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THE ROLE OF THE CARBOXYLATE GROUP IN OCTAHEDRAL SUBSTITUTION

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A INTRODUCTION

The occurrence of stereochemical change in the substitution reactions of cobalt(III) complexes of the type $Co(L_4)AX^{n+}$ (X is the ligand replaced) depends upon the nature of the reaction, the nature and position of ligand A and the steric requirements of the four nitrogen donor system, L_4 Of the monodentate ligands so far examined, only A = OH, F, Cl, Br, and NCS have definitely been shown to lead to steric change, and there is reasonably good evidence to suggest that A = H_2O should also be included It has been suggested[1] that all of these ligands have in common the potentialities of acting as π donors, using a lone pair on the donor atom or else a suitably orientated occupied π orbital on the ligand This should provide a conjugative assistance for the dissociation of X^-, especially if the five-coordinate intermediate then assumes a trigonal bipyramidal geometry, and may thereby lead to stereochemical change

More recently[2] it was observed that, in the solvolytic aquation of complexes of the type *trans*-$[M(L_4)ACl]^{n+}$ (M = Cr^{III}, Co^{III}, Rh^{III}, Ir^{III}), the occurrence of stereochemical change is, in general, associated with an entropy of activation some 15 cal deg^{-1} · mole^{-1} more positive than that found for reactions that take place with complete retention of configuration In recent years, many more conforming systems have been discovered and also some that do not conform[3] All of the new systems involve either a variation of L_4 or M, and no new A ligands that lead to stereochemical change have been reported

We have recently started to prepare complexes with a new range of ligands A which are expected to cause stereochemical change, in order to test the validity of the hypotheses relating to stereochemical change reactions Oxygen donors should present a fruitful area for further study, and in the search for suitable oxyanions which did not have a marked tendency to act as chelates, our attention was drawn to the carboxylate anions, $RCOO^-$. These have the added advantage of the presence of substituent R which can be varied extensively and thereby allow the relationship between the basicity of the ligand and the labilising and orienting properties of the ligand to be determined In this paper we report the kinetics and steric course of the catalysed and uncatalysed solvolytic reactions of $[Co(en)_2RCOO(X)]^+$.

B RESULTS

(i) The isomerisation of cis *and* trans-*[Co(en)$_2$CH$_3$COO(H$_2$O)]$^{2+}$*

In any study of the steric course of a reaction it is necessary, first of all, to determine the stereochemical lability of the product Carunchio and Ortaggi[4] have measured the kinetics of the isomerisation of *trans*-$[Co(en)_2CH_3COO(H_2O)]^{2+}$ in aqueous solution over a range of temperature, pH and ionic strength, and in methanol. We have reexamined this reaction and find that, although we are in reasonable agreement as to the magnitude of the rate constants and the activation parameters for approach to equilibrium, we find that at equilibrium the aquoacetato complex comprises 75% *cis* and 25% *trans* isomer This is confirmed by approaching equilibrium from the *cis*-$[Co(en)_2CH_3COO(H_2O)]^{2+}$ complex as well as the *trans* isomer The kinetics were followed spectrophotometrically and the rate was found to be independent of acid concentration in the range $10^{-3}\ M < [H^+] < 2\ M$, although at higher acidities acid-catalysed displacement of the acetato group presented further problems The position of equilibrium was independent of temperature The kinetic data can be summarised as

$$trans\text{-}[Co(en)_2CH_3COO(H_2O)]^{2+} \underset{k_c}{\overset{k_t}{\rightleftharpoons}} cis\text{-}[Co(en)_2CH_3COO(H_2O)]^{2+}$$

$k_c + k_t\,(25°) = 2\ 5 \times 10^{-5}\ sec^{-1}$

$\Delta H^{\ddagger} = 28\ 5$ kcal mole^{-1}

$\Delta S^{\ddagger} = +15\ 6$ cal deg^{-1} mole^{-1}

These are fairly typical values for isomerisation reactions of this type and it is reasonable to believe that the isomerisation is the result of a dissociative water-for-water exchange with stereochemical change.

(ii) The aquation of trans-*[Co(en)$_2$CH$_3$COO(Cl)]$^+$*

Parallel spectrophotometric and titrimetric studies indicate that the reaction in water consists of displacement of chloride to form $[Co(en)_2CH_3COO(H_2O)]^{2+}$ Parallel or subsequent loss of acetate does not interfere except at higher acid concentrations and until these conditions are reached, the rate of reaction is independent of the concentration of acid (at pH > 9 the base-catalysed displacement of chloride can be observed) The change of spectrum as a function of time indicates clean isosbestic points throughout the reaction at 553, 432, 379 and 337 nm. These correspond exactly to the crossing points of the spectra of *trans*-$[Co(en)_2CH_3COO(Cl)]^+$ and the 75% *cis* + 25% *trans* equilibrium $[Co(en)_2CH_3COO(H_2O)]^{2+}$ mixture and indicates that the subsequent isomerisation is either very much faster than the aquation or else that it does not occur. The latter possibility can only be achieved if the product is actually formed at, or very close to, its equilibrium composition The semilogarithmic plots of $\log_{10}(D_\infty - D_t)$ against time (D_t and D_∞ are the optical densities of the reaction mixture at 490 nm, or any other suitable wavelength, at time t and at the end of the reaction, respectively) are linear over at least three half-lives and the derived rate constants are independent of the wavelength used and in very close agreement to those determined from the rate of release of chloride The rate data can be summarised by

$k_{25} = 3\ 1 \times 10^{-6}$ sec^{-1} (see ref. 5 for detailed kinetics)

$\Delta H^{\ddagger} = 27\ 2$ kcal mole^{-1}

$\Delta S^{\ddagger} = +7\ 6$ cal deg$^{-1}\cdot$mole^{-1}

The *trans*-$[\mathrm{Co(en)_2C_6H_5COO(Cl)}]^+$ complex behaves in a very similar manner, the spectral changes also being characterised by well-defined isosbestic points The spectrophotometric and titrimetric rate data are in close agreement and can be summarised by

$k_{25} = 1\ 2 \times 10^{-6}$ sec^{-1} (ref 5)

$\Delta H^{\ddagger} = 29\ 0$ kcal$\cdot$mole^{-1}

$\Delta S^{\ddagger} = +12$ cal deg^{-1} mole^{-1}

This now allows an expansion of the reactivity sequence for the aquation of complexes of the type *trans*-$[\mathrm{Co(en)_2A(Cl)}]^+$, which aquate with stereochemical change, so that A = OH(160) > Br(4 5) > Cl(3 9) > $\mathrm{CH_3COO}$(0 31) > $\mathrm{C_6H_5COO}$(0 12) > NCS(0 005) (The values in parentheses are $10^5\ k$, measured at 25 0°)

A discussion of the relative labilising powers of $\mathrm{CH_3COO}$ and $\mathrm{C_6H_5COO}$ is premature with only two examples for consideration but the effect is in the right direction for an electron donation labilising effect The more basic acetate (pK_a of acetic acid = 4 74) labilises the chloride a little more strongly than benzoate (pK_a = 4 22)

It is clear that the specific rate constant for the approach to isomerisation equilibrium ($k_c + k_t = 2\ 5 \times 10^{-5}$ sec^{-1} at 25°) is some eight times greater than the rate constant for aquation of the *trans* chloroacetato complex The difference is not so great as to account for the observed sharpness of the isosbestic points, and an independent determination of the steric course indicates that the actual act of aquation produces 75 ± 10% *cis*- and 25 ± 10% *trans*-$[\mathrm{Co(en)_2CH_3COO(H_2O)}]^{2+}$ directly The analysis consists of calculating curves for the relationship between observed extinction coefficient at a suitable wavelength and time assuming a reaction

$$\textit{trans-}[\mathrm{Co(en)_2CH_3COO(Cl)}]^+ \rightarrow \underset{(f\%\ \textit{cis} + (100-f)\%\ \textit{trans})}{[\mathrm{Co(en)_2CH_3COO(H_2O)}]^{2+}} \rightarrow \underset{(75\%\ \textit{cis} + 25\%\ \textit{trans})}{[\mathrm{Co(en)_2CH_3COO(H_2O)}]^{2+}}$$

and using appropriate values for the rate constants The treatment is set out in full in ref. 5

Lack of detailed knowledge of the spectra and the isomerisation kinetics of the aquo-benzoato system precludes an accurate evaluation of the steric course of aquation of the chloro–benzoato complex. However, published data[6] indicate a close similarity between the aquoacetato and aquobenzoatobis(ethylenediamine)cobalt(III) complexes, and it seems reasonable to believe that aquation of the *trans*-chlorobenzoato complex is accompanied by extensive steric change.

The observation of entropies of activation in the region of +8 to +12 $\text{cal} \cdot \text{deg}^{-1}\ \text{mole}^{-1}$ in association with extensive stereochemical change is fully consistent with our previous correlation[2]

(iii) The Hg^{2+}-catalysed hydrolysis of trans-*$[Co(en)_2CH_3COO(Cl)]^+$*

In order to overcome the unfavourable relationship between the rate of formation of the aquo complex and the rate of its subsequent isomerisation, attempts were made to increase the former while holding the latter constant The addition of $Hg(ClO_4)_2$ allows this readily and the kinetics of solvolysis follow the well-established rate law

$$\text{Rate} = (k_{aq} + k_{Hg}[Hg^{II}])[\text{complex}]$$

With sufficient excess of Hg^{2+}, it is possible to ignore the catalysis by $HgCl^+$, but at relatively low mercuric ion concentrations this plays quite a significant part. The spectral changes in the presence of Hg^{2+} are identical with those of the uncatalysed solvolysis, except of course that the rate of change is much greater The isosbestic points remain even when the rate of solvolysis is some twenty times faster than the subsequent isomerisation This indicates quite clearly that the product is formed exactly in the equilibrium composition 75 ± 2% *cis* + 25 ± 2% *trans* as a direct result of the Hg^{2+}-catalysed solvolysis The rate constant, $k_{Hg} = 0.40\ \text{mole}^{-1} \cdot \text{sec}^{-1}$ at 39°, $[H^+] = 0.01\ M$

(iv) Acid-catalysed hydrolysis of trans-*$[Co(en)_2(CH_3COO)_2]^+$*[★]

As in the previous two cases, the progress of the reaction is defined by a set of spectra with very well-defined isosbestic points In contrast to the observations with the Hg^{2+} catalysis of the chloroacetato complex, the positions of the isosbestic points are somewhat dependent on the concentration of the acid used Closer examination shows that this is because the spectrum of the *trans*-$[Co(en)_2CH_3COO(H_2O)]^{2+}$ ion, in the near ultraviolet, is sensitive to acid concentration The final spectrum is unaffected, and corresponds to that of the 75% *cis* + 25% *trans*-$[Co(en)_2CH_3COO(H_2O)]^{2+}$ equilibrium mixture The rate of reaction is very sensitive to the concentration of acid, and in neutral solution the change is very slow indeed The slowest reactions studied were considerably slower than the subsequent isomerisation, but increasing the acid concentration did not increase the rate of

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[★] See ref 7 for full details of the kinetics

TABLE 1

Derived kinetic and equilibrium parameters for the acid-catalysed hydrolysis of *cis*- and *trans*-$[Co(en)_2(CH_3COO)_2]^+$ (μ = 2.0 $NaClO_4$)

	Temp (°C)	K_{spec} [a] (M^{-1})	K_{kin} [b] (M^{-1})	10^3k (sec^{-1})	$\Delta H°$ (kcal mole^{-1})	$\Delta S°$ (cal deg^{-1} mole^{-1})	$\Delta H^‡$ (kcal mole^{-1})	$\Delta S^‡$ (cal deg^{-1} mole^{-1})
trans	26.0	1.08						
	30.0	1.16						
	35.0	1.35			+3.7	+12	23.0	+1
	39.0	1.44	1.05	0.98				
	50.0		1.22	3.7				
	60.0		1.48	10.3				
cis	30.0		6.5	142				
	39.0		7.4	290	+1.7	+9	15.4	+13
	50.0		8.2	710				

[a] Determined from the dependence of the initial optical density at 300 nm upon $[H^+]$

[b] Determined from the kinetic analysis

solvolysis indefinitely A limiting rate was approached that was only some 2–3 times faster than the subsequent isomerisation This was sufficient to allow a very accurate spectrophotometric analysis, along the lines indicated above and once again, the initial product ratio was shown to be 80 ± 5% *cis* + 20 ± 5% *trans* The kinetics, at constant ionic strength, obeyed the rate law

$$\frac{-d[\text{complex}]}{dt} = \frac{kK[\text{complex}]\,[\text{H}^+]}{1 + K[\text{H}^+]}$$

and at a particular hydrogen ion concentration the reaction was first order and the pseudo first-order rate constant, k_{obs}, could be measured spectrophotometrically Thus, $k_{\text{obs}} = kK[\text{H}^+]/1 + K[\text{H}^+]$, and a plot of $1/k_{\text{obs}}$ vs $1/[\text{H}^+]$ should be linear with a slope of $1/Kk$ and an intercept of $1/k$ The values of k and K are collected in Table 1 It is proposed that the kinetics result from a pre-equilibrium protonation, step (1), followed by dissociation of the new weakly bonded protonated ligand

$$[\text{Co(en)}_2(\text{CH}_3\text{COO})_2]^+ + \text{H}_3\text{O}^+ \overset{K}{\rightleftharpoons} [\text{Co(en)}_2(\text{CH}_3\text{COO})(\text{CH}_3\text{COOH})]^{2+} + \text{H}_2\text{O}$$

$$[\text{Co(en)}_2(\text{CH}_3\text{COO})(\text{CH}_3\text{COOH})]^{2+} + \text{H}_2\text{O} \xrightarrow{k} [\text{Co(en)}_2\text{CH}_3\text{COO}(\text{H}_2\text{O})]^{2+} + \text{CH}_3\text{COOH}$$

The kinetic form will also allow an alternative mechanism in which H_3O^+ attacks the unprotonated ligand, but this is considerably less likely in the light of the available evidence The pre-equilibrium protonation was also examined spectrophotometrically and values of K were obtained from the change of initial absorbance at 300 nm as a function of acid concentration. These agree closely with those obtained from the kinetic analysis

The conclusion to be drawn from the study of the steric course of aquation of *trans*-$[\text{Co(en)}_2\text{CH}_3\text{COO(X)}]^{n+}$, where X = Cl^-, ClHg^+ and CH_3COOH is that in all cases, the initial product contains 75% *cis* and 25% *trans*-$[\text{Co(en)}_2\text{CH}_3\text{COO}(\text{H}_2\text{O})]^{2+}$, and that this is strongly indicative of a dissociative mechanism with a common five-coordinate intermediate The occurrence of stereochemical change in the acid-catalysed hydrolysis of *trans*-$[\text{Co(en)}_2(\text{CH}_3\text{COO})_2]^+$ is incontrovertible evidence of Co–O bond fission

(v) The acid-catalysed hydrolysis of cis-$[Co(en)_2(CH_3COO)_2]^{+}$*

The *cis* diacetato complex undergoes acid-catalysed hydrolysis very much faster than its *trans* isomer As a consequence, the steric course could be established without need for any correction due to the subsequent isomerisation, and the actual kinetics of the process could only be followed by stopped-flow techniques Direct examination of the initial reaction product showed that the substitution was stereoretentive and the initial product was 100% *cis*-$[\text{Co(en)}_2\text{CH}_3\text{COO}(\text{H}_2\text{O})]^{2+}$ The rate law was of the same form as that found for the *trans* isomer except at the highest acid concentrations Here there was some indication of

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*See ref 7 for full details of the kinetics further protonation leading to decrease in reactivity, especially at the lowest temperature. It has not yet been possible to examine these deviations in detail as they occur at the limits of usefulness of the adopted techniques The derived rate and equilibrium constants are collected in Table 1, from which it will be seen that the higher rate of reaction compared with the *trans* isomer arises from an increased basicity (K) and a considerably greater dissociative lability It is far less easy to assign a mechanism to the reaction of the *cis* isomer The retention of configuration does not provide an answer, since it is consistent both with carbon–oxygen bond fission, which, of necessity, requires retention of configuration at cobalt, and with Co–O bond fission, which, apart from a couple of possibly equivocal exceptions, is shown to take place with complete retention of configuration for aquation of complexes of the type *cis*-$[Co(en)_2AX]^{n+}$ In a similar situation, Deutsch and Taube[8] proposed that the enthalpy of activation for the acid-catalysed aquation of $Cr(H_2O)_5CH_3COO^{2+}$ (19 kcal mole^{-1}) was so much smaller than the values normally observed for solvolysis at Cr^{III} (~ 23 kcal mole^{-1}) that C–O bond fission was indicated (It was pointed out that the enthalpy of activation for the acid hydrolysis of methyl acetate, which involves C–O bond fission, was 16 4 kcal mole^{-1}) If this reasoning was applied to the reaction of *cis*-$[Co(en)_2(CH_3COO)_2]^+$ ($\Delta H^{\ddagger}$ = 15 4 kcal mole^{-1}), carbon–oxygen bond fission would be clearly indicated However, in many of the cases where the *trans* isomer of a pair aquates with stereochemical change and the *cis* isomer reacts with complete retention of configuration, not only is the entropy of activation of the former considerably more positive than that of the latter, but the enthalpy of activation is considerably greater in compensation In these examples there is no ambiguity about the position of bond fission It is thus not possible to state unequivocally whether the *cis*-diacetato complex hydrolyses with C–O or Co–O bond fission

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