

Kinetics and Mechanism of Equilibration Between Bidentate and Monodentate Carbonate in a Macrocyclic Chromium(III) Complex

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Equilibration between complexes with bidentate and monodentate carbonate coordinated to *cis*-(*rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)-chromium(III) has been investigated at a range of temperatures in 1 M (H,Na) (Br,OH) at range of acidities from strongly acidic to strongly basic solution. Chelation and dechelation reactions occur in the entire acidity range, but in strongly acidic or strongly basic solutions decarboxylation reactions dominate and the carbonate complexes are not stable. Kinetic parameters are given and discussed in a mechanistic context.

Aminecarbonato complexes are easily prepared and have long been known for a number of transition-metal ions, but it was not until recently that the first tetraaminecarbonato-chromium(III) complex was characterized.¹ The crystal structure of *cis*-[Cr(cycb)(O₂CO)]₂(S₂O₆)·4H₂O [cycb = *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane] showed no anomalies for the coordinated bidentate carbonate ligand when compared to a number of *cis*-tetraaminecarbonatocobalt(III) complexes,² and it was therefore decided to investigate the chromium(III) complex further in an attempt to clarify the cause of the apparent sparsity of carbonatochromium(III) complexes and the efficient carbonate ion catalysis of substitution reactions at a chromium(III) centre.

The Cr(cycb) moiety is exceptionally stable in aqueous solution, and reactions at the two coordination positions not occupied by the macrocyclic tetraamine can be investigated free from competitive amine ligand aquation or isomerization.³ This work describes a detailed reaction kinetic investigation of equilibration between bidentate and monodentate carbonate at a range of acidities from strongly acidic to strongly basic solution.

Results and discussion

Stoichiometry. The *cis*-[Cr(cycb)(O₂CO)]⁺ ion is well characterized in the solid state.² Salts containing this cation can be dissolved in water and reprecipitated without decomposition of the complex. In acidic solution, however, *cis*-[Cr(cycb)(OH)₂]³⁺ and CO₂ are rapidly formed. In basic solutions the red colour due to the carbonato complex slowly changes to blue-violet. From such blue-violet solutions, ion-exchange fractionation experiments allow the isolation

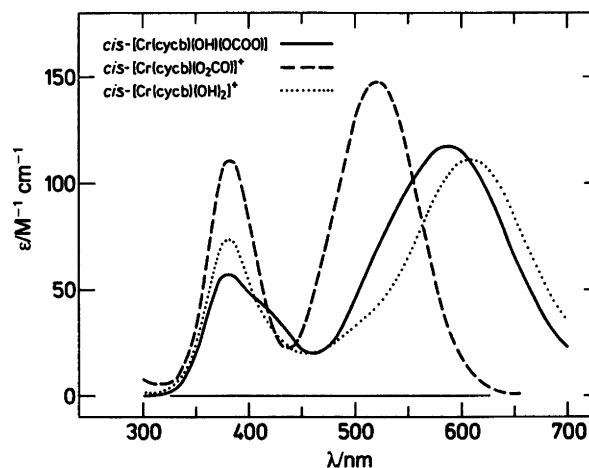
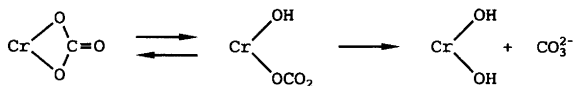


Fig. 1. Visible absorption spectra of *cis*-[Cr(cycb)(O₂CO)]⁺, *cis*-[Cr(cycb)(OH)(OCO₂)] and *cis*-[Cr(cycb)(OH)₂]⁺ in 1.0 M Na(OH,Br) at 25 °C. The spectrum of the bidentate carbonate complex is measured in neutral solution, and the spectra of complexes with coordinated hydroxide ion in solutions with [OH⁻] ≈ 0.1 M.

of an uncharged component. This species regenerates the parent *cis*-[Cr(cycb)(O₂CO)]⁺ complex at intermediate acidities and gives blue *cis*-[Cr(cycb)(OH)₂]⁺ by a very slow process in basic solution. The mode of formation, the further reactions and the visible absorption spectrum (Fig. 1) make it likely that the uncharged complex is *cis*-[Cr(cycb)(OH)(OCO₂)], i.e. a complex with a monodentate carbonate ligand.

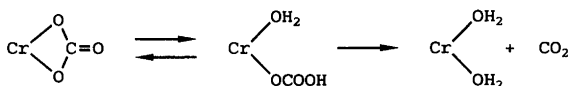
Reactivity in basic solution. Spectral measurements of basic solutions of the *cis*-[Cr(cycb)(O₂CO)]⁺ ion indicate two

first-order processes with significantly different rate constants. A multi-wavelength analysis of the spectral changes shows that the faster reaction is an equilibration between complexes with bidentate and monodentate carbonate followed by a slower 'irreversible' formation of the dihydroxo complex, i.e. the transformations take place according to Scheme 1.



Scheme 1.

Reactivity in acidic solution. Spectral measurements on acidified solutions of $\text{cis-}[\text{Cr}(\text{cycb})(\text{O}_2\text{CO})]^+$ show two rather fast first-order kinetic processes with rate constants of the same order of magnitude. Two processes are also observed when solutions of $\text{cis-}[\text{Cr}(\text{cycb})(\text{OH})(\text{OCO}_2)]$ are made acid, and the reactions therefore occur by a stoichiometric scheme analogous to that found for basic solutions, but here involving the protonated intermediate and reaction product (Scheme 2).

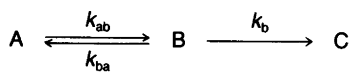


Scheme 2.

Fig. 2 shows the hydrogen ion concentration dependence of the two observed rate constants, k_1 and k_2 , obtained by approximating the observed absorbance vs. time dependence, $A(t)_{\text{obsd}}$, by eqn. (1).

$$A(t)_{\text{obsd}} \approx A(t)_{\text{calcd}} = a_0 + a_1 e^{-k_1 t} + a_2 e^{-k_2 t} \quad (1)$$

For a reaction scheme which can formally be written as in Scheme 3,



Scheme 3.

observed rate constants obtained by approximating the experiments using eqn. (1) are given by eqn. (2).

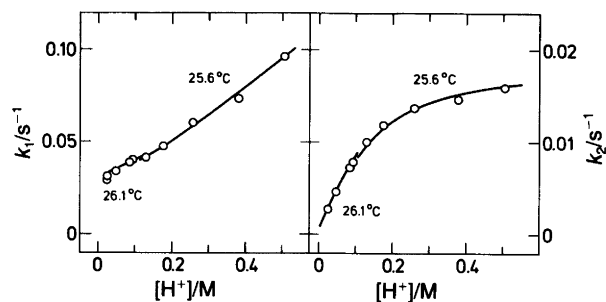


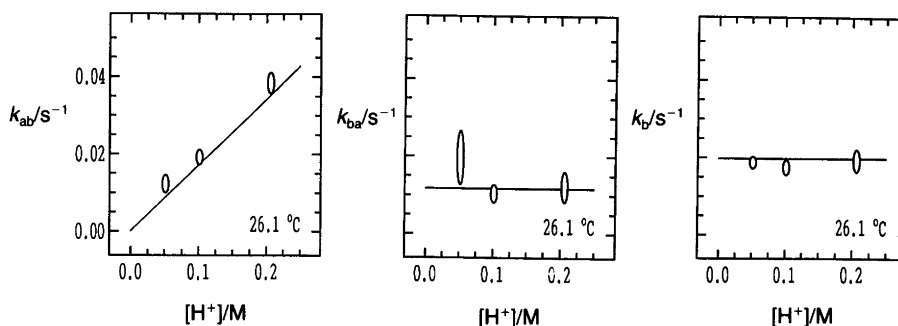
Fig. 2. Hydrogen ion concentration dependence of the two observed first-order rate constants, k_1 and k_2 [eqn. (1)], for the hydrolysis of carbonate complexes in 1.0 M (H,Na)Br solution. The circles represent experimental data and the solid curves are calculated from eqns. (2) and (3) using the parameters of Table 1.

$$(k_1, k_2) = \frac{1}{2} [k_{\text{ab}} + k_{\text{ba}} + k_{\text{b}} \pm \sqrt{(k_{\text{ab}} + k_{\text{ba}} + k_{\text{b}})^2 - 4k_{\text{ab}}k_{\text{b}}}] \quad (2)$$

The hydrogen ion dependence of the individual rate constants is not easily resolved from this type of measurement, and to supplement the data obtained by following the reaction at a single wavelength, a series of experiments were performed in which samples of the reacting solution were withdrawn and quenched by the addition of base. From the visible absorption spectra of such solutions the content of complexes with bidentate, with monodentate and without coordinated carbonate was calculated from the spectra of the pure components (Fig. 1). These concentration vs. time relationships allow the calculation of all three constants k_{ab} , k_{ba} and k_{b} . Some representative examples are shown in Fig. 3. k_{ab} is seen to depend linearly on the hydrogen ion concentration, whereas both k_{ba} and k_{b} are constant within this range of acidities.

Reactivity at intermediate acidities. $\text{cis-}[\text{Cr}(\text{cycb})(\text{O}_2\text{CO})]^+$ is stable at intermediate acidities and is formed from $\text{cis-}[\text{Cr}(\text{cycb})(\text{OH})(\text{OCO}_2)]$ when basic solutions of this complex are adjusted to a higher hydrogen ion concentration. This process is first order in complex concentration; Fig. 4 shows rate constants at a series of hydrogen ion concentrations and temperatures.

Fig. 3. Hydrogen ion concentration dependence of k_{ab} , k_{ba} and k_{b} (Scheme 3) in 1.0 M (H,Na)Br at 26.1°C. Experimental data are indicated by contour ellipses of the probability density function drawn at the 95% level. Solid curves are calculated from eqns. (2) and (3) using the parameters of Table 1.



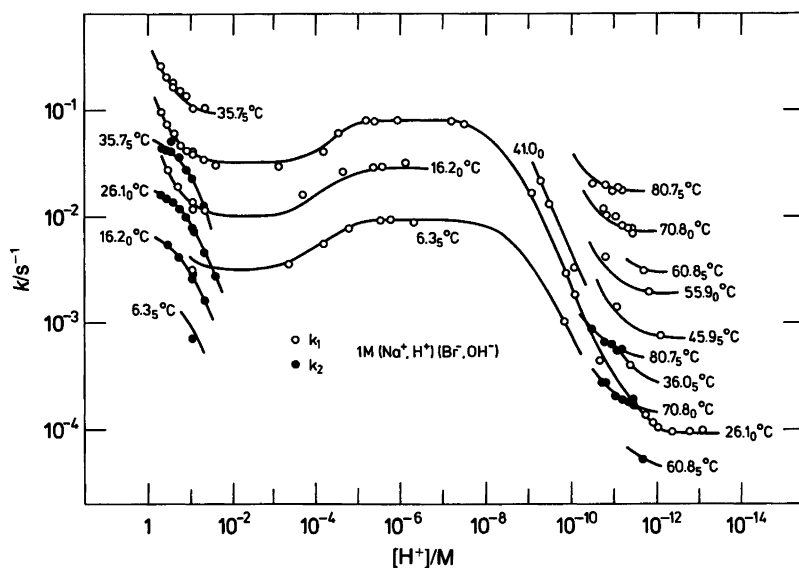


Fig. 4. Temperature and hydrogen ion concentration dependence of the first-order rate constants for equilibration between bidentate and monodentate carbonate complexes and the aquation of the monodentate complex. Circles represent experimental data and the solid curves are calculated from eqns. (2) and (3) using the parameters of Table 1.

Stoichiometric reaction scheme. From the data presented in Fig. 4 it is clear that the kinetics of the investigated transformations conform to a reaction sequence given by the formal Scheme 3, and that one and two hydrogen ion dependent equilibria are involved for the initial complex, A, and the intermediate, B, respectively. This accords with the detailed Scheme 4, for which eqn. (3) can be derived when the protonation constant $K \ll 1 \text{ M}^{-1}$.

$$k_{ab} = k_{ab1} + k_{ab0}K[\text{H}^+]$$

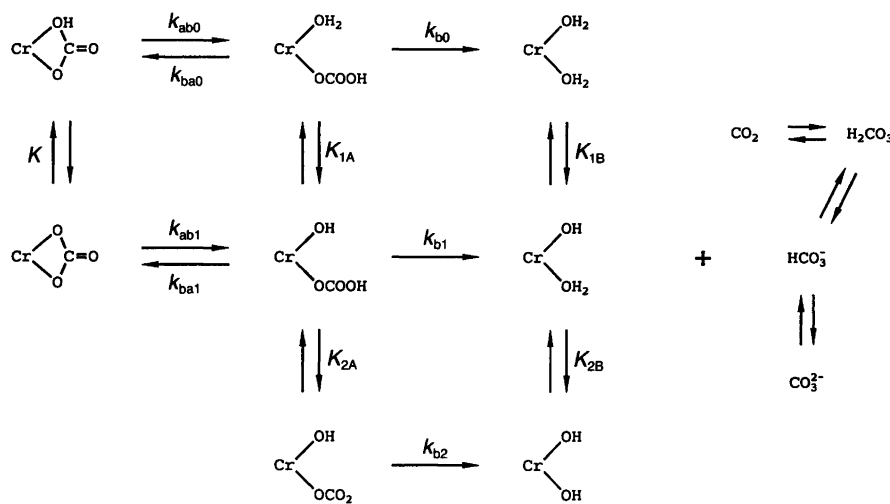
$$k_{ba} = \frac{k_{ba0} + k_{ba1}K_{1A}/[\text{H}^+]}{1 + K_{1A}/[\text{H}^+] + K_{1A}K_{2A}/[\text{H}^+]^2} \quad (3)$$

$$k_b = \frac{k_{b0} + k_{b1}K_{1A}/[\text{H}^+] + k_{b2}K_{1A}K_{2A}/[\text{H}^+]^2}{1 + K_{1A}/[\text{H}^+] + K_{1A}K_{2A}/[\text{H}^+]^2}$$

Parameters obtained from the kinetic data in the entire acidity range and the equilibrium constants for the basic solutions (Scheme 1) are given in Table 1, and the agreement between observed and calculated quantities is shown in Figs. 2–4.

The ring-opening reaction, k_{ab} , is seen to be accelerated substantially in acidic solution, corresponding to the uptake of one proton of the reactant. In Scheme 4 the site of protonation is taken to be the coordinated oxygen atom. This gives a stoichiometric reaction mechanism analogous to that of depolymerization of dihydroxy-bridged dimeric metal ion systems.⁴ Arguments can, however, also be advanced in favour of protonation of the uncoordinated oxygen atom.⁵ This ambiguity seems at present unsettled.

Comparisons with data for other systems. The overall stoichiometric scheme derived for carbonate ligand aquation in the present chromium(III) complexes is in agreement with



Scheme 4.

Table 1. Kinetic and thermodynamic parameters for aquation of $cis\text{-}[\text{Cr}(\text{cycb})(\text{O}_2\text{CO})]^+$ in 1.00 M (Na,H)(Br,OH) (Scheme 4). Standard deviations in parenthesis.

Parameter	Value at 25 °C	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{JK}^{-1} \text{mol}^{-1}$
$k_{\text{ab0}}/M^{-1} \text{s}^{-1}$	0.155(3)	72.4(13)	-18(5)
$k_{\text{ab1}}/\text{s}^{-1}$	$7.8(3) \times 10^{-5}$	81.7(9)	-50(3)
$k_{\text{ba0}}/\text{s}^{-1}$	$1.01(3) \times 10^{-2}$	77(2)	-24(10)
$k_{\text{ba1}}/\text{s}^{-1}{}^b$	$7.1(2) \times 10^{-2}$	73.4(13)	-21(5)
k_{b0}	$1.70(4) \times 10^{-2}$	81(3)	-9(8)
k_{b1}	$1.5(12) \times 10^{-3}{}^c$	102(13)	42(40)
k_{b2}	$2.7(10) \times 10^{-7}{}^c$	114(6)	10(20)
$-\log(K_{1A}/M)$	4.15(3)	13(3)	-35(10)
$-\log(K_{2A}/M)$	8.447(14)	42(3)	-21(8)
$-\log(K_{1B}/M)$	3.486(12)	27(3)	24(10)
$-\log(K_{2B}/M)$	7.112(15)	42(4)	5(13)

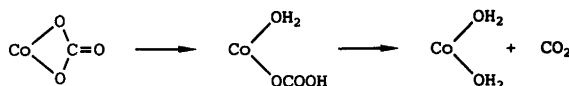
^a ΔH^\ddagger , ΔH^\ddagger or $\Delta H^\ddagger + \Delta H^\ddagger$ and analogously for ΔS^\ddagger depending upon the parameter. ^b k_{ba1} calculated from $k_{\text{ba1}} = k_{\text{ba0}}k_{\text{ab1}}/(Kk_{\text{ab0}}K_{1A})$. ^c These rate constants are significantly correlated with K_{1A} and K_{2A} , but more well defined at higher temperatures: $k_{\text{b1}}K_{1A}$ (70 °C): $5.4(10) \times 10^{-5} \text{ M s}^{-1}$; $k_{\text{b2}}K_{1A}K_{2A}$ (70 °C): $5.8(11) \times 10^{-16} \text{ M}^2 \text{ s}^{-1}$.

the general scheme established on the basis of data for other carbonate complexes predominantly of cobalt(III) and rhodium(III).

Reactions in acid of the present chromium(III) system are faster than those of the corresponding cobalt(III) complex: $cis\text{-}[\text{Co}(\text{cycb})(\text{O}_2\text{CO})]^+$,⁶ but in basic solution this relative order is reversed.⁷ The detailed stoichiometry of the chromium(III) reactions is well established through structure determinations of the $cis\text{-}[\text{Cr}(\text{cycb})(\text{O}_2\text{CO})]^+$ and $cis\text{-}[\text{Cr}(\text{cycb})(\text{OH})_2]^+$ cations, which both have the same conformation of the coordinated amine. The cobalt(III) system is much more complicated, and several isomerization reactions have been reported.⁶⁻⁸ This has limited the tractability of the latter system, and a detailed interpretation of the rate differences is not possible on the basis of the presently available data.

A significant number of complexes with simpler amine ligands have been investigated in greater detail, particularly in acidic solutions. Most cobalt(III) complexes react significantly faster than the $cis\text{-}[\text{Cr}(\text{cycb})(\text{O}_2\text{CO})]^+$ ion, and this apparently has prevented an accurate characterization of the fast step (k_1 in Fig. 2), although it has been seen in the aquation of the $cis\text{-}[\text{Co}(\text{tren})(\text{O}_2\text{CO})]^+$ complex [tren = tris(2-aminoethyl)amine].⁹ The slow step (k_2 in Fig. 2) has been measured in detail for a large number of tetraamine-carbonato complexes, and these data conform well to those for the present chromium(III) complex. In most cases only the linear portion of k_2 vs. $[\text{H}^+]$ has been observed, but in other systems such as $cis\text{-}[\text{Cr}(\text{en})_2(\text{O}_2\text{CO})]^+$ [en = 1,2-ethanediamine] a limiting rate at higher hydrogen ion concentrations is also apparent.¹⁰

Aquation of bidentate carbonate is usually described as two consecutive first-order processes, i.e. Scheme 5, and chelation of the aquahydrogencarbonato complex clearly demonstrated in this work has not been demonstrated to



Scheme 5.

occur in the previously investigated cobalt(III) and rhodium(III) systems. Whether this results from a lack of accurate data for the k_1 path of the earlier investigated systems (Fig. 2), or is a real difference which results from this path being much more dominant in the present system than for the previously studied cobalt(III) and rhodium(III) complexes, remains to be demonstrated. However, the latter alternative could give an explanation of why tetraaminecarbonatochromium(III) ions of simpler amine ligands have not previously been characterized: removal of a ligand in a position *cis* to coordinated hydrogen carbonate is an efficient process which could rapidly remove a coordinated amine ligand. This would also explain the well documented carbonate ion catalysis of substitution reactions at a chromium(III) centre. It is tempting to ascribe this difference in substitution kinetic behaviour to the change in intimate mechanism between chromium(III) and cobalt(III), as an uncoordinated oxygen atom of a carbonate ligand is well suited for an 'associative' attack at a chromium(III) centre. Interpreted in this way the present data are additional evidence for significant differences in the substitution kinetic behaviour of metal ions.

Experimental

Chemicals. $cis\text{-}[\text{Cr}(\text{cycb})(\text{O}_2\text{CO})]\text{Cl} \cdot \text{H}_2\text{O}$ was prepared according to Ref. 1. Other chemicals were the best available commercial grades, which were purified as necessary.

$cis\text{-}[\text{Cr}(\text{cycb})(\text{OH})(\text{OCO}_2)]$ solutions. 50 mg $cis\text{-}[\text{Cr}(\text{cycb})(\text{O}_2\text{CO})]\text{Cl} \cdot \text{H}_2\text{O}$ was left for 20 h in 10 ml 0.1 M NaOH at about 20 °C. The resulting solution was charged onto a 10×2 cm Sephadex SP-C-25 filled column which had previously been treated with 0.1 M NaOH. A blue-violet component was clearly separated from $cis\text{-}[\text{Cr}(\text{cycb})(\text{O}_2\text{CO})]^+$ and $cis\text{-}[\text{Cr}(\text{cycb})(\text{OH})_2]^+$ by elution with 0.1 M NaOH. The ionic strength of the eluate was adjusted to 1.00 M by dissolution of solid NaBr \cdot 2H₂O or NaClO₄ \cdot H₂O. The visible absorption spectrum of a solution thus prepared is shown in Fig. 1. Solutions for kinetic runs were prepared analogously but using 0.01 M NaOH. This gave solutions with almost identical spectral characteristics. However, at this lower hydroxide concentration, chelation on the column to form the bidentate carbonate complex is noticeable.

The majority of the work reported here was done using the monodentate complex prepared in the above way. It was later found, however, that a solid compound containing the diprotonated form of the above cation could be isolated from perchloric acid solutions as follows:

$cis\text{-}[\text{Cr}(\text{cycb})(\text{OH}_2)(\text{OCO}_2)](\text{ClO}_4)_2 \cdot x\text{HClO}_4 \cdot y\text{H}_2\text{O}$.
0.25 g $cis\text{-}[\text{Cr}(\text{cycb})(\text{O}_2\text{CO})]\text{Cl} \cdot \text{H}_2\text{O}$ was kept in 1.0 ml 1.0

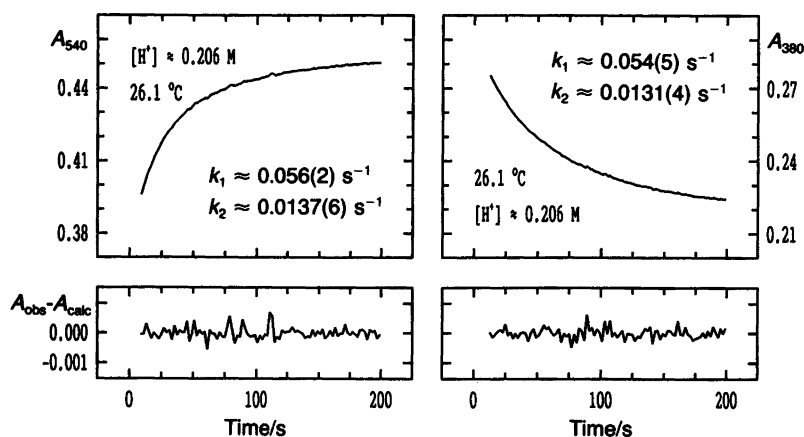


Fig. 5. Upper part: absorbance vs. time profile at 540 and 380 nm, respectively, for the aquation of $\text{cis-}[\text{Cr}(\text{cycb})(\text{O}_2\text{CO})]^+$ in 1.00 M (H,Na)Br. Lower part: differences between the observed and calculated absorbance vs. time using the rate constants given in the figure [eqn. (1)].

M NaOH(aq) at 65 °C for 10 min. The resulting solution was cooled to 0 °C and 1.0 ml 1.0 M NaClO₄(aq) was added. Unreacted carbonate complex was removed by filtration as the perchlorate salt, and the filtrate was rapidly added to 2.0 ml 1.0 M HClO₄(aq) at 0 °C. The pink precipitate was filtered off and dried in air. Yield: 0.2 g of a product containing the pure chromium(III) species as judged from the visible absorption spectrum, but also varying amounts of perchloric acid and water. Typical preparations gave $x \approx 0.5$ and $y \approx 2-4$. Analyses: Cr, Cl, N, C and H. This compound is not stable for an extended period of time as it decarboxylates slowly in the solid state.

Kinetic measurements. The reactions were followed spectrophotometrically using either a Cary 118C or an RC-Partner computer-controlled Perkin-Elmer Lambda-17 spectrophotometer both equipped with Perkin-Elmer digital temperature controllers. The transformations were usually followed at a single wavelength. Two such examples are

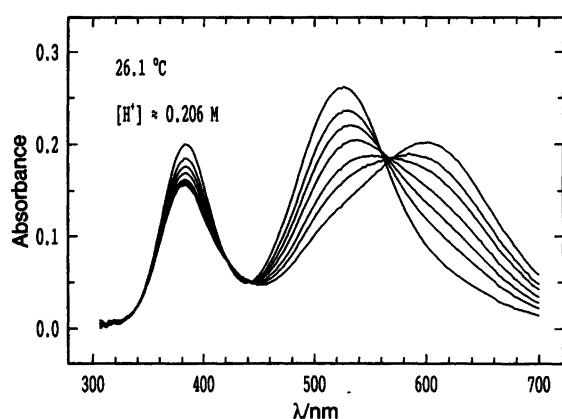


Fig. 6. Spectra of $\text{cis-}[\text{Cr}(\text{cycb})(\text{O}_2\text{CO})]^+$ hydrolysed in 1.00 M (H,Na)Br, and quenched by the addition of an excess of 1 M NaOH. These spectra as a function of time give $k_{\text{ab}} \approx 0.0384$ (14) s⁻¹, $k_{\text{ba}} \approx 0.0121$ (20) s⁻¹ and $k_{\text{b}} \approx 0.0192$ (15) s⁻¹ (Fig. 3). By use of eqn. (2) $k_1 \approx 0.057$ s⁻¹ and $k_2 \approx 0.0130$ s⁻¹ are calculated. This is seen to be in good agreement with the data in Fig. 5.

shown in Fig. 5. In some experiments acidic reaction mixtures were quenched by addition of base, and absorption spectra from 300 to 700 nm were measured and used for the determination of individual complex concentrations as a function of time. One such kinetic run is shown in Fig. 6. A range of nitrogen bases were used as buffers to maintain a suitable constant hydrogen ion concentration at intermediate acidities. Both pyridine- and amine-type buffers are suitable, as neither reacts with the chromium(III) species. This was judged both from the absence of spectral changes and the absence of buffer concentration dependences on reaction rates.

The range of buffers included 3-chloropyridine, 4-chloropyridine, pyridine, 2-methylpyridine, 2,6-dimethylpyridine and 1,2-ethanediamine (Table 2 and the data in Fig. 4). The use of 4-chloropyridine is somewhat problematical, as it decomposes and solutions develop an intense yellow colour. Apparently this does not affect spectral measurements at higher wavelengths or reaction rates, and as a readily available non-interfering alternative was not found a few measurements around $[\text{H}^+] \approx 10^{-4}$ M were performed despite the shortcomings of this buffer system.

Hydrogen ion concentration measurements. Hydrogen ion concentrations were measured with a Radiometer PHM 52 pH-meter equipped with standard glass and reference electrodes. The electrodes were calibrated by titrations of

Table 2. Acid dissociation constants at 25.0 and 40.0 °C in 1.00 M NaBr for the buffer substances used in this work. Standard deviations in parenthesis.

Basic form	$-\log[K(25^\circ\text{C})/\text{M}]$	$-\log[K(40^\circ\text{C})/\text{M}]$
3-Chloropyridine	3.310(8)	3.165(14)
4-Chloropyridine	4.238(3)	4.064(3)
Pyridine	5.601(7)	5.350(4)
2-Methylpyridine	6.374(8)	6.035(7)
2,6-Dimethylpyridine	7.194(8)	6.851(8)
2-Aminoethylammonium ion	7.481(12)	7.036(11)
1,2-Ethanediamine	10.290(17)	9.737(15)

strong acid with strong base in 1.00 M NaBr solution. All measurements of solutions from the kinetic runs were performed at 25 °C relative to a 0.001000 M HBr + 0.999 M NaBr solution and corrected to the temperature of the kinetic experiment by the temperature dependence of the buffer substances given in Table 2.

Determination of acid dissociation constants. This was performed as described previously.¹¹ Results for the buffer systems used are given in Table 2, and results for *cis*-[Cr(cycb)(OH₂)₂]³⁺ are given in Table 1. *cis*-[Cr(cycb)(OH₂)(OCCOOH)]²⁺ was too labile to be titrated, and the acid dissociation constants for this species were determined from the kinetic measurements (Table 1 and Fig. 4).

Methods of calculation. All parameter values were determined by minimizations within the framework of non-linear regression analysis. Rate constants for kinetic runs followed at a single wavelength were determined by minimization of

$$\sum_i [A(t)_{\text{obsd}} - A(t)_{\text{calcd}}]^2 / \sigma^2 [A(t)_{\text{obsd}}]$$

where $A(t)_{\text{obsd}}$ and $\sigma[A(t)_{\text{obsd}}]$ are the absorbance and standard deviation upon absorbance, respectively, at time t , and $A(t)_{\text{calcd}}$ is given by eqn. (4) or (5).

$$A(t)_{\text{calcd}} = a_0 + a_1 \exp(-k_1 t) + a_2 \exp(-k_2 t) \quad (4)$$

$$A(t)_{\text{calcd}} = a_0 + a_1 \exp(-k_1 t) + a_2 t \quad (5)$$

The latter alternative was used in those cases with intermediate hydrogen ion concentrations where only the faster equilibration reaction was followed, cf. the data in Fig. 4. The minimizations were carried out as a function of a_0 , a_1 , a_2 , k_1 and k_2 . The agreement between the experimental and calculated data is shown with two examples in Fig. 5. The method used to derive rate constants from the multi-wavelength spectral experiments such as that shown in Fig. 6 are described in detail in Ref. 12.

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