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THE BASE HYDROLYSIS OF CARBONATO-, OXALATO-, AND MALONATO-BIS(ETHYLENEDIAMINE)COBALT(III) IONS

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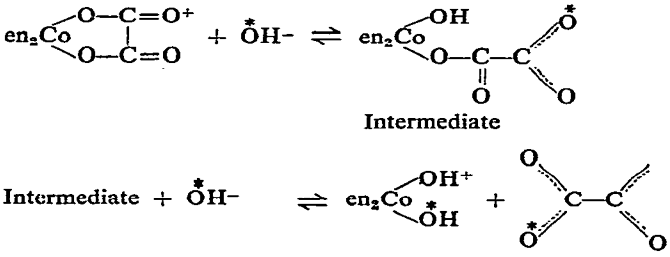
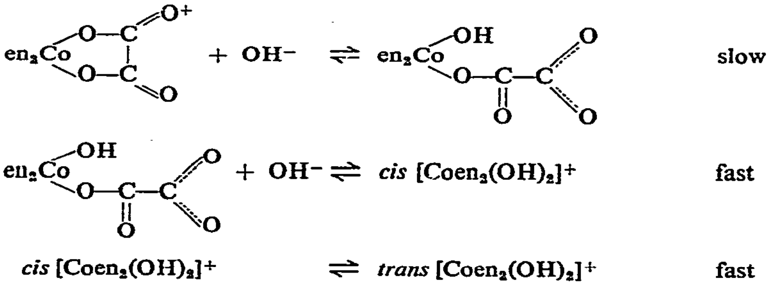
Some results of the investigations into the base hydrolysis at high hydroxyl ion concentration (*i.e.* up to 3.7 *M*) of the carbonato-, oxalato-, and malonato-bis(ethylenediamine)cobalt(III) ions are presented in this paper.

The base hydrolysis of the carbonato and of the oxalato ions have been postulated to go by ring opening reactions by Harris[1] in 1963 and Taube[2] in 1964.

It was suggested[2] that the oxalate chelate ring is ruptured by OH^- attack on carbon, with carbon–oxygen fission. Thus the following series of reactions can explain the ^{18}O exchange:



The following mechanism for the base hydrolysis of the oxalato ion in dilute alkali (up to 0.1 *M*) was put forward by Harris[1].



At the hydroxyl ion concentrations used by Harris and his co-workers the final product was the *cis–trans* equilibrium mixture of the dihydroxo ions.

The present work has shown that at high hydroxide concentrations, *i.e.* one to four *M*, the intermediate can be detected spectrophotometrically, and that the dihydroxo product has the *cis* configuration which subsequently isomerises to the *cis–trans* equilibrium mixture. Under similar conditions of high hydroxyl ion concentration the change of optical activity in the optically active complex is in three steps. The first mutarotation can be identified with ring opening, the second with removal of the oxalate ring and the last with the equilibration of the dihydroxo products. Further work on the oxalato system at high hydroxide concentration is at present being carried out.

In the case of the carbonatobis(ethylenediamine)cobalt(III) cation the hydroxo monodentate carbonato species is relatively long-lived. Thus on the addition of base to a solution of the bromide salt of the carbonato cation, there is a change in the spectrum to that of an intermediate. The spectrum of the intermediate then gives way to that of the *cis*-dihydroxobis(ethylenediamine)cobalt(III) cation. The proposal for a monodentate carbonato intermediate is supported by the fact that at an hydroxyl ion concentration of 0.006 *M*, the spectral change in the solution is exactly paralleled by an increase in the electrical resistance during the formation of the non-charged species. The spectrophotometric and conductometric rate constants calculated from these data are identical.

It can be seen from Figure 1 that at 30,000 cm^{-1} the absorbance of the hydroxo carbonato compound is higher than that of either the carbonato starting material or the dihydroxo products. The absorbance thus first rises and then falls as the reaction progresses. The final absorbance corresponds to that of the *cis*[Coen$_2$(OH)$_2$]$^+$ ion.

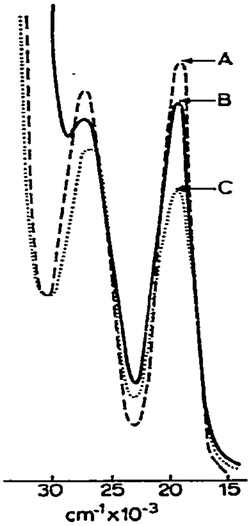


Fig. 1. A. [Coen$_2$CO$_3$]Br; B. [Coen$_2$CO$_3$OH]; C. [Coen$_2$(OH)$_2$]$^+$.

Pseudo first order and hence second order rate constants have been calculated for both reactions from the spectrophotometric data.

For the reaction:

$$[Coen_2CO_3]^+ + OH^- \xrightarrow{k'} [Coen_2CO_3OH]$$

at low hydroxyl ion concentration the rate is directly proportional to the concentration of OH^-, but as the hydroxide concentration is increased the rate becomes independent of the OH^- concentration, and eventually a limiting rate is reached.

The rate for the second reaction:

$$[Coen_2CO_3OH] + OH^- \xrightarrow{k''} [Coen_2(OH)_2]^+ + CO_3{}^{2-}$$

remains first order with respect to hydroxide (see Table 1).

TABLE I

SPECTROPHOTOMETRIC RATE CONSTANTS FOR THE BASE HYDROLYSIS OF THE $Coen_2CO_3^+$ ION
(A) FORMATION OF $Coen_2CO_3OH$ AT 24.8 °C

OH^- Molarity	*k'_1 (min^{-1})*	*k'_2 ($min^{-1}l.mole^{-1}$)*
3.71	0.361	0.097
3.69	0.365	0.099
3.03	0.355	0.127
2.73	0.328	0.130
1.66	0.215	0.128
0.96	0.130	0.135
0.55	0.072	0.131

(B) BASE HYDROLYSIS OF $Coen_3CO_3OH$ AT 47.5 °C

OH^- Molarity	*k''_1 (min^{-1})*	*k''_2 ($min^{-1}l.mole^{-1}$)*
3.71	0.248	0.067
2.76	0.196	0.071
1.38	0.0957	0.069
0.966	0.0690	0.071
0.55	0.0376	0.068
0.55	0.0380	0.069
0.276	0.0182	0.067

The ratio of the two rate constants $K = k''/k'$ thus becomes larger with increasing OH^- concentration once k' reached a limiting rate. The time, t_{max}, at which the concentration of $[Coen_2CO_3OH]$ is a maximum, becomes smaller and the maximum less pronounced as the concentration of OH^- is increased to 4 *M*. (See Fig. 2.) The variation of the rate constants with temperature fit the Arrhenius equations:

$$k_2' = 2.6 \cdot 10^{15} \exp(-22{,}000/RT)\ 1\ mole^{-1}sec^{-1}$$
$$k_2'' = 1.9 \cdot 10^{13} \exp(-24{,}000/RT)\ 1\ mole^{-1}sec^{-1}$$

It is postulated that the carbonatobis(ethylenediamine)cobalt(III) cation

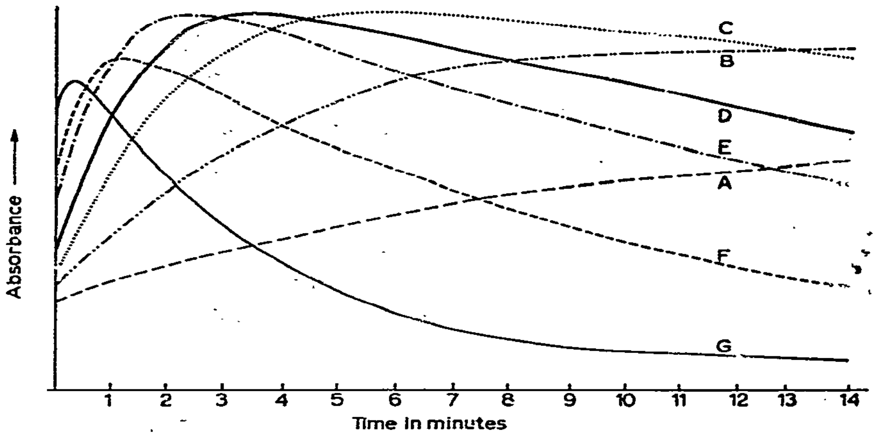


Fig. 2. Reaction of [Coen$_2$CO$_3$]Br with OH$^-$ ions: variation of absorbance with time at 30,000 cm^{-1}. Temp.: 47.5 °C. A. OH$^-$ = 0.014 *M*; B. OH$^-$ = 0.069 *M*; C. OH$^-$ = 0.276 *M*; D. OH$^-$ = 0.550 *M*; E. OH$^-$ = 0.970 *M*; F. OH$^-$ = 1.380 *M*; G. OH$^-$ = 3.710 *M*.

undergoes a ring opening reaction by cobalt–oxygen fission, as predicted by Taube.

The reactions which take place by cobalt–ligand bond breaking seem to reach a limiting rate somewhere around 3M alkali concentration. This limiting rate could come about by an SN$_1$CB mechanism, where a limiting rate is predicted at high enough OH$^-$ concentrations to give only the amido complex; or by an ion-pair mechanism in which the [Coen$_2$CO$_3$]$^+$ · OH$^-$ ion-pair is the reactive species. However, OH$^-$ attack on the carbon giving C–O fission, would not be expected to give a limiting rate.

With the carbonato complex, therefore, the first step takes place with cobalt–oxygen fission. The limiting rate is reached when the complex is in the form of the ion-pair or perhaps the amido complex. The second step takes place by carbon–oxygen fission.

With the oxalato complex, however, it seems likely that the ring opening takes place with carbon–oxygen fission. The second step then occurs with Co–O bond breaking and reaches a limiting rate. The hydroxo–oxalato intermediate can thus be observed at high OH$^-$ concentrations.

The base hydrolysis of the malonatobis(ethylenediamine)cobalt(III) ion was studied over a wide range of hydroxyl ion concentration. In dilute alkali, up to 0.1 *M*, the results are similar to those of the oxalatobis(ethylenediamine)cobalt(III) ion under analogous conditions[3]. The products of the reaction are the *cis* and *trans*[Coen$_2$(OH)$_2$]$^+$ ions in equilibrium proportions. The reaction is first order in complex and in OH$^-$. Good second order rate constants were computed from the standard integrated form of the second order rate equation. The reaction was followed spectrophotometrically and polarimetrically. The second order polarimetric rate constants calculated from the loss of optical activity in basic solution were in good agreement with those determined spectrophotometrically.

The variation of rate with temperature fits the Arrhenius equation:

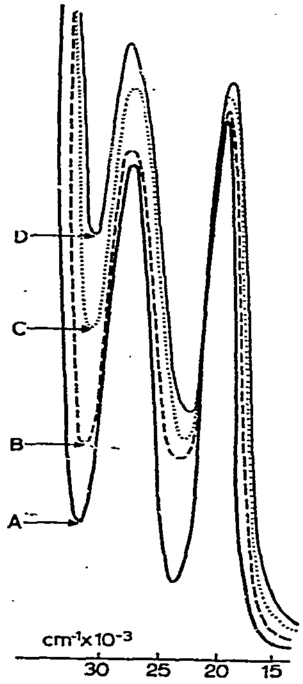
$$k_2 = 5 \cdot 10^{19} \exp(-29.300/RT) \text{ l. mole}^{-1}\text{sec}^{-1}.$$

The Arrhenius parameters may be compared with those for the oxalato complex[3], where:

$$k_2 = 6.5 \cdot 10^{19} \exp(-38{,}000/RT) \text{ l. mole}^{-1}\text{sec}^{-1}$$

The difference in the velocity of the two reactions comes about as a result of different activation energies.

At about 1 *M* hydroxide the rate of reaction of the malonato ion can be pushed high enough so that it becomes considerably faster than the *cis–trans* equilibrium reaction of the dihydroxo products. *cis*$[\text{Coen}_2(\text{OH})_2]^+$ can now be identi-



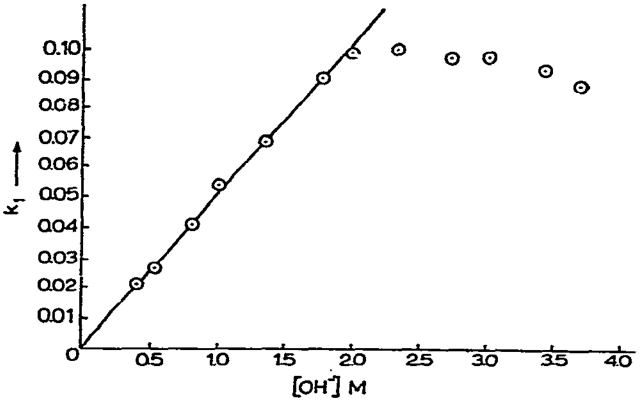
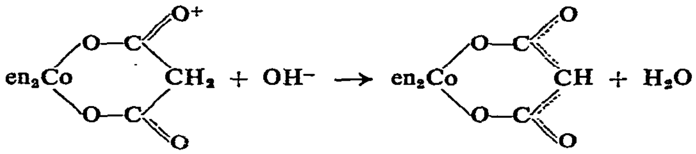


Fig. 3. Reaction of $[\text{Coen}_2\text{OOCCH}_2\text{COO}]\text{Br}$ with OH^- ions. Variation of initial spectrum with change in OH^- ion concentration. Temp.: 24.8 °C. A. $\text{OH}^- = 0.00$ *M*; B. $\text{OH}^- = 0.55$ *M*; C. $\text{OH}^- = 2.00$ *M*; D. $\text{OH}^- = 3.71$ *M*.

Fig. 4. Reaction of $[\text{Coen}_2\text{OOCCH}_2\text{COO}]\text{Br}$ with OH^- ions. Variation of pseudo first order spectrophotometric rate constants with change in OH^- ion concentration. Temp.: 37.5 °C.

fied as the product by its spectrum, and the loss of optical activity falls into two distinct parts; the first a mutarotation to the *cis* hydroxo complex followed by a loss of optical activity while the *cis–trans* equilibrium is established. Above about 2 *M* alkali, the initial spectrum obtained in the runs becomes dependent on the initial hydroxide concentration (see Fig. 3). The pseudo first order spectrophotometric rate constants reach a limiting value at about 2 *M* hydroxide (see Fig. 4).

A possible explanation of the results is proton removal from the coordinated malonato group:



The species so formed, which would be resonance-stabilized, is expected to be unreactive, thus a limiting rate would be reached. Further work on this system is at present in progress.

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