J. CHEM. SOC. DALTON TRANS. 1982

Equilibria and Mechanism of the Interaction of In^{III} with the Indicator Ferron †

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The interaction between In^{III} and the indicator ferron (H_2L) has been investigated at 25 °C, ionic strength of 0.2 mol dm^{-3}, and $[H^+] = 0.008$—0.2 mol dm^{-3}. Two complexes were observed, namely, $[InL]^+$ with $K_1 = 237 \pm 7$ and $[In(HL)]^{2+}$ with $K_1' = 688 \pm 65$ dm^3 mol^{-1}. The formation of the complexes proceeds *via* three parallel paths differing in their $[H^+]$ dependences. One of these can be uniquely assigned to the reaction between In^{3+} and H_2L with a forward rate constant of $(1.1 \pm 0.1) \times 10^3$ dm^3 mol^{-1} s^{-1}; each of the other two is in fact a proton-ambiguous pair, one involving In^{3+} and HL^-, and/or $[In(OH)]^{2+}$ and H_2L, and the other (which makes a smaller contribution) involving $[In(OH)]^{2+}$ and HL^-, and/or $[In(OH)_2]^+$ and H_2L. For these pairs, only upper limits for the rate constants can be given. Nevertheless, it can be concluded unequivocally that the hydrolysed species react faster than In^{3+}. The results are compared with previous data involving In^{III} and are discussed in terms of the dissociative Eigen mechanism *vs.* an associative mechanism.

In order to serve as an indicator in complexometric titrations of metal ions a compound must form complexes which are strong, but not too strong. Furthermore, the colour of the complex must differ from that of the free indicator so that complex formation can be detected visually. These properties make indicators especially suitable for the investigation of the mechanism of complex formation involving metal ions which do not absorb in the visible or accessible u.v. range.

We decided to make use of this fact in the continuation of our program [1] of studying substitution reactions on tervalent metal cations. Whereas for *bi*valent cations the dissociative Eigen mechanism seems to be almost universally [2] accepted (see, however, ref. 3), the position with respect to *ter*valent cations is much less clear.

As we pass from Al^{III} to Ga^{III} the rate constants increase. On the other hand, the difference between the reactivity of the aqua-ions and the hydrolyzed species becomes less pronounced. In order to enable additional comparisons to be made, we have now extended our investigation to In^{III}, a cation which has been comparatively little investigated.[4–7]

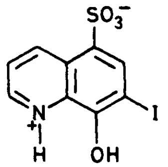
We found a suitable ligand in ferron (8-hydroxy-7-iodoquinolinium-5-sulphonate), a diprotic acid which we shall abbreviate as H_2L.

Experimental

The indium perchlorate solution was prepared by dissolving a weighed amount of the pure metal in a known excess of perchloric acid. The concentration was checked by titrating with ethylenediaminetetra-acetate (edta) (using 1-(2′-pyridylazo)-naphth-2-ol as an indicator), and was found to correspond exactly to that calculated from the weight of the metal. The ferron was BDH AnalaR.

The concentrations of the cation, c_M, ranged between 10^{-3} and 5×10^{-3} mol dm^{-3} and were always in excess over those of the ligand, c_L, which ranged between 5×10^{-5} and 2×10^{-4} mol dm^{-3}. The hydrogen-ion concentration ranged between 0.008 and 0.2 mol dm^{-3}; its change during the reaction was therefore negligibly small. Furthermore, under these conditions the formation of binuclear forms of In^{III} can be neglected.[8]

Equilibrium constants were determined by spectrophotometric titration, using a Perkin-Elmer E200 spectrophotometer.



The kinetic results were obtained by the stopped-flow technique, using a Durrum model D-110 stopped-flow spectrophotometer. From the exponential change of the absorbance A with time we evaluated $k_{obs.}$, the pseudo-first-order rate constant, using $k_{obs.} = d\ln(A_t - A_\infty)/dt$. The results of duplicate runs exhibited a spread of 10% at most, usually much less.

Unless otherwise stated, experiments were carried out at a wavelength of 400 nm, where the difference in absorption between complex and free ligand has its largest relative value.

The temperature was 25.0 °C and the ionic strength was 0.2 mol dm^{-3}, regulated by the addition of sodium perchlorate.

Results

Equilibrium Constants.—The value of K_{A1}, the first dissociation constant of H_2L, was determined at 360 nm, using a method of calculation described earlier.[1c] We found $K_{A1} = (4.19 \pm 0.07) \times 10^{-3}$ mol dm^{-3}, in good agreement with previous data.[9]

For the formation constant of our complex we again [1] define an apparent, $[H^+]$-dependent, quantity, as in equation (i) with $\alpha = 1 + ([H^+]/K_{A1})$ and $\beta = 1 + (K_{OH1}/[H^+])$, where

$$K_{app} = \frac{[\text{complex}]}{[\text{free ligand}][\text{free metal}]} = \frac{[\text{complex}]}{[HL^-][In^{3+}]\alpha\beta} \quad (i)$$

K_{OH1} is the hydrolysis constant of indium. Widely differing values are quoted in the literature [10] for this constant. However, with any of the possible data, the value of β is very nearly unity. We decided to base our calculations on $K_{OH1} = 5.2 \times 10^{-4}$ mol dm^{-3}, a value obtained at $I = 0.1$ mol dm^{-3}, an ionic strength nearest to ours.[10b]

Figure 1 shows a typical example of a spectrophotometric titration ($[H^+] = 0.05$ mol dm^{-3}). Nine titrations of this kind

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† 8-Hydroxy-7-iodoquinolinium-5-sulphonate.

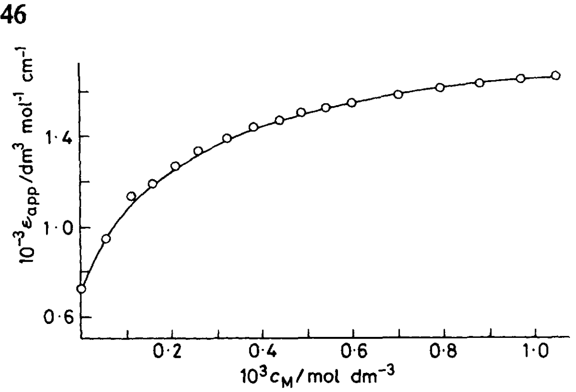


Figure 1. An example of a spectrophotometric titration: the change of ε_{app} with metal ion concentration (where ε_{app} is the absorbance divided by c_L, the stoicheiometric concentration of the ligand); $[H^+] = 0.05$ mol dm^{-3}, $c_L = 2 \times 10^{-4}$—1.5×10^{-4} mol dm^{-3}

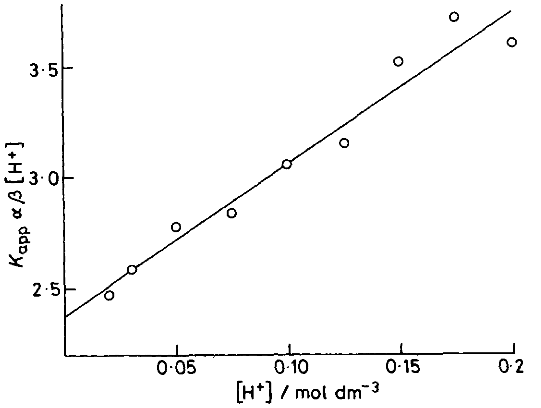


Figure 2. Dependence of $K_{app}\alpha\beta[H^+]$ on hydrogen-ion concentration, where K_{app} is defined in equation (i)

were carried out, at different hydrogen-ion concentrations. From these data, values of K_{app} and $\varepsilon_{complex}$ were evaluated, using the Benesi–Hildebrand method.[1b,11]

If only one complex, $[InL]^+$, were formed, then $K_{app}\alpha\beta[H^+]$ would be a true constant. Instead, this quantity increased linearly with increasing $[H^+]$, as shown in Figure 2. We conclude that two complexes are formed, differing in their degree of protonation so that, again,[1b] $K_{app}\alpha\beta[H^+] = K_1 + K_1'[H^+]$. From the intercept and slope of our figure, we obtain $K_1 = [InL^+][H^+]/[In^{3+}][HL^-] = 237 \pm 7$ and $K_1' = [In(HL)^{2+}]/[In^{3+}][HL^-] = 688 \pm 65$ dm^3 mol^{-1}.

The values of $\varepsilon_{complex}$ were also found to depend somewhat on $[H^+]$. This is because $\varepsilon_{complex}$ is made up of the weighted contributions of the two complexes.[1b] A plot of $\varepsilon_{complex}(K_1 + K_1'[H^+])$ as a function of $[H^+]$ was linear; from its intercept and slope, together with the above values of K_1 and K_1', we found $\varepsilon_{ML} = (1.95 \pm 0.07) \times 10^3$ and $\varepsilon_{M(HL)} = (1.25 \pm 0.15) \times 10^3$ dm^3 mol^{-1} cm^{-1} at 400 nm.

Kinetic Results.—Representative results are given in Figure 3 which shows the observed pseudo-first-order rate constant $k_{obs.}$ as a function of $[H^+]$ for $c_M = 2 \times 10^{-3}$ mol dm^{-3}.

In order to calculate the forward rate constants from $k_{obs.}$, we again [1] found it convenient to define a quantity B as in (ii).

$$B \equiv [H^+](K_{app}c_M + 1)/(K_1 + K_1'[H^+]) = (c_M/\alpha\beta) + [H^+]/(K_1 + K_1'[H^+]) \quad \text{(ii)}$$

The expression $k_{obs.}/B$ is independent of concentration, but depends on $[H^+]$ if more than one reaction path is operative.

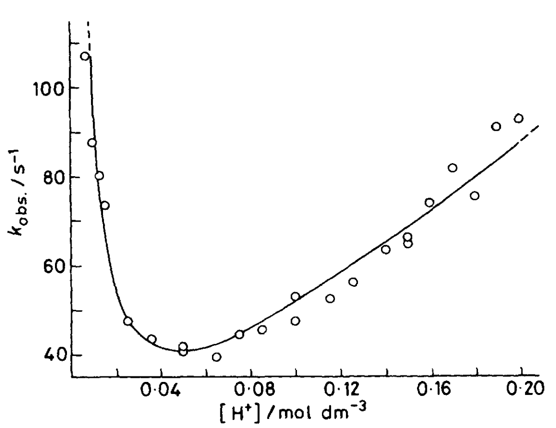


Figure 3. Dependence of $k_{obs.}$ on the hydrogen-ion concentration, at $c_M = 2 \times 10^{-3}$ mol dm^{-3}. The line is calculated from the parameters obtained using the results at *all* values of c_M

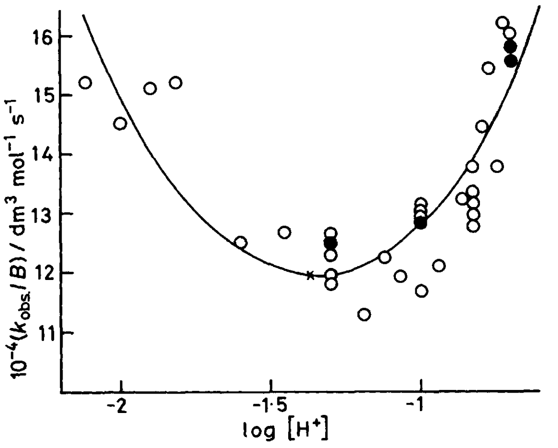
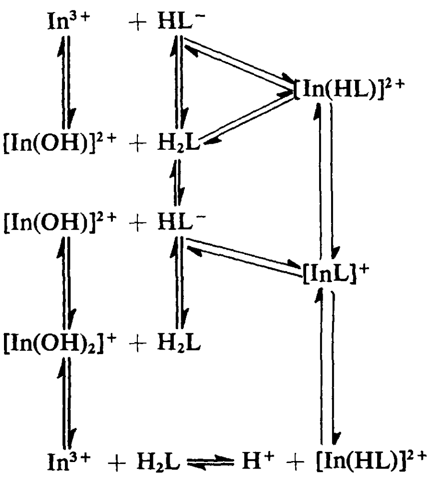


Figure 4. Dependence of $k_{obs.}/B$ on $\log[H^+]$, where B is defined as in equation (ii): ●, two experiments coinciding; ×, calculated minimum



In Figure 4 we have plotted $k_{obs.}/B$ as a function of $\log[H^+]$. The form of the curve suggests [1e] that it should be possible to write $k_{obs.}/B$ as a linear regression, as in (iii). A

$$k_{obs.}/B = a + b[H^+]^{-1} + c[H^+] \quad \text{(iii)}$$

reaction scheme compatible with this assumption (omitting water molecules) is shown in equations (1)—(3), where the

Table. Comparison of rate constants for In^{3+}

Ligand	$10^{-4}k$/ dm^3 mol^{-1} s^{-1}	I/ mol dm^{-3}	z	K_{os}/ dm^3 mol^{-1}	k/K_{os}/ s^{-1}	Ref.
H_2L	0.108	0.2	+1	0.04 [a]	2.7×10^4	This
			0	0.3 [a]	3.5×10^3	work
HL^-	$\leqslant 9.69$	0.2	0	0.3 [a]	$\leqslant 3.1 \times 10^5$	This
			−1	3 [a]	$\leqslant 3.8 \times 10^4$	work
Murexide ion	60		−1	*ca.* 5 [a]	1.2×10^5	7
Semixylenol orange dianion	28	0.1	−1	5 [a]	5.7×10^4	6
			−2	8×10 [a]	3.7×10^3	
SO_4^{2-}	26	0	−2	10^3 [b]	2.6×10^2	5
H_2O					2×10^4	14

[a] Calculated from the Fuoss equation with $a = 5$ Å and corrected for ionic strength using the Davies equation. [b] Ref. 5.

vertical equilibria can again be assumed to be rapid. Reactions (1) and (1a), and (2) and (2a), respectively, are seen to be proton-ambiguous. An additional reaction, namely that between In^{3+} and L^{2-}, proton-ambiguous with (2) and (2a), has been excluded because of the low relative concentration of L^{2-} ($pK_{A2} = 7.08$ [9]). The regression coefficients of equation (iii) are $a = k_1 + (k_{1a}K_{OH1}/K_{A1}) = (9.69 \pm 0.41) \times 10^4$ dm^3 mol^{-1} s^{-1}, $b = k_2K_{OH1} + (k_{2a}K_{OH1}K_{OH2}/K_{A1}) = (5.0 \pm 0.6) \times 10^2$ s^{-1}, and $c = k_3/K_{A1} = (2.59 \pm 0.28) \times 10^5$ dm^6 mol^{-2} s^{-1}, where K_{OH2} is the hydrolysis constant of $[In(OH)]^{2+}$. The value of k_3 is readily calculated from c. For the rate constants pertaining to proton-ambiguous paths we can only estimate upper limits. Furthermore, it must be remembered that the considerable uncertainty in K_{OH1} and K_{OH2} is reflected in k_{1a}, k_2, and k_{2a}. The results are as follows: $k_1 \leqslant (9.69 \pm 0.41) \times 10^4$, $k_{1a} \leqslant 80 \times 10^4$, $k_2 \leqslant 10^6$, $k_{2a} \leqslant 10^7$ (using [10b] $K_{OH2} = 9.6 \times 10^{-5}$ mol dm^{-3}), $k_3 = (1.08 \pm 0.12) \times 10^3$ dm^3 mol^{-1} s^{-1}; $k_{-1} = k_{-1a} = 141 \pm 15$, $k_{-2} = k_{-2a} = 2.1$ s^{-1}; $k_{-3} = 376 \pm 74$ dm^3 mol^{-1} s^{-1}.

Discussion

Equilibrium Constants.—The complex $[InL]^+$ may be expected to be stabilized by chelate formation. The protonated complex $[In(HL)]^{2+}$, although less likely to be stabilized in this way, is nevertheless present in appreciable concentrations. It is interesting to note that in the gallium(III)–5-nitrosalicylate system, too, a protonated complex was found to be present,[1b] but not in the analogous aluminium(III) system.[1g] If the ratio K_1'/K_1 were the same in the two latter systems, the formation of the protonated complex ought to have made itself felt {although $[H^+]$ was lower in the aluminium(III) than in the gallium(III) system}. We suggest that this might be connected with the decreasing ionic radius [12] as we pass from In^{3+} *via* Ga^{3+} to Al^{3+}, the smaller radius entailing a higher charge density on the central ion with a concomitant stronger repulsion for the proton attached to the ligand. A similar connection between the stability of the protonated complex and the ionic radius can be seen, for instance, in lanthanide–malonate systems.[13]

Rate Constants.—If the reaction proceeds *via* the Eigen mechanism [2] then the forward rate constant divided by the ion-pair formation constant K_{os} should be constant and equal to 2×10^4 s^{-1}, the first-order rate constant for the exchange of water between the inner co-ordination sphere and bulk water,[14] multiplied [15] by a statistical factor of 0.75. Even if a different mechanism is operative, the quantity k/K_{os} is still meaningful because it should provide a suitable means for correcting for the charge effect and for ionic strength. Unfortunately, for ferron, and also for the dianion of semixylenol orange, the calculation of K_{os} is not entirely unambiguous, because it is difficult to decide to what extent the charge on the SO_3^- group should be taken into account, since it is rather far removed from the reaction site (see, for instance, ref. 1*e* and references cited therein). We have calculated k/K_{os} for the two extreme possibilities. Some further uncertainty is inherent in the calculation of K_{os} because the distance of closest approach can only be rather arbitrarily assumed. The Table shows the results for all available data.

All values are higher than those found for similar reactions involving Ga^{3+} (see, for example, Figure 5 of ref. 1*b*) which, in turn, are higher than those obtained for substitution on Al^{3+}, an effect also observed [16] for dimethyl sulphoxide exchange on these three metals. This result is to be expected [17] on the basis of the decrease of charge density as we pass from Al^{3+} *via* Ga^{3+} to In^{3+}.

Instead of being equal for all ligands, as required by the Eigen mechanism, the values of k/K_{os} cover a wide range. Although, so far, no pattern emerges which would connect the rate constants with nucleophilic properties such as base strength or polarizability,[18] the very existence of this wide range is strongly indicative of an associative mechanism. Again, this is to be expected: for Al^{3+}, we found indications for an associative mechanism,[1g] but the discussion is not yet closed. For Ga^{3+}, the evidence for an associative mechanism is still stronger,[1b] although not undisputed.[17] For In^{3+}, which has the highest ionic radius, all evidence so far obtained points in the direction of an associative mechanism.

Because of proton ambiguity, no unique values can be given to the rate constants involving the hydrolysed species. This is because k_1 and k_{1a}, and k_2 and k_{2a}, are interconnected through expressions a and b, respectively, and any assignment of the relative contributions of the two pathways within the proton-ambiguous pairs would be entirely arbitrary, the upper limits reported resulting from two extreme, mutually exclusive, assumptions, namely that either *one*, or the *other*, pathway makes no contribution whatsoever. However, a comparison between these upper limits for k_{1a}, k_2, and k_{2a} on the one hand, and k_1 on the other, leads to the conclusion that, with any possible assignment, either $[In(OH)]^{2+}$, or $[In(OH)_2]^+$, or, more probably, both, must react with considerably higher rate constants than does In^{3+}. Similar results were obtained for the indium(III)–murexide [6] and –semixylenol orange [5] systems. Towards the sulphate ion,[4] the effect is somewhat more pronounced. The enhanced reactivity of the hydrolysed species resembles that found [1a,c] for Ga^{III}, and is less dramatic than that involving Al^{III}. As we have pointed out before,[1f] the enhanced reactivity of the hydrolysed form is no proof for an S_N1 mechanism for the aqua-ion.

Acknowledgements

We thank the Kultusministerium Niedersachsen, West Germany, for financial support, and are indebted to R. Corigli for carrying out part of the calculations and to Dr. H. Diebler, Max Planck Institute for Biophysical Chemistry, Göttingen, West Germany, for helpful discussions.

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Received 7*th October* 1981; *Paper* 1/1551