of thioglycolic acid at 30° and an ionic strength of 0.10, corresponding to an ionization constant of 2.82×10^{-4} compared to our 20° value of 3.89×10^{-4}, it is consistent that the rare earth complex stability constants observed at 30° are larger than those observed at 20° at a comparable ionic strength.

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The Kinetics of Formation of Some Divalent Transition Metal–Dye Complexes, Studied by the Temperature-Jump Relaxation Method

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The kinetics of reaction of pyridine-2-azo-*p*-dimethylaniline (I) with bivalent cobalt, nickel, copper, zinc, and cadmium have been measured by the temperature-jump relaxation method. The values for the second-order formation constant are compared with kinetic data for the reaction of other ligands with these metals, and the importance of dissociation of water from the metal aqua ion in the formation reaction is further substantiated.

Introduction

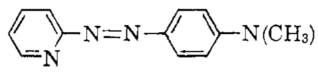
Divalent metal ions of the first transition series (vanadium–zinc) form metal complexes with simple ligands rapidly. The second-order formation rate constants are now known for the manganese–zinc series and especially for the slower reacting Ni(II) ion with a number of ligands.[2] These values have been determined by flow, relaxation, and competitive methods[3] and in some cases from a combination of dissociative rate and thermodynamic data. More information is required however, especially for the earlier members, bivalent vanadium and chromium, and for zinc (for comparison with cadmium) as well as the determination of Arrhenius parameters.

In the application of the temperature-jump method[4,5] to a metal–complex equilibrium

$$M + L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ML \qquad K, \text{ formation constant} \qquad (1)$$

One of the prerequisites for success is that the increase of temperature of some 10° promotes an easily detectable change in the concentration of one of the species present in the equilibrium.

This is most simply achieved by using a ligand (L) which does not complex too strongly with the metal. Since spectral is the most convenient detection method, it should also have a high molar extinction coefficient or produce a complex ML with a high absorption. This enables dilute solutions to be used with concomitant slower relaxation times (see Results). Examination of the literature for quantitative thermodynamic data[6] reveals that few metal–ligand systems fulfill these requirements, however. Nevertheless the dye, pyridine-2-azo-*p*-dimethylaniline (I), does chelate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weakly in aqueous solution with transition metal ions ($5 < K < 10^6$), and the complexes have strong absorption bonds ($\epsilon \sim 3 \times 10^4$) at about 550 m$\mu$, shifted some 80 m$\mu$ from those of the free ligand.[7] In addition, there is a small, but calculably sufficient, heat of reaction. Finally, if experiments are performed in the neutral pH region, protonated forms of the dye are not important ($\mathrm{p}K_1 \sim 4.5$) and equilibria involving these (which may even be rate-controlling) need not be considered.[8] Consequently the reaction rate constants k_1 and k_{-1} were determined from measurements on the cobalt(II), nickel(II), copper(II), zinc(II), and cadmium(II) *mono* complexes of I. Unfortunately, vanadium(II), chromium(II), and silver(I) ions rapidly decolorized the dye and could not be investigated. With iron(II), some slow color changes were observed on addition of the dye; without further investigation, it was therefore decided not to include this ion in the temperature-jump experiments.

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TABLE I

KINETIC DATA

Metal	Temp., °C.	$C_M \times 10^4$, M	$C_L \times 10^5$, M	τ, msec.	k_1, M^{-1} sec.$^{-1}$	k_{-1}, sec.$^{-1}$
Co^{2+}	14	14.0	2.0	20	3.2×10^4	5.3
	16	2.9	1.8	55	4.3×10^4	7.0
		14.0	1.8	16		
		14.0	1.8	15^a		
		43.0	3.0	5.8		
		86.0	1.8	2.5		
	22	14.0	2.0	13	5.0×10^4	9.2
	29	14.0	2.0	8.3	7.5×10^4	15
	42	14.0	2.0	3.2	1.9×10^5	43
Ni^{2+}	15	10.0	3.0	250	4.0×10^3	0.2
Cu^{2+}	15	0.22	1.8	0.36	0.9×10^8	0.9×10^3
		0.22	1.8	0.35^b	1.0×10^8	1.0×10^3
		0.40	1.5	0.19	1.2×10^8	1.2×10^3
		0.50	1.7	0.13	1.5×10^8	1.5×10^3
Zn^{2+}	15	1.0	16.2	0.09	4.1×10^6	1.0×10^4
		1.0	16.2	0.10	3.7×10^6	0.9×10^4
Cd^{2+}	15	1.0	16.2	~0.03	~1.3×10^7	~2.6×10^4

[a] pH adjusted to 7.2, all other Co work at 6.2 ± 0.1. [b] Observation at 470 mμ (dye peak), others at 570 mμ (Cu–dye peak).

Experimental

Materials.—The dye was prepared by the method of Faessinger and Brown.[9] The spectral characteristics of the dye and of the protonated and metal complex species were substantially those reported previously.[7] All inorganic chemicals were reagent grade, the metal salts used being hydrated nitrates or sulfates. Double distilled water was used in all experiments.

Kinetic Measurements.—The temperature-jump apparatus was that described by Czerlinski and Eigen.[4] The light beam from a tungsten lamp, passed through filters, was split into two portions, one of which passed through the solution in the cell. Both light components impinged on IP 28 photomultiplier tubes, which were linked to an oscilloscope. Changes in optical density of the solution as a result of the jump were shown as current changes on the oscilloscope. The trace was photographed and enlarged for measurement. In all cases these relaxation spectra were characterized by a single relaxation time, τ, defined by $d/dt(\Delta c) = -\Delta c/\tau$, where Δc indicates the deviation of the concentrations from their equilibrium values, directly related to the oscilloscope trace. τ was insensitive to the pH of the solution in the range 5.8–7.0. Nearly all the experiments were performed at pH ~6 and solutions contained 0.1 M KNO_3 for lowering the resistivity of the system. Fresh dye solutions were continually prepared since slight instability of dye solutions was observed. In the majority of runs, the cell was thermostated at 5 ± 1° and the temperature jump was approximately 10°. The wave length of observation corresponded to the metal dye complex absorption peak, which varied slightly with different metals (540–580 mμ). The results are collected in Table I. Quoted relaxation times were often the mean of several runs. The error in relaxation times is about ±10%, and somewhat higher for the shortest times quoted.

Results

Cobalt.—Because of the magnitude of the effect and the suitability of the relaxation times, the cobalt(II)–dye was the most thoroughly studied system. For reaction 1

$$\tau^{-1} = k_{-1} + k_1([M] + [L]) \qquad (2)$$

where τ is the relaxation time and [M] and [L] are the concentrations of *free* metal ion and ligand. In all experiments a relatively high ratio of total metal ion (C_M) to total dye concentration (C_L) was used. This not only ensured the presence in solution of the *mono* species only, but allowed an approximate form of (2) to be used

$$\tau^{-1} = k_{-1} + k_1(C_M - C_L) \qquad (3)$$

A series of experiments was performed at 16° using different total concentrations of metal ion (Table I). From the linear plot of τ^{-1} against $(C_M - C_L)$ (Fig. 1), $k_{-1} = 7$ sec.$^{-1}$, $k_1 = 4.3 \times 10^4$ M^{-1} sec.$^{-1}$, and $K = k_1/k_{-1} = 6 \times 10^3$ M^{-1}. The latter value is in reasonable agreement with that determined by Klotz and Loh Ming with different conditions (2.1×10^3 at 25°, $I = 0.15$).[7] It was also possible to investigate the cobalt(II) complex at higher temperatures (to 42°), the time losses due to cavitational effects in the cell solution at the highest temperatures (approximately 0.5 msec.) being unimportant compared with the relaxation times. Equation 3 can be rewritten

$$\tau^{-1} = k_1/K + k_1(C_M - C_L) \qquad (4)$$

so that k_1 can be estimated from the observed relaxation times at each temperature using values for the formation constant, determined above and modified for each temperature using a $\Delta H \sim 2$ kcal./mole.[7] This is very much a second-order correction, the energy of activation obtained being insensitive to the choice of K. A reasonable Arrhenius plot was obtained from the data in Table I (14, 22, 29, and 42°) yielding an energy of activation of 10 ± 2 kcal./mole.

Nickel.—The nickel–dye complex was somewhat too stable and slowly reacting to give good effects. If relaxation times much exceeded about 0.2 sec. then serious difficulties arose from temperature readjustment by conduction and convection within the cell. Flow methods would be more suitable for measuring the nickel–dye reaction.

Copper.—Klotz and Loh Ming[7] observed that the position and intensity of the absorption bands and the value of the formation constant of the copper–dye complex differed at pH 6.2 and 7.0. They ascribed

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(9) R. W. Faessinger and E. V. Brown, *J. Am. Chem. Soc.*, **73**, 4606 (1951).

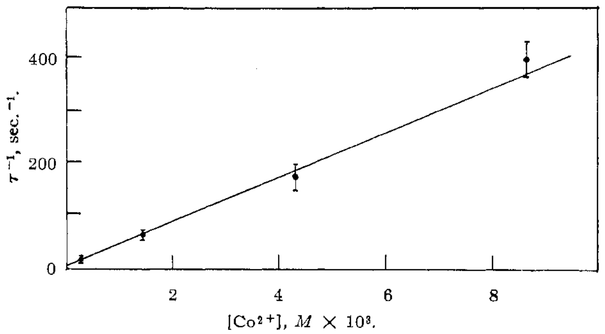

Fig. 1.—Effect of [Co^{2+}] on relaxation time of Co–dye complex.

this to the participation of hydroxy species in the equilibria. We have found relaxation times to be independent of the acidity from pH 5.7 to 6.6 so that reaction proceeds through the aqua complex and metal–hydroxy species appear not to be important kinetically. Values of k_1 in Table I are estimated from expression 2 substituting values for k_{-1} ($=k_1/K$), [M], and [L] calculated from the value of K (1.0×10^5).

Zinc and Cadmium.—Relaxation times for these metal systems were the fastest measured. Those for cadmium were close to the limiting values measurable with the temperature-jump apparatus used (~10 μsec.). The values of k_1 were estimated using a value of K for Zn–dye of 4.2×10^2. The formation constant for Cd–dye ($\sim 5 \times 10^2$) had not previously been determined but its measured value, although approximate, indicated that the formation rate constant for the cadmium complex exceeded that of the zinc by at least a factor of three.

Manganese.—Although relaxation times can be modified by adjusting reactant concentrations (see eq. 2), the value of k_{-1} may be of overriding importance if the formation constant is low, *i.e.*, $k_{-1} \sim k_1$. This is the situation with manganese for which $K = 5$, and a small effect was observed, too rapid to measure, indicating that $k_1 \geqslant 5 \times 10^5$ M^{-1} sec.$^{-1}$.

Discussion

The rate constants at 15° are collected in Table II, which also includes a comparable set of data for the reactions of the metal ions with sulfate[10] or acetate[11] (by sound-absorption experiments) and for water exchange (by nuclear magnetic resonance ^{17}O exchange studies),[12] the cited first-order rate constants corresponding to process 6.

Table II

Rate Constants for Metal Complex Formation

Metal	15° k_{dye}, M^{-1} sec.$^{-1}$	20° $k_{SO_4^{2-}}$, sec.$^{-1}$	20° $k_{CH_3COO^-}$, sec.$^{-1}$	25° k_{H_2O}, sec.$^{-1\,c}$
Co^{2+}	4.0×10^4	$2 \times 10^{5\,a}$	...	1.1×10^6
Ni^{2+}	4×10^3	$1.5 \times 10^{4\,a}$	...	2.7×10^4
Cu^{2+}	1×10^6	$>10^{7\,a}$	$4.3 \times 10^{8\,b}$	2×10^8
Zn^{2+}	4×10^6	$3 \times 10^{7\,b}$	$3 \times 10^{7\,b}$	...
Cd^{2+}	$\approx 1 \times 10^7$	$>10^{8\,b}$	$3 \times 10^{8\,b}$	...

[a] Reference 10. [b] Reference 11. [c] Reference 12.

It is now fairly clear[2,10,13] that the formation of complexes of bivalent and possibly tervalent[14] transition metal ions, so far examined, is dominated by the release of water molecules from the metal aqua ion. In the reaction of a hydrated metal ion (signified M_{aq}, with charges omitted) with a ligand (L_{aq}), prior formation of an ion pair or loose complex $[M(H_2O)L]_{aq}$ can be invoked from which water dissociates, in a rate-determining step, to form the complex $[ML]_{aq}$.[10]

$$M_{aq} + L_{aq} \rightleftharpoons [M(H_2O)L]_{aq} \qquad K_0 \qquad (5)$$

$$[M(H_2O)L]_{aq} \rightleftharpoons [ML]_{aq} + H_2O \qquad k_0,\ k_{-0} \qquad (6)$$

If this mechanism is correct, the experimental second-order constants for the formation of the metal dye complex k_1 ($=K_0k_0$) should differ from the first-order water exchange values (k_0) by a small factor (K_0) representing the formation constant of the intermediate $[M(H_2O)L]_{aq}$. For the dye ligand this factor can be estimated[5b] as very approximately 0.1, and by comparing the values in column 1 (Table II) with those in columns 2–4, which measure directly k_0, this is seen to be the case. The present study thus further substantiates the idea that for a particular metal, the rate-limiting step of complex formation is almost independent of the nature of the entering ligand, neutral or charged, large or small. In addition, the energy of activation for the cobalt–dye reaction (10 ± 2 kcal./mole) is close to that for cobalt(II) aqua ion exchange ($\Delta H^* = 8.0$ kcal./mole).[12]

The second and third row transition elements usually react slower than their first period counterparts.[15] Where crystal field effects are no longer operative, however, as with the d^{10} ions, this appears no longer to be true and cadmium reacts more rapidly than zinc with sulfate and acetate,[11] the azo dye used in the present study, and tripyridyl.[16]

Although we must be prepared for surprises, it now seems clear that we know the formation rate constants for the reactions of these metals with most ligands, and provided thermodynamic data are available for the system, the dissociative rate data can also be estimated. Data now are needed for reactions with these metals in different oxidation states and for other elements (transition and nontransition).

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