by which base hydrolysis of such a chelate complex takes place. Let $[Co(en)_2chel]^+$ be a complex where "chel" represents a chelate with two carboxylate donors. The mechanism of ring opening will probably be similar to that of the oxalato complex



(3)

The second stage, complete loss of the carboxylato ligand, can take place in a similar way, i e with carbon–oxygen fission, or can proceed by cobalt–oxygen fission The latter reaction could be dissociative and independent of base concentration, or it could involve the hydroxide ion either in an attack on cobalt or in the S_N1CB mechanism[8].

It seems possible that either step, ring opening or ligand loss, could take place by the path second-order in hydroxide, suggested by Taube[2] for highly basic media, viz.



(4)

The overall reaction can now be considered.

(1) Ring opening is a fast pre-equilibrium

$$[Co(en)_2chel]^+ + OH^- \overset{K_{eq}}{\rightleftharpoons} [Co(en)_2chel(OH)]^0 \qquad (5)$$

(a) The second step is slow and dissociative

$$[Co(en)_2chel(OH)]^0 \xrightarrow[k]{slow} \{[Co(en)_2OH]\}^{2+} + chel^{2-} \qquad (6)$$

$$[Co(en)_2(OH)]^{2+} + OH^- \xrightarrow{fast} [Co(en)_2(OH)_2]^+ \qquad (7)$$

The reaction will appear to be one stage, since this is an example of an S_N1CB mechanism, the reaction will be either second-order (first in complex, first in hydroxide concentration), or will be first-order (zero in hydroxide), depending on the equilibrium constant and on the conditions.

(b) The loss-of-ligand step follows at a rate which is dependent on the hydroxide concentration, viz.

$$[Co(en)_2chel(OH)]^0 + OH^- \xrightarrow[k]{slow} [Co(en)_2(OH)_2]^+ + chel^{2-} \qquad (8)$$

The limiting cases are, depending on K_{eq}, either

$$\left.\begin{aligned} &\text{Rate} = k_{obs}\,[\text{complex}]\,[OH^-]^2 \\ &\text{or} \\ &\text{Rate} = k_{obs}\,[\text{complex}]\,[OH^-] \end{aligned}\right\} \qquad (9)$$

(2) Ring opening is slow

$$[Co(en)_2chel]^+ + OH^- \xrightarrow{slow\ k} [Co(en)_2chel(OH)]^0 \qquad (10)$$

(a) The second step is fast and dissociative, viz

$$[Co(en)_2chel(OH)]^0 \xrightarrow{fast} [Co(en)_2(OH)]^{2+} + chel^{2-} \qquad (11)$$

$$[Co(en)_2(OH)]^{2+} + OH^- \xrightarrow{fast} [Co(en)_2(OH)_2]^+ \qquad (12)$$

The reaction is again single step, second-order (rate = k_{obs} [complex] [OH^-]), but no limiting rate is expected.

(b) The rate of loss of ligand is dependent on hydroxide concentration but is fast compared with reaction (10). the kinetics would be as in mechanism *2*(a).

(c) The rate of loss of the ligand is dependent on hydroxide concentration, but is slower than, or comparable with, the rate of reaction (10) In these circumstances, a two-stage mechanism could be observed, each stage first-order in complex and first-order in hydroxide concentration.

Either stage could be susceptible to the path shown in eqn. (4), which is second-order in hydroxide concentration.

Thus the assignment of mechanism from the observed kinetics appears to be difficult.

The steric course of the reaction can also provide information about the mechanism. In this case, the criterion we have is that carbon–oxygen fission produces *no* steric change but a reaction via cobalt–oxygen fission *can* produce steric change, i e if steric change is observed in the reaction, C–O fission is ruled out.

A further complicating factor in considering the steric change is the stereochemistry of the products, the $[Co(en)_2(OH)_2]^+$ ions These ions can exist in either *cis* or *trans* forms and undergo isomerisation in basic media to an equilibrium mixture which contains approximately 50% of each isomer[9,10] The rate of isomerisation is independent of the base concentration[10]. When, therefore, the rate of hydrolysis is less than that of equilibration, the $[Co(en)_2(OH)_2]^+$ ions in the product will be in their equilibrium proportions and no information about the steric course is gained.

A study of the base hydrolysis of the $[Co(en)_2C_2O_4]^+$ ion in basic media[6] shows that the hydrolysis reaction takes place in two stages under certain conditions. At low temperatures and in concentrated base, the loss of oxalate becomes greater than first-order in hydroxide, and under these conditions a 1 1 mixture of the *cis*- and *trans*-$[Co(en)_2(OH)_2]^+$ ions is obtained even when the rate of hydrolysis is faster than the equilibration The steric course in concentrated base contrasts with that in more dilute base where the initial product is only *cis*-$[Co(en)_2(OH)_2]^+$.

The mechanism put forward for this reaction[6] was that under conditions of low base concentrations and high temperatures, ring opening is a fast pre-equilibrium However, as the temperature is lowered the relative activation energies are such that the ring opening can be observed and the reaction becomes two-stage (mechanism *2*(c))

At high temperatures, the loss of ligand was postulated to go via mechanism *1*(b), above. At high base concentrations and low temperatures, a path was postulated, second-order in hydroxide but with Co–O fission, to account for steric change

As a continuation of the study of such reactions of bis(ethylenediamine)cobalt(III) cations in highly basic media, the work has been extended to ions containing malonato and substituted malonato ligands

The malonato ligand is interesting because it contains a potentially active methylene group.

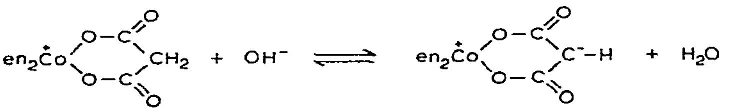
(13)

The base hydrolysis of the bis(ethylenediamine)cobalt(III) complex containing this simple malonate group has been studied[4]. In dilute base, $[OH^-] < 1\ M$ and $\mu = 1\ M$ (perchlorate media), the hydrolysis is single stage.

Because the hydrolysis is slower than the equilibration of the dihydroxo ions, the product is a *cis/trans* equilibrium mixture[9,10] of the $[Co(en)_2(OH)_2]^+$ ions. The reaction is second-order and the activation parameters are $\Delta H^\ddagger = 28.7$ kcal.mole^{-1} and $\Delta S^\ddagger = +20$ e.u.

In concentrated base, $[OH^-]$ up to 3.7 *M* (perchlorate media), the *cis*-$[Co(en)_2(OH)_2]^+$ is the usual product and a limiting rate, zero-order in hydroxide, is reached at about 2 *M* NaOH at 37 5°.

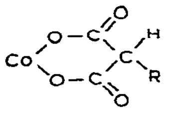
Two stages have not been observed in the hydrolysis of the malonate complex, although the initial spectrum changes with the hydroxide concentration, consistent with an initial fast equilibrium. Mechanism *1*(a) would be consistent with these observations. However, malonate may be a special case and a second mechanism which takes this into account is also feasible. Such a mechanism is *2*(a) or *2*(b) and an additional fast pre-equilibrium in which a proton is removed from the malonate ring This produces a non-reactive resonance-stabilised ring, which effectively removes the complex from participation in the second step, viz.



(14)

Consistent with reaction (14), the protons from the methylene group have been found by PMR studies to exchange with deuterium from the solvent in both acidic and basic media. In acid the reaction is first-order in D_3O^+ and first-order in complex For $[Co(en)_2mal]^+$ the activation parameters are $\Delta H^\ddagger = 27.5 \pm 3$ kcal.mole^{-1} and $\Delta S^\ddagger = 27 \pm 6$ e.u. The effect has been confirmed for the ion $[Co(bipy)_2mal]^+$, where $\Delta H^\ddagger = 18 \pm 4$ kcal mole^{-1}, $\Delta S^\ddagger = -1 \pm 5$ e u

In order to investigate further the mechanisms of the reactions of such malonato complexes, substituted malonato ligands were used, and complexes of the type $[Co(en)_2Rmal]^+$ where R is ethyl or benzyl, were prepared. These contain the ring



The base hydrolyses of these substituted malonato complexes are found to be two stage, and both dechelation and loss of malonato ligand can be studied separately. In solutions where $[OH^-] < 1$ *M*, both stages are found to be second-order and the initial product is *cis*-$[Co(en)_2(OH)_2]^+$. The final product is a mixture of 90% $[Co(en)_2(OH)_2]^+$ and 10% $[Co(en)_2Rmal(OH)]^0$ Activation parameters are shown in Table 1.

TABLE I

Activation parameters for the base hydrolysis of some bis(ethylenediamine)cobalt(III) complexes containing substituted malonate ligands
(R = ethyl, R' = benzyl)

Complex	$\Delta H^{\ddagger}$ (kcal mole^{-1})	$\Delta S^{\ddagger}$ (e.u.)
$[Co(en)_2Rmal]^+$	14.5 ± 1	−22 ± 3
$[Co(en)_2Rmal(OH)]^0$	25.5 ± 1	+ 7 ± 3
$[Co(en)_2R'mal]^+$	17.5 ± 1	−12 ± 3
$[Co(en)_2R'mal(OH)]^0$	27.5 ± 1	+ 13 ± 3

In concentrated base (NaOH up to 4 M, μ = 4 M chloride medium), deviations from second-order kinetics occur in both stages of the reaction, when $[OH^-] > 2\,M$. It appears that instead of a limiting rate, as with the simple malonato complex, terms higher than first-order in hydroxide ion are entering into the rate equation. Such a situation also occurs in the oxalato system, $[Co(en)_2C_2O_4]^+$, in concentrated base[6], except that under these conditions the reaction product changes from *cis*- to a mixture of *cis*- and *trans*-$[Co(en)_2(OH)_2]^+$ ions. In the substituted malonato systems, however, no such change in the steric course is noticed and the initial product is always *cis*-$[Co(en)_2(OH)_2]^+$

The reactions of the substituted malonato complexes seem to indicate that the hydrolysis of the simple malonato ring proceeds via mechanism *2*(b) together with reaction (14) The presence of substituents slows down the bimolecular attack by hydroxide on the neutral complex, so that the second stage is observable. This is a reasonable consequence of the steric effect. The inductive effect of substituents would also tend to make the hydrogen less acidic, so that reaction (14) no longer plays a prominent role.

The alternative explanation is that mechanism *1*(a) operates in the case of the simple malonate. The presence of substituents now slows down the initial ring opening reaction, but the second step must change from dissociative to associative, which does not appear to be a likely effect. Further investigations into the kinetics and steric course of the hydrolysis of dicarboxylato complexes are continuing

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