

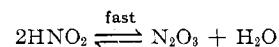
shielded by the four ethyl groups preventing it from interacting with HNO_2 along the z axis.¹³ Reactions of the analogous complex $[\text{Pt}(\text{dien})\text{Cl}]^+$, where Pt(II) is accessible, are catalyzed by HNO_2 . This observation is important because it supports the view that interaction with Pt(II) is involved rather than an electrophilic attack on the departing Cl^- .

We have also observed qualitatively that there is a nitrous acid catalysis of the reactions of nitrite ion with *trans*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ and with PtCl_4^{2-} . In aqueous solution at $\text{pH} > 7$ these reactions are much slower than previously reported.⁸ This suggests that the more rapid rates are due to catalysis by small amounts of HNO_2 resulting from the solvolysis of NO_2^- .

That boric acid and acetic acid, which can behave as electrophiles, are also catalysts for these reactions affords support to the proposed mechanism. However, alternative mechanisms for the catalysis by HNO_2 have been considered and some experiments were done that show these to be unlikely. The possibility exists of an oxidation-reduction catalysis involving labile Pt(III) species¹⁴ formed as a result of the reaction of Pt(II) with HNO_2 . In order to test this possibility, duplicate experiments were carried out in the presence of added Ce(IV) or Pt(IV) and in every case the values of k_{obsd} were the same as was found in the absence of these substances.

Nitrosyl-platinum complexes of the types PtA_4NOX

and $\text{PtA}_2\text{V}_2\text{NOX}$ can be prepared by the reaction of NOX with platinum(II) complexes.¹⁵ Here NOX is a species such as N_2O_3 or NOCl . The form of rate law 1 argues against a rate-determining step with either of these possible reactants. When only nitrous acid is present, for example, there is no reaction whatever (see Table I). A reaction with N_2O_3 would give a rate dependent on the square of the HNO_2 concentration, e.g.



Furthermore, the complex $[\text{Pt}(\text{pip})_2\text{NONO}_2\text{Cl}]_2$, which might be an intermediate in the nitrous acid catalyzed reaction, was prepared according to the directions in the literature¹⁵ and it was found to be unreactive under our reaction conditions. Hydrazoic acid was found not to be a catalyst in spite of potential π bonding capability. This suggests that hydrogen bonding of H in HA to the leaving halide ion at the same time that A is π bonded to Pt(II) may be important. This same suggestion was made earlier¹ to explain why methyl acetate and methyl borate were not catalysts.

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The Kinetics of Replacement Reactions of Complexes of the Transition Metals with 1,10-Phenanthroline and 2,2'-Bipyridine

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The kinetics of formation and dissociation of metal complexes of 1,10-phenanthroline, 2,2'-bipyridine, and some related ligands have been measured by the stopped-flow method. The second-order formation rate constant for the mono complex increases in the sequence $\text{Ni}^{2+} < \text{Co}^{2+} < \text{Fe}^{2+} \sim \text{Mn}^{2+} < \text{Zn}^{2+} < \text{Cu}^{2+} \sim \text{Cd}^{2+} < \text{Ag}^+ < \text{Hg}^{2+}$. Although most attention was directed to the 1:1 complexes, some of the reactions of the higher species were examined also. Agreement between thermodynamic data obtained from kinetic and equilibrium studies was good. The results are discussed in terms of current ideas on the mechanism of complex ion reactions.

Introduction

When this work was commenced it was becoming apparent that the rate constants for the formation of nickel complexes with a variety of ligands were similar and that dissociation of the complex controlled its stability.² At the same time, it was clearly emerging

that the formation of complexes of the bivalent transition metals, at least with simple ligands, was controlled by the water exchange rate of the aquated metal ion, and that once again the ligand had a minimal influence.³

It seemed worthwhile then to investigate the general

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validity of this important and simplifying concept using as wide a range of metals and ligands as possible, and in addition to explore the effect of ligands already coordinated to the metal ion on the rates of their subsequent uptake. A start was made on the problem by investigating by a temperature-jump relaxation method the reactions of an azo dye with bivalent cobalt, nickel, copper, zinc, and cadmium ions.⁴ The present, more extensive work is concerned with the kinetics of formation in aqueous solution of complexes of 1,10-phenanthroline and 2,2'-bipyridine with the manganese-zinc group of metals, as well as with the zinc, cadmium, and mercury triad. In general, the formation of the mono complex has been studied but, where feasible, the higher species have been examined also. A subsequent paper will examine the corresponding reactions of 2,2',2''-terpyridine.

The heterocyclic amines, 1,10-phenanthroline and 2,2'-bipyridine, have played an important role in the development of coordination chemistry.⁵ Kinetic studies have been made of certain slowly reacting iron(II),⁶⁻¹⁰ cobalt(II),¹¹ and nickel(II)¹²⁻¹⁶ complexes with these ligands, in particular the rates of dissociation, but a detailed and systematic study of formation rates with the labile transition metal ions has not been attempted, largely because of the rapid rates involved. These ligands are particularly suitable for studying the kinetics of metal complex formation. The complex systems have been thoroughly examined thermodynamically^{17,18} so that the nature and concentration of the species present in solution is well characterized. The ligands have absorption bands in the near-ultraviolet, sufficiently well separated from those of their metal complexes. This fact, together with the large extinction coefficients and the high stability of the complexes, ensures that on mixing even micromolar aqueous solutions of metal ion and ligand reactants, complex formation is complete and can be followed by spectroscopic methods. This use of low concentrations usually brings the formation rates into the milliseconds, and thus the flow region of measurement. In the event that rates are still too rapid, formation data can sometimes be obtained from a combination of dissociative rate constants and thermodynamic parameters.

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Finally, the ligands are weakly basic with pK values in the region 4.5-5.0. Thus studies in the neutral or weakly acid region obviate interference and difficulties in interpretation arising from the presence of protonated species.^{7,10,14}

Experimental

Materials.—The source and treatment of bipyridine, phenanthroline, and the substituted phenanthrolines were described previously.¹⁵ $Ni(bipy)_2Cl_2$ was prepared by the controlled heating *in vacuo* of $Ni(bipy)_3Cl_2 \cdot 7H_2O$.¹⁹ The analysis of all materials was satisfactory. The metal perchlorates used were purchased from G. F. Smith. Other reagents were A.R. grade. Metal salt solutions were estimated complexometrically with EDTA.²⁰ Standard solutions of the ligands were prepared by weight and occasionally checked colorimetrically with ferrous ion. All solutions were freshly prepared for a set of kinetic runs.

Spectra.—These were determined with a Cary Model 14 spectrophotometer. They were used to (a) find the most suitable wave length for observation of the formation and decomposition processes and (b) check that complete reaction occurred and the nature of the species involved. Our results for the free bases and the mono complexes (and the few tris species we examined) are in excellent agreement with the values in the literature.²¹⁻²⁵ Spectra for $Zn(bipy)^{2+}$, $bipy$, $Zn(phen)^{2+}$, and $phen$ are shown in Figure 1. Changes in optical density as the base is converted into the mono complex are, in general, poorer for phenanthroline than for bipyridine.²¹ Observations in all runs were in the 270 (py, phen, or substituted phen) or 300 $m\mu$ (bipy) regions. The

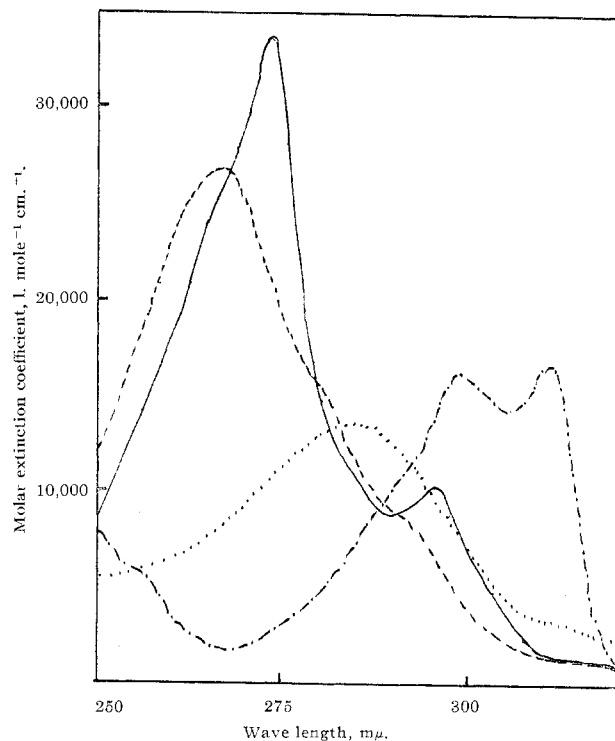


Figure 1. — — —, phen; ———, $Zn(phen)^{2+}$; ·····, bipy; - · - · - ·, $Zn(bipy)^{2+}$.

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dissociation of the higher copper(II) phenanthroline species was investigated more conveniently using the visible region and the spectra of $\text{Cu}(\text{phen})_3^{2+}$, $\text{Cu}(\text{phen})_2^{2+}$, $\text{Cu}(\text{phen})^{2+}$, and Cu^{2+} were determined using computed concentrations of metal ion and base. The results were in agreement with those reported²⁸ for $\text{Cu}(\text{phen})_3^{2+}$ and $\text{Cu}(\text{phen})_2^{2+}$ and those expected from a consideration of the spectra of the three copper bipyridine species recently carefully measured.²⁷ The extinction coefficient of the bis is higher than the tris and the mono over the region investigated (600–1000 $\text{m}\mu$).

Kinetic Runs.—A stainless-steel Gibson stopped-flow apparatus employed in previous studies^{28,29} could not be used for the present work since it was found that solutions of this ligand type attacked the metal easily, in particular leeching iron from the steel. Consequently an apparatus was constructed in which the solution paths were completely free of metal, but which was basically the same design as previously.³⁰ The present work, started at Sheffield with this apparatus, was continued at Buffalo with a glass-lucite stopped-flow apparatus.³¹ No problems were encountered with these instruments and the agreement in results obtained from the two was reasonable.

In the formation studies pseudo-first-order kinetics (rate constant k_1) were realized by using relatively high concentrations of metal ion, although these were varied (in the case of the nickel-bipyridine system widely) without significant change in the computed second-order rate constant ($k_2 = k_1/[\text{M}^{2+}]$). This latter fact, plus spectral examination of the product and considerations of the approximate rate constants for the formation of the higher species, confirmed that we were concerned solely with the formation of the mono complex.

For the dissociation experiments the complex was first formed from the appropriate amounts of M and L in neutral or weakly acid solutions. Once again, ligand concentration was 5% or less of metal concentration. Its dissociation was then effected by decomposition with another metal ion, which reacted more rapidly and formed a more stable complex with L than did M. Thus from a consideration of stability constants and probable formation rate constants, Cu(II) was a suitable decomposing ion for $\text{Mn}(\text{phen})^{2+}$, $\text{Zn}(\text{bipy})^{2+}$, $\text{Zn}(\text{phen})^{2+}$, $\text{Cd}(\text{phen})^{2+}$, and $\text{Ag}(\text{phen})_2^+$ while Hg(II) could be used for $\text{Cu}(\text{bipy})^{2+}$ and $\text{Cu}(\text{phen})^{2+}$.³²

The direction of the reaction $\text{Cu}(\text{bipy})^{2+} + \text{Hg}^{II} \rightleftharpoons \text{Hg}(\text{bipy})^{2+} + \text{Cu}^{2+}$ could be reversed by using relatively large concentrations of Cu(II), and the dissociation of $\text{Hg}(\text{bipy})^{2+}$ was determined by this means. It was possible to decompose $\text{Cu}(\text{phen})_3^{2+}$ with large amounts of Zn^{2+} ion, which being colorless and forming nonabsorbing complexes did not interfere spectrally. A rapid increase of optical density at 800 $\text{m}\mu$ (tris \rightarrow bis) was followed by a measurable decrease (bis \rightarrow mono), before the mono species precipitated in the presence of the large amounts of electrolyte. Spectra were used to show that these various metal replacement reactions did occur. Good first-order kinetic plots for at least 2–3 half-lives were obtained and the rate constant was shown to be independent of the concentration of the complex and the concentration (and nature) of the decomposing metal ion. This indicated that dissociation alone controlled, and was measured by, the metal exchange.

Little effect was observed of small changes in $[\text{H}^+]$, ionic strength, or the nature of the anion, in low concentrations, on either formation or dissociation rates, and thus no attempt was made to maintain a constant ionic strength or buffered medium in the study. The majority of runs were in the pH region 6.0–6.8 but those involving Cu(II) and Hg(II) complex ions were carried out in somewhat higher acidities. The probable errors in the kinetic parameters have been mentioned previously.²⁹ All runs quoted are the mean of several individual determina-

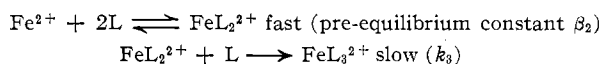
tions. Temperature control of the reactions was $\pm 0.2^\circ$. The results are collected in Tables I and II. In studies involving $\text{Ag}(\text{phen})_2^+$ ion, a sulfate medium was necessary since the complex nitrate and perchlorate precipitated.³³ Copper sulfate was used in the decomposition experiments. Otherwise, nitrate or perchlorate anions could be used replaceably.

Results

Rate constants and activation parameters are collected in Table III, which also includes values for dissociation of cobalt and nickel complexes obtained from previous exchange studies.^{11,15} The extensive thermodynamic results of Irving and his co-workers¹⁷ and Anderegg¹⁸ have been used as a basis for our comparisons and calculation of results. The results of these careful measurements, which are in excellent agreement with each other, have been invaluable in the present study.

Manganese.—The bipyridine complexes were too unstable to allow measurement of their formation at the low reactant concentrations necessary, and dissociation rate constants were too high for determination by flow methods. More success was obtained using the phenanthroline complexes, although even with these only a single formation rate constant could be measured at lowered temperatures. However, a reasonable study of the dissociation of $\text{Mn}(\text{phen})^{2+}$ was possible.

Iron.—The formation of the deep red tris species $[\text{FeL}_3]^{2+}$ from reactants in acid solution (which slows down the rate) was studied some years ago.^{5–7} The fourth-order kinetics were explained in terms of the mechanism



Thus the rate = $\beta_2 k_3 [\text{Fe}^{2+}] [\text{L}]^3$. We now¹⁷ have information on the values of β_2 not available at the time of the original studies and can thus calculate values for k_3 of $1.4 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ (L = bipy) and $1.5 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$ (L = phen). Since in addition Bell and Sutin¹⁰ have measured the formation of $\text{Fe}(\text{phen})^{2+}$ by flow methods, we confined our attentions solely to the kinetics of formation of $\text{Fe}(\text{bipy})^{2+}$. By using relatively large concentrations of ferrous ion and flow methods we were able to measure the formation of the mono species before the subsequent formation of higher species. This was indicated by an initial optical density which corresponded to the free base; *i.e.*, there was no very rapid formation of any complex. In addition there was a lack of optical density change at 523 $\text{m}\mu$, a wave length where the tris species, but not the mono, absorbs appreciably.

Cobalt.—Combining rate constants and Arrhenius parameters for the formation of the mono phenanthroline complex with dissociative data obtained from metal exchange¹¹ gives thermodynamic constants in excellent agreement with literature values (Table III). This success gave us confidence in calculating formation rate constants for other systems in this way. The kinetic parameters for the formation of tris(phenan-

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TABLE I
 KINETIC DATA FOR METAL COMPLEX FORMATION

[metal ion], mM	Temp., °C.	$t_{1/2}$, msec.	k_2 , $M^{-1} \text{ sec.}^{-1}$	[metal] ion, mM	Temp., °C.	$t_{1/2}$, msec.	k_2 , $M^{-1} \text{ sec.}^{-1}$
Mn ²⁺ -phen				Ni ²⁺ -phen			
0.50	11.0	12	1.2×10^5	10.2	0.2	142	4.7×10^2
				5.1	0.2	266	5.1×10^2
				2.5	0.2	600	4.6×10^2
0.25	0.2	96	2.8×10^4	2.5	15.0	160	1.7×10^3
0.25	0.2	102	2.8×10^4	2.5	25.0	74	3.9×10^3
0.50	0.2	51	2.7×10^4	Ni ²⁺ -5-NO ₂ phen			
1.00	0.2	28	2.5×10^4	5.0	0.2	690	2.0×10^2
0.25	10.0	50	5.6×10^4	5.0	15.0	170	8.0×10^2
0.25	20.0	25	1.1×10^5	5.0	25.0	70	1.9×10^3
Co ²⁺ -bipy ^a				Ni ²⁺ -5-CH ₃ phen			
0.50	0.2	93	1.5×10^4	2.5	25.0	89	3.1×10^3
0.50	15.0	35	4.0×10^4	Ni ²⁺ -5-Clphen			
0.50	25.0	20	7.2×10^4	2.1	0.2	118	2.8×10^2
Co ²⁺ -phen				Ni ²⁺ -2-Clphen			
0.24	0.2	56	5.1×10^4	2.5	25.0	270	1.0×10^3
0.48	0.2	28	5.4×10^4	2.5	40.0	83	3.3×10^3
0.32	7.5	25	8.4×10^4	Cu ²⁺ -bipy			
0.24	10.0	25	1.2×10^5	0.025	0.2	N.o. ^e	$\geq 5 \times 10^6$
0.32	15.0	15	1.4×10^5	Cu ²⁺ -phen			
Co ²⁺ -5-NO ₂ phen				0.01 ^d	11.0	~3	$\sim 2 \times 10^7$
0.25	0.2	110	2.5×10^4	Zn ²⁺ -bipy			
0.50	0.2	57	2.4×10^4	0.104	8.0	13	5.1×10^3
0.50	9.3	25	5.5×10^4	0.104	12.5	9	7.4×10^3
0.50	15.0	18	7.8×10^4	0.047	17.5	19	8.0×10^3
Ni ²⁺ -py				0.093	17.5	9	8.3×10^3
100	3.8	8	9×10^2	0.186	17.5	5	8.3×10^3
100	8.8	7	10^3	0.104	20.0	~8	$\sim 8.3 \times 10^3$
100	15.0	4	2×10^3	0.104	30.2	6	1.2×10^4
Ni ²⁺ -bipy ^a				0.052	38.2	8	1.8×10^4
5.0	0.2	740	1.9×10^2	Zn ²⁺ -phen			
2.5	15.0	460	6.1×10^2	0.104	6.5	12	5.6×10^3
2.5	25.0	207	1.4×10^3	0.052	13.0	12	1.1×10^4
5.1	25.0	91	1.5×10^3	0.104	14.5	7	9.5×10^3
5.1	25.0	81	1.6×10^3	0.104	25.0	N.o. ^e	$\geq 3.0 \times 10^3$
0.15	25.0	2.2 sec. ^b	2.1×10^3	0.040	7.5	12	3.0×10^3
Ni(bipy) ₂ ²⁺ -bipy ^c				Cd ²⁺ -phen			
0.015	25.0	9.6 sec. ^b	2.1×10^3	0.050	13.0	~3	$\sim 5. \times 10^3$
				Ag ⁺ -phen			
				0.050	12.5	N.o. ^e	$\geq 5 \times 10^6$

^a [bipy] $\approx 10^{-3} M$. ^b Using a Cary spectrophotometer. ^c [bipy] = $3.5 \times 10^{-3} M$. ^d [phen] = $10^{-5} M$. ^e N.o. indicates a reaction trace was nonobservable and $k_1 \geq 200 \text{ sec.}^{-1}$.

throline)cobalt(II) ion from the bis analog using published ¹⁴C-phenanthroline exchange (dissociation) results¹¹ were thus obtained. The second-order rate constant equals $4 \times 10^5 M^{-1} \text{ sec.}^{-1}$ at 25° with an energy of activation of 12 kcal. mole⁻¹.

Nickel.—Because the reactions of nickel(II) are relatively slow, most detailed studies so far have been with this metal. The reactions of nickel(II) ion with some thirty ligands have been studied in the past few years. The effect of substitution within the phenanthroline molecule on the rate of formation of the nickel complex is shown in Table III and augments data for the dissociation process obtained from radionickel exchange

studies.¹⁵ Not perhaps surprisingly, little effect of 5-substitution on the rates is observed. Of more interest is the fact, however, that 2-chlorophenanthroline reacts only about three times more slowly with nickel ion than does phenanthroline, although dissociation of the complex is some thousand times more rapid.¹⁵ It is apparent that electronic and steric effects due to substitution at the 2 position¹⁵ are showing up in the dissociative, and not in the formation, process. Since the higher species are stable, the reaction of [Ni-(bipy)₂]²⁺ with bipyridine is easily studied. The formation rate constant ($2.1 \times 10^3 M^{-1} \text{ sec.}^{-1}$ at 25°) is very similar to that for the formation of the mono

TABLE II
KINETIC DATA FOR METAL COMPLEX DISSOCIATION

[metal ion], mM	[decomposing metal ion], mM	Temp., °C.	k_t , sec. ⁻¹
Ligand = phen			
Mn ²⁺	Cu ²⁺		
0.50	5.0	6.0	28
0.50	5.0	6.5	28
0.50	20.0	11.0	33
0.50	5.0	18.5	58
0.50	20.0	25.0	~120
Ligand = bipy			
Cu ²⁺	Hg ²⁺		
0.50	5.0	13.5	0.07
0.50	5.0	25.0	0.18
0.50	5.0	39.5	0.58
0.50	5.0	39.5	0.63
0.50	50.0	39.5	0.58
Ligand = phen			
Cu ²⁺	Hg ²⁺		
1.0	20	25.0	0.04 ^a
Cu ²⁺	Zn ²⁺		
2.0 ^b	500	14.5	≥200 ^c
2.0 ^b	500	14.5	58 ^d
Ligand = bipy			
Zn ²⁺	Cu ²⁺		
0.2	0.2	16.0	9.6
0.1	0.1	20.5	15
0.1	0.1	25.0	19
0.2	0.2	30.5	25
0.1	0.1	34.0	30
Ligand = phen			
Zn ²⁺	Cu ²⁺		
0.4	0.4	15.5	2.0
0.4	0.4	25.0	5.0
0.4	0.4	35.0	6.9
Zn ²⁺	Fe ²⁺		
0.4	25.0	35.5	6.0 ^e
Cd ²⁺	Cu ²⁺		
0.5	20.0	4.8	8.7
0.5	20.0	9.5	10
0.5	20.0	16.0	20
Ligand = bipy			
Hg ²⁺	Cu ²⁺		
0.5	100	9.0	7.7
0.5	100	9.0	7.7
0.5	100	25.3	23
0.5	~500	25.3	~50
Ligand = phen			
Ag ⁺	Cu ²⁺		
1.0 ^f	20	25.0	≥200
0.05 ^g	20	3.5	30
0.05	20	5.0	37
0.05	20	9.5	69
0.05	20	10.0	87
0.05	20	13.0	87
0.05	20	18.0	174

^a Using a Cary spectrophotometer, λ 286 m μ . ^b [phen] = 8 \times 10⁻³ M. ^c Refers to decomposition of tris, no trace observable. ^d Refers to decomposition of bis. ^e λ 510 m μ . ^f [phen] = 5 \times 10⁻⁵ M. ^g [phen] = 1.5 \times 10⁻⁴ M.

species (1.4 \times 10³ M⁻¹ sec.⁻¹ at 25°), indicating little effect of coordinated bipyridine on the metal-water exchange rate.

Copper.—The formation rates with this metal are too rapid for direct measurement, but the high association constants of these complexes imply that dissociation rates are more easily measurable. The dissociation of Cu(phen)₃²⁺ is too fast for measurement, the half-life of that of Cu(phen)₂²⁺ is some 10 msec. or so at 15°, while the dissociation of Cu(phen)²⁺ can be measured without resort to flow methods. This increased kinetic stability parallels increased thermodynamic stabilities, indicating that successive formation rate constants are appreciably constant, a situation that has been frequently observed with nickel(II),² but this is the first observation for copper(II).

Zinc, Cadmium, and Mercury.—Approximate values for the rates of formation of phenanthroline complexes of these metals can be obtained from direct mixing experiments. Accurate data are best obtained, however, by combining kinetic dissociative results with formation constants. Both approaches indicate the sequence Zn < Cd < Hg for increasing formation rates, but the computed second-order formation rate constant for Hg(bipy)²⁺ is alarmingly high (~10¹¹). It was difficult to decompose the latter ion without using relatively large concentrations of Cu(II), and it may well be that these enhanced dissociation of the mercury complex, although no such effect was observed with other metals. Either this, leading to too high an estimate for k_d , or an error in the literature value for K_1 could lead to the high calculated value for k_t . Some experiments in which a solution containing a mixture of Zn(bipy)²⁺ and Zn(bipy)₂²⁺ was treated with a bipyridine solution indicated that the higher species were formed with similar rate constants to that for the mono. Similarly, there was no evidence of a slowing down in rate after the Zn(phen)²⁺ species was formed and reacted further with phenanthroline.

Silver(I).—As far as the authors are aware, these represent the first kinetic data for a silver(I) complex. The dissociation of Ag(phen)₂⁺ obeys the rate equation $R = k[\text{Ag}(\text{phen})_2^+]$. At 25°, $k = 300$ sec.⁻¹, and in conjunction with the stability constant for the bis³³ species $k_f = 3 \times 10^9$ M⁻¹ sec.⁻¹ at 25°. Only a limit can be placed on the second-order rate constant ($\geq 10^7$ M⁻¹ sec.⁻¹) for the formation of the mono species (by direct measurement and indirect calculations from the dissociative data). These results replace provisional ones reported earlier.³⁴ Unfortunately, no enthalpy data are available so that no estimate of the energy of activation for the formation of Ag(phen)₂⁺ can be made. However, since this is likely to be small in view of its high, near diffusion-controlled rate constant, then the high energy of activation for dissociation must signify that a high enthalpy accompanies the formation of bis(phenanthroline)silver(I) ion.

Discussion and Summary

It is now believed that the second-order rate constant for the formation of many metal complexes (k_f)

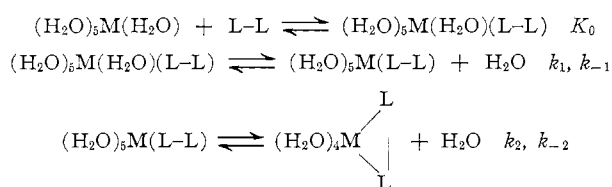
(34) C. D. Hubbard, P. Moore, and R. G. Wilkins, Proceedings of the 8th International Conference on Coordination Chemistry, Vienna, 1964, p. 286.

TABLE III
 KINETIC AND THERMODYNAMIC PARAMETERS FOR FORMATION AND DISSOCIATION OF
 METAL-BIPYRIDINE AND -PHENANTHROLINE COMPLEXES AT 25.0°

Ion	Ligand	Log k_f^b	Log A_f	E_f	Log k_d^c	Log A_d	E_d	Log K^a	Log K ($=k_f/k_d$)	$-\Delta H^a$	$-\Delta H$ ($E_d - E_f$)
Mn ²⁺	phen	5.1 ^d			1.5 ^d	9.6	10.4	4.0	3.6 ^d	3.5	
Fe ²⁺	bipy	5.2	13.5	11.3				4.3			
Co ²⁺	bipy	4.8	12.5	10.4				6.0		8.2	
	phen	5.5	13.7	11.2	-1.8 ^e	12.4 ^e	19.4 ^e	7.2	7.3	9.1	8.2
	5-NO ₂ phen	5.2	13.9	11.8							
Ni ²⁺	py	~3.6		~12	1.6 ^g	13.6 ^g	16 ^g	2.1 ^f	~2.0	3 ^f	~4
	bipy	3.2	13.3	13.8	-4.3 ^h	13.2 ^h	23.7 ^h	7.1	7.5	9.6	9.9
	phen	3.5	13.6	13.7	-5.0 ^h	13.0 ^h	24.5 ^h	8.8	8.5	11.2	10.8
	5-NO ₂ phen	3.2	13.8	14.4	-4.2 ^h	13.1 ^h	23.5 ^h		7.4		9.1
	5-CH ₃ phen	3.5			-5.2 ^h	12.8 ^h	24.4 ^h	8.3	8.7		
	5-Clphen	2.4			-4.6 ^h	13.1 ^h	23.9 ^h		7.0		
	2-Clphen	3.0	13.1	13.7	-2.0 ^h	~10.5 ^h	~17 ^h		~5.0		~4
Ni(bipy) ₂ ²⁺	bipy	3.3			-2.5 ⁱ	13.8 ⁱ	22.2 ⁱ	6.5	5.8	9.2	
Cu ²⁺	bipy	≥7.0			-0.7	9.6	14.1	8.0	≥7.7	11.9 ^j	
	phen	≥7.0			-1.4			9.0	≥8.4	11.7	
Cu(phen) ₂ ²⁺	phen				1.8			6.7			
Cu(phen) ₂ ²⁺	phen				≥2.3			5.0			
Zn ²⁺	bipy	6.0	11.1	6.9	1.2	10.1	12.1	5.2	4.8	7.1	5.2
	phen	~6.3			0.6	9.7	12.3	6.5	~5.7	7.5	
Cd ²⁺	phen	~7.0			1.6	12.2	14.4	5.8	~5.4	6.3	
Hg ²⁺	bipy				1.4	9.2	10.7	9.6			
Ag ⁺	phen	>6.5			≥2.3			5.0 ^k			
Ag(phen) ⁺	phen				2.5	15.7	18.0	7.0 ^k			

^a Ref. 17 and 18. ^b Formation rate constant, $M^{-1} \text{sec}^{-1}$. ^c Dissociation rate constant, sec^{-1} . ^d 11.0°. ^e Ref. 11. ^f G. Atkinson and J. E. Bauman, Jr., *Inorg. Chem.*, **2**, 64 (1963). ^g Ref. 29. ^h Ref. 15. ⁱ P. Ellis and R. G. Wilkins, unpublished exchange studies. ^j This value appears a little high when compared with the phen analog. ^k Ref. 33.

is a composite value, the product of an outer-sphere association constant K_0 and a first-order rate constant k_1 for water exchange of the outer-sphere complex; *i.e.*, $k_f = K_0 k_1$.³⁵ Furthermore, it has been tacitly assumed that the formation of a chelate compound is usually controlled by the rate of the first water molecule released from the metal ion.³⁶⁻³⁸ Thus in the detailed picture (L-L representing the donor atoms of the bidentate ligand)



this follows if $k_2 \gg k_{-1}$, whence $k_f = K_0 k_1$. Since we are concerned in this paper exclusively with chelate formation, it is necessary to look at this relationship more closely. Sufficient information is now available for us to assign plausible values to the various rate constants in the detailed picture for the formation of $[\text{Ni}(\text{bipy})(\text{H}_2\text{O})_4]^{2+}$ and to test these values for internal consistencies.

We can equate, not unreasonably, the limiting rate constant for dissociation of $\text{Ni}(\text{bipy})^{2+}$ in strong acid to the value of k_{-2} .⁸ Further, we have studied previously²⁹ the dissociation of several nickel complexes

with unidentate ligands, including pyridine, and can approximate the rate constant for dissociation of $\text{Ni}(\text{py})^{2+}$ to that of $\text{Ni}(\text{L-L})^{2+}$ where L-L is the bipyridine attached only at one end. The values of k_{-2} and k_{-1} obtained in this way are 3.4×10^{-3} and 38 sec^{-1} , respectively, at 25°. We have measured $K_0 k_1$ for pyridine in the present study, and we can also use the value $4 \times 10^3 M^{-1} \text{sec}^{-1}$ at 25° as a reasonable approximation for the corresponding process for bipyridine. We are left with the assignment of a value for k_2 , the first-order rate constant for the process involving completion of the chelate ring. Since there appears to be little effect of nitrogen-donating ligands, already present, on water-exchange values for the metal ion,³⁵ then using a value of 10^4sec^{-1} at 25° for k_2 is justified. Alternatively, we can calculate k_2 from the ratio of rate constants for the dissociation of $\text{Ni}(\text{bipy})^{2+}$ in acid (k_a) and in neutral solution (k_n), for on the current ideas of acid dissociation of these types of chelates, $k_a/k_n \sim k_2/k_{-1}$. Since the ratio is approximately 70, $k_2 \sim 70k_{-1} \sim 3 \times 10^3$. The use of either value of k_2 (10^4 or $3 \times 10^3 \text{sec}^{-1}$) leads to a value for the stability constant of $\text{Ni}(\text{bipy})^{2+}$ ($=K_0 k_1 k_2 / k_{-1} k_{-2}$) of $1-3 \times 10^3$. This value, considering the various approximations implied in its derivation, is in reasonable agreement with that measured (2×10^7). Obviously if we used the value $1.4 \times 10^3 M^{-1} \text{sec}^{-1}$ at 25° for $K_0 k_1$ for the bipyridine complex, which we can now conclude is equal to the measured second-order formation rate constant, the agreement would be even better. Finally, probably the most convincing evidence that formation of these chelates is dominated by the first step of coordination comes from a compari-

(35) M. Eigen and R. G. Wilkins, *Advances in Chemistry Series*, to be published, contains an account and full tabulation of kinetics and mechanism of formation of metal complexes.

(36) G. G. Hammes and J. I. Steinfeld, *J. Am. Chem. Soc.*, **84**, 4639 (1962).

(37) G. G. Hammes and M. L. Morrell, *ibid.*, **86**, 1497 (1964).

(38) G. H. Nancollas and N. Sutin, *Inorg. Chem.*, **3**, 360 (1964).

son of the formation rates of $\text{Ni}(\text{py})_2^{2+}$, $\text{Ni}(\text{bipy})_2^{2+}$, and $\text{Ni}(\text{terpy})_2^{2+}$ with similar conditions. Thus, the respective formation half-lives are 9, 12, and 15 msec., respectively, when 0.2 M nickel(II) ion is mixed with $\sim 10^{-4} M$ ligand in water at 7.0° (see also ref. 29).

Margerum, Bystroff, and Banks¹⁴ studied the formation of monophenanthroline nickel(II) ion in acid solution, and their formation rate constant, extrapolated to neutral pH ($2 \times 10^3 M^{-1} \text{sec.}^{-1}$ at 25°) is in good agreement with our directly determined value (4×10^3). This constant was, however, equated to $K_0 k_1 k_2 / k_{-1} + k_2$ (on our scheme) and only the limiting value in high acidities ($4 \times 10^4 M^{-1} \text{sec.}^{-1}$) was considered to represent $K_0 k_1$. For similar reasons to those outlined above, we believe that in this system also $k_2 \gg k_{-1}$ (and not $k_{-1} \sim 20k_2$ which emerges from the Margerum, Bystroff, and Banks mechanism). We are not able to account for their increasing rate constant, with increasing acidity.

The formation rate constants for phenanthroline and bipyridine complexes are collected in Table III. The following points emerge from examining the results.

(1) For the reaction with phenanthroline and/or bipyridine, the order of reactivity observed is $\text{Ni}^{2+} < \text{Co}^{2+} < \text{Fe}^{2+} \sim \text{Mn}^{2+} < \text{Zn}^{2+} < \text{Cu}^{2+} \sim \text{Cd}^{2+} < \text{Ag}^+ < \text{Hg}^{2+}$. This sequence parallels that observed for the water-exchange rate for the metal ion and/or the sulfation reaction studied by ultrasonics and provides yet further evidence for the paramount role of water exchange in the ligand reactions.³⁵ Aspects of this order have been previously discussed in terms of the metal electronic configuration (see ref. 35 for references). The sequence for the d^{10} ions, $\text{Zn}^{\text{II}} < \text{Cd}^{\text{II}} < \text{Hg}^{\text{II}}$, is substantiated, although the value for $\text{Hg}(\text{II})$ is obviously too high. Interesting, and perhaps not unexpected, is the higher rate constant for $\text{Ag}(\text{I})$ than for the isoelectronic $\text{Cd}(\text{II})$. The second-order rate constants for phenanthroline and bipyridine are consistently lower than these for the other ligands; bipyridine invariably reacts slower than does phenanthroline but this difference only in a small degree accounts for the lower stability of bipyridine complexes. Since we must remember that $k_f = K_0 k_1$, these small

differences probably arise from differing values of K_0 , slightly less than unity, as well as values for k_1 slightly different for each complex and for the water-exchange value of the aquated metal ion. It is extremely difficult to calculate values for K_0 for the outer-sphere complexes for these and similar ligands.³⁶⁻³⁸ Indeed it may be more justifiable to calculate K_0 from the observed values for k_f and k_1 .³⁷ The higher energies of activation for the phenanthroline and bipyridine complexes than for the water exchange or sulfation process will arise from a small contribution from the heat of outer-sphere complex formation.³⁸

(2) Attention is being currently directed to the effect which coordinated ligands have on rates of substitution of the remaining coordinated water. Quite small differences have so far been observed.^{39,40} The formation rate constants for the reaction of ligand with $\text{Fe}(\text{phen})_2^{2+}$, $\text{Fe}(\text{bipy})_2^{2+}$, $\text{Co}(\text{phen})_2^{2+}$ ($4 \times 10^5 M^{-1} \text{sec.}^{-1}$), $\text{Ni}(\text{phen})_2^{2+}$ ($3 \times 10^2 M^{-1} \text{sec.}^{-1}$), and $\text{Ni}(\text{bipy})_2^{2+}$ ($1.5 \times 10^3 M^{-1} \text{sec.}^{-1}$ at 25°) are extremely similar to the corresponding reactions with metal ion. Although accurate measurements for the formation of $\text{Cu}(\text{phen})_3^{2+}$ and $\text{Zn}(\text{phen})_3^{2+}$ were not possible, it was easily shown that with these also, second-order rate constants could not have been smaller than for the lower species. This is interesting in view of the suggestion that polyamines coordinated to copper(II) may lower significantly the remaining water-exchange rate.⁴¹ The constancy of these formation rates for the complexes of a particular metal complex is in marked contrast to some observations with terpyridine complexes to be reported later.

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(39) E. Blatt and R. E. Connick, Proceedings of the 8th International Conference on Coordination Chemistry, Vienna, 1964, p. 284.

(40) D. W. Margerum and M. Eigen, *ibid.*, p. 289.

(41) D. B. Rorabacher and D. W. Margerum, *Inorg. Chem.*, **3**, 382 (1964).