Kinetics and Equilibria of 1:1 Complex Formation of Hexa-aquatitanium(III) with Malonic and Methylmalonic Acid

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Equilibria and kinetics of the 1:1 complex formation of Ti^{III} with malonic acid and methylmalonic acid have been investigated at 15 °C, ionic strength $I = 0.5$ mol dm^{-3} (LiCl). Spectrophotometric measurements yielded for the complex stability constant $K_c = [TiL^+]/[Ti^{3+}][L^{2-}]$ values of 3.4×10^6 (malonic acid) and 4.0×10^6 dm^3 mol^{-1} (methylmalonic acid). The kinetics of the complex-formation process show simple behaviour within the acidity range $[H^+] = 0.05$—0.30 mol dm^{-3}, the apparent second-order rate constant being of the form $k_a = k[H^+]$. It is concluded that under these conditions only the reaction path $Ti^{3+} + HL^- \xrightarrow{k_2} [TiL]^+ + H^+$ contributes to the complex formation, with $k_2 = 4.2 \times 10^5$ (malonic acid) and 3.2×10^5 dm^3 mol^{-1} s^{-1} (methylmalonic acid), respectively. Together with data obtained earlier, the results indicate an associative-interchange mechanism for substitution at $[Ti(H_2O)_6]^{3+}$.

Kinetic studies of the 1:1 complex formation reactions of $[Ti(H_2O)_6]^{3+}$ with thiocyanate,[1] oxalate,[2] acetate,[3] monochloroacetate and dichloroacetate[3] have previously been reported. The kinetic data strongly suggest an associative type of mechanism (I_a) for substitution at $[Ti(H_2O)_6]^{3+}$, probably a consequence of the high positive charge at the metal centre and of the low occupancy of the t_{2g} orbitals, both of which favour the formation of a transition state of increased co-ordination number. Additional information on this subject is provided by the present study in which the kinetics of the complex-formation reactions of Ti^{III} with malonic and methylmalonic acid are reported.

Experimental

The carboxylic acids and other chemicals used were of the best grade available (E. Merck, Fluka) and were used without further purification. The preparation and standardization of titanium(III) solutions have already been described.[2] In order to avoid aerial oxidation of Ti^{III}, all experiments were performed under an atmosphere of nitrogen, and the ligand solutions were purged thoroughly with nitrogen before mixing with Ti^{III}. Measurements of pH and the conversion of pH values into hydrogen-ion concentrations were carried out as described before.[3] A Cary 118 instrument was used for the spectrophotometric studies. The kinetics of the complex-formation reactions were investigated by means of the temperature-jump relaxation technique with spectrophotometric detection, using an instrument built at our Institute. At least four individual measurements were made with each solution. The relaxation curves were evaluated by means of an electronic simulator. The deviations of the individual time constants from the mean were always smaller than 10%. All measurements were carried out at 15 C, ionic strength $I = 0.5$ mol dm^{-3} (adjusted with LiCl).

Results and Discussion

For the hydrolytic dissociation constant of Ti^{III}, $K_H = [Ti(OH)^{2+}][H^+]/[Ti^{3+}]$, a value of 1.12×10^{-2} mol dm^{-3} has been reported at 15 C, $I = 0.5$ mol dm^{-3}.[3,4]

The dissociation constants of the ligands are defined by $K_{L1} = [H^+][HL^-]/[H_2L]$ and $K_{L2} = [H^+][L^{2-}]/[HL^-]$. where L^{2-} denotes the dianion of either malonic or methylmalonic acid. Values of K_{L1} were evaluated from pH

Table 1. Acid dissociation constants (K_{L1}, K_{L2}) of malonic and methylmalonic acid, and stability constants (K_c) of the 1:1 complexes of these ligands with Ti^{III} (15 °C, $I = 0.5$ mol dm^{-3})

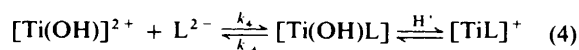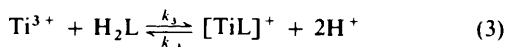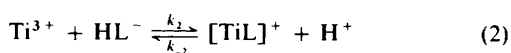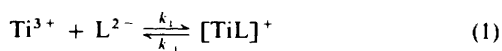| Acid	$\dfrac{10^3 K_{L1}}{\text{mol dm}^{-3}}$	$\dfrac{10^6 K_{L2}}{\text{mol dm}^{-3}}$	$\dfrac{10^{-6} K_c}{\text{dm}^3 \text{ mol}^{-1}}$
Malonic	3.68 ± 0.2	12.6 ± 1.2	3.4 ± 0.3
Methylmalonic	2.40 ± 0.1	8.7 ± 0.2	4.0 ± 0.3

measurements of solutions containing various concentrations of the dicarboxylic acid (0.005—0.02 mol dm^{-3}). The dissociation constants K_{L2} were determined from pH measurements of 0.01 mol dm^{-3} solutions of the dicarboxylic acid to which varying amounts of NaOH (0.012—0.016 mol dm^{-3}) had been added. The two dissociation constants are so far apart that one equilibrium can always be neglected under our conditions. Results are given in Table 1, and are consistent with literature values[5,6] reported for somewhat different conditions.

The stability constants of the complexes of Ti^{3+} with these ligands, $K_c = [TiL^+]/[Ti^{3+}][L^{2-}]$, have been determined spectrophotometrically (2-cm cells), measuring the absorption due to the complex species at 270 nm. The individual reactants absorb only very slightly at this wavelength. The equilibrium studies have been carried out under the following concentration conditions: $[Ti]_T = 0.002, [L]_T = 0.02$—$0.1,$ and $[H^+] = 0.1$—0.3 mol dm^{-3} where $[Ti]_T$ and $[L]_T$ denote the total concentrations of Ti^{III} and ligand, respectively. An evaluation of the spectrophotometric data according to Bent and French[7] confirmed that only 1:1 complexes are formed under these conditions. The complex stability constants have been determined using the procedure described previously.[3] The values obtained are included in Table 1. Significant concentrations of protonated complex species, $[Ti(HL)]^{2+}$, are not formed under our conditions.

The stability constants K_c (Table 1) are about one order of magnitude smaller than those of the corresponding iron(III) complexes.[6] This difference, which has been pointed out before[2,3] with respect to other ligands, is apparently due to the somewhat larger radius of the Ti^{3+} ion as compared to Fe^{3+}.

The kinetic investigations have been carried out using the following reactant concentrations: $[Ti]_T = 2.07 \times 10^{-3}$, $[malonic\ acid]_T = (2$—$10) \times 10^{-2}$, $[H^+] = 0.05$—0.25, and

$[Ti]_T = 2.02 \times 10^{-3}$; [methylmalonic acid]$_T = 6 \times 10^{-2}$, $[H^+] = 0.05$—0.30 mol dm^{-3}. The general reaction scheme shown in equations (1)—(6) was considered for the formation of

$$Ti^{3+} + L^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [TiL]^+ \qquad (1)$$

$$Ti^{3+} + HL^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [TiL]^+ + H^+ \qquad (2)$$

$$Ti^{3+} + H_2L \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [TiL]^+ + 2H^+ \qquad (3)$$

$$[Ti(OH)]^{2+} + L^{2-} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} [Ti(OH)L] \overset{H^+}{\rightleftharpoons} [TiL]^+ \qquad (4)$$

$$[Ti(OH)]^{2+} + HL^- \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} [TiL]^+ \qquad (5)$$

$$[Ti(OH)]^{2+} + H_2L \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} [TiL]^+ + H^+ \qquad (6)$$
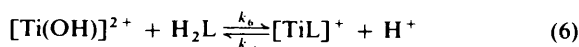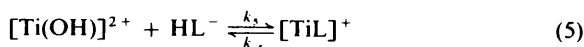
the 1:1 complexes. The individual pathways are coupled to each other by protolytic processes. The protolytic steps are assumed to equilibrate very rapidly as compared to the complex-formation reactions, and the species [Ti(OH)L] was considered to be a steady-state intermediate. Only one reaction effect for the complex formation should then be observed, and the rate equation is of the form (7) with k_a and k_b defined as in equations

$$d[TiL^+]/dt = k_a[Ti^{3+}][L^{2-}] - k_b[TiL^+] \qquad (7)$$

(8) and (9) and where $K_{COH} = [Ti(OH)L][H^+]/[TiL^+]$.

From equations (7)—(9) the expression (10) for the reciprocal

$$k_a = k_1 + \frac{k_2[H^+]}{K_{L2}} + \frac{k_3[H^+]^2}{K_{L1}K_{L2}} + \frac{k_4 K_H}{[H^+]} + \frac{k_5 K_H}{K_{L2}} + \frac{k_6 K_H[H^+]}{K_{L1}K_{L2}} \qquad (8)$$

$$k_b = k_{-1} + k_{-2}[H^+] + k_{-3}[H^+]^2 + k_{-4}K_{COH}[H^+]^{-1} + k_{-5} + k_{-6}[H^+] \qquad (9)$$

relaxation time is derived, where under our conditions {i.e. with $K_{L2} \ll [H^+]$ and $[Ti(OH)^{2+}] \ll [H^+]$}, A and B are defined as in equations (11) and (12). The somewhat complicated form of

$$1/\tau = k_a(A[L^{2-}] + B[Ti^{3+}]) + k_b \qquad (10)$$

$$A = [H^+]/(K_H + [H^+]) \qquad (11)$$

$$B = \frac{(K_H + K_{L1} + 2[H^+])(K_{L1}[L^{2-}] + 2[H^+][L^{2-}])}{(K_H + [H^+])(K_{L1} + [H^+] + [HL^-])(K_{L1} + [H^+])} + \frac{K_{L1}K_{L2}}{K_{L1}[H^+] + [H^+]^2} \qquad (12)$$

B is due to the fact that the concentration of H^+ cannot be considered as constant during the relaxation process.

As expected, only one relaxation effect was observed, $\tau = 0.3$—0.8 ms (270 nm). The kinetic data were evaluated by substituting k_b by k_a/K_c and plotting the left-hand side of equation (13) versus $[H^+]$, see Figure. The concentrations of the individual reactant species were calculated from $[Ti]_T$, $[L]_T$,

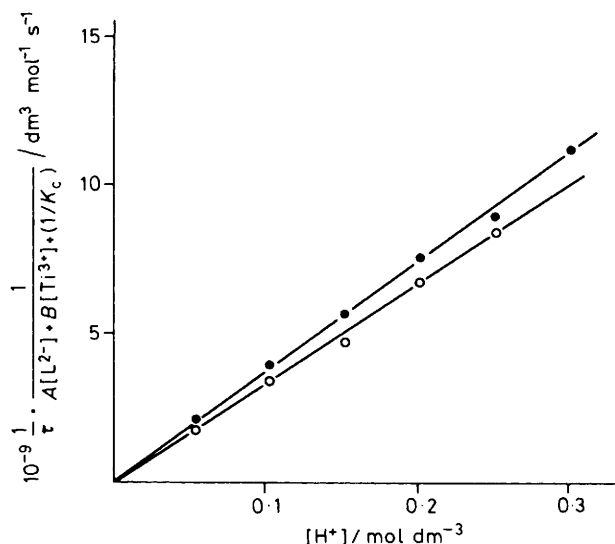$$\frac{1}{\tau} \cdot \frac{1}{A[L^{2-}] + B[Ti^{3+}] + (1/K_c)} = k_a \qquad (13)$$

Figure. Dependence of $k_a = \tau^{-1}\{A[L^{2-}] + B[Ti^{3+}] + (1/K_c)\}^{-1}$ on $[H^+]$ for Ti^{III} + malonic acid ($\bigcirc$) and Ti^{III} + methylmalonic acid ($\bullet$)

and $[H^+]$ and the known equilibrium constants (Table 1). Within the experimental accuracy the data yield straight lines with zero intercepts (intercept $\leq 2 \times 10^8$ dm^3 mol^{-1} s^{-1}) and thus demonstrate that under our conditions the rate terms with k_1, k_3, k_4, and k_5 do not contribute measurably to the overall rate constant k_a, see equation (8). The slopes of the straight lines yield $k_2/K_{L2} + k_6 K_H/K_{L1}K_{L2} = 3.34 \times 10^{10}$ dm^6 mol^{-2} s^{-1} for malonic acid and 3.67×10^{10} dm^6 mol^{-2} s^{-1} for methylmalonic acid. Assuming that only one of the two pathways (2) and (6) is of significance, the following rate constants are obtained: Ti^{III} + malonic acid, $k_2 = 4.2 \times 10^5$ dm^3 mol^{-1} s^{-1} or $k_6 = 1.4 \times 10^5$ dm^3 mol^{-1} s^{-1}, and Ti^{III} + methylmalonic acid, $k_2 = 3.2 \times 10^5$ or $k_6 = 6.8 \times 10^4$ dm^3 mol^{-1} s^{-1}. While these two pathways cannot be distinguished kinetically, previous observations allow certain conclusions. For instance, it had been observed [3] that Ti^{3+} reacts with a deprotonated carboxylic group much faster (100—1 000-fold) than with the protonated form. Now, if in the present systems k_6 were close to 1×10^5 dm^3 mol^{-1} s^{-1} and k_5 only 10-fold higher, then clearly detectable intercepts of ca. 1×10^9 dm^3 mol^{-1} s^{-1} should be obtained for the plots shown in the Figure, contrary to our findings. Also, it has been observed that $[Ti(OH)]^{2+}$ does not react much faster than Ti^{3+} with a given ligand; [1,2] since the linearity of the plots in the Figure indicates that $k_3 \leq 5 \times 10^2$ dm^3 mol^{-1} s^{-1}, values near 1×10^5 dm^3 mol^{-1} s^{-1} for k_6 appear to be too high by several orders of magnitude. Therefore, one may safely conclude that the rate law observed is due to the pathway Ti^{3+} + HL^-, and that the true values of k_6 are much lower than the upper limits quoted above. This conclusion is readily rationalized: the fully protonated ligand, H_2L, is a much weaker nucleophile than HL^-. On the other hand, the concentration of L^{2-} is far too low to contribute appreciably to the overall reaction. From the near-zero intercepts it follows that $k_5 \leq 2 \times 10^5$ dm^3 mol^{-1} s^{-1}.

These dicarboxylic acids have also been used as ligands in studies of the kinetics of 1:1 complex-formation reactions with Fe^{III}.[6] At the same hydrogen-ion concentration, the apparent second-order rate constants k_a are about 50 times smaller in the reactions with Fe^{III} as compared to those involving Ti^{III}. However, it is well known that complex-formation reactions of $[Fe(OH)]^{2+}$ are much faster than those of Fe^{3+}, and therefore

Table 2. Complex-formation rate constants for the reaction of $[Ti(H_2O)_6]^{3+}$ with various ligands

Ligand	k_f/dm^3 $mol^{-1} s^{-1}$	Conditions [a]	Ref.
$ClCH_2CO_2H$	0.7×10^3	15, 0.5	3
CH_3CO_2H	1×10^3	15, 0.5	3
NCS^-	8×10^3	8—9, 1.5	1
H_2O	1×10^{5} [b]	25, ca. 0.1	c
Cl_2CHCO_2	1.1×10^5	15, 0.5	3
$ClCH_2CO_2^-$	2.1×10^5	15, 0.5	3
Methylmalonate(1 −)	3.2×10^5	15, 0.5	This work
$HC_2O_4^-$	3.9×10^5	10, 1.0	2
Malonate(1 −)	4.2×10^5	15, 0.5	This work
$CH_3CO_2^-$	1.8×10^6	15, 0.5	3

[a] Temperature in °C, ionic strength in mol dm^{-3}. [b] Water-exchange rate, k_{ex}/s^{-1}. [c] A. M. Chmelnick and D. Fiat, *J. Chem. Phys.*, 1969, **51**, 4238.

the interpretation in terms of individual reaction pathways is different [6] from the one given here for Ti^{III}.

The results of the present study together with earlier data for substitution at Ti^{3+} are compiled in Table 2. The variation of the formation rate constants k_f over more than three orders of magnitude and the general increase of k_f with the ligand's basicity provide strong evidence for an associative-interchange mechanism (I_a) [8] in substitution processes at $[Ti(H_2O)_6]^{3+}$. The negative values of the volumes of activation for the

exchange of H_2O between bulk solvent and several hexa-aquametal(III) ions, including $[Ti(H_2O)_6]^{3+}$, obtained recently [9] by high-pressure oxygen-17 n.m.r. experiments also indicate the formation of a transition state of increased co-ordination number in these reactions.

Acknowledgements

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