909. *Exchange Studies of Certain Chelate Compounds of the Transitional Metals. Part IV.* The Rates of Dissociation of Bis- and Mono-(1 : 10-phenanthroline)nickel*(II) *Ion determined by* $^{63}Ni^{2+}$ *Exchange.*

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The rate constants for dissociation of $[Ni\ phen_2]^{2+}$ and $[Ni\ phen]^{2+}$ have been determined from exchange experiments with ^{63}Ni. The values $10^{14}\exp(-23{,}100/\boldsymbol{R}T)$ and $10^{16}\exp(-26{,}200/\boldsymbol{R}T)$ respectively are compared with that of the $[Ni\ phen_3]^{2+}$ species, $10^{15\cdot2}\exp(-25{,}200/\boldsymbol{R}T)$, obtained from previous [^{14}C]phenanthroline exchange studies (all values are in min.$^{-1}$). The results for the bisphenanthroline species are established by adding $*Ni_{aq}^{2+}$ to an equilibrium mixture containing Ni_{aq}^{2+}, $[Ni\ phen]^{2+}$, and $[Ni\ phen_2]^{2+}$, and by following the specific activity of each species at various times.

Work on the exchange of $[Ni\ phen_3]^{2+}$ with 1 : 10-phenanthroline, [^{14}C]-labelled materials being used, indicated that in the pH range 5·7—11·7 the exchange rate constant (k_{exch}) and the pH-independent acid-dissociation rate constant (k_a) were identical.[1] This result requires that the exchange takes place only through the first dissociative equilibrium represented in eqn. (1) (co-ordinated water molecules are not included in the equations or considered in the subsequent discussion) and that subsequent stages do not assist in the introduction of labelled phenanthroline into the trisphenanthroline ion. If this were not the case, k_{exch} would have a value such that $3k_a \geqslant k_{exch} > k_a$ with the limiting case of $k_{exch} = 3k_a$ when $R_2, R_1 \gg R_3$.[2]

$$\left.\begin{array}{llll}[Ni\ phen_3]^{2+} & \overset{R_3}{\rightleftharpoons} [Ni\ phen_2]^{2+} & + \text{phen} \ldots\ldots & k_3, k_{-3} \\ [Ni\ phen_2]^{2+} & \overset{R_2}{\rightleftharpoons} [Ni\ phen]^{2+} & + \text{phen} \ldots\ldots & k_2, k_{-2} \\ [Ni\ phen]^{2+} & \overset{R_1}{\rightleftharpoons} Ni^{2+} & + \text{phen} \ldots\ldots & k_1, k_{-1}\end{array}\right\} \quad . \quad . \quad (1)$$

Since the concentrations of the bis- and mono-phenanthrolinenickel(II) species will be very small under the conditions of ligand exchange with the tris-derivative, the value of k_2 and k_1 may still be much higher than that of k_3 and yet the condition R_2 ($= k_2$ [Ni phen$_2$]) and R_1 ($= k_1$ [Ni phen]) $\ll R_3$ still hold.

A value of $k_2 \sim 10k_3$ was indicated by acid-dissociation experiments [3] on $[Ni\ phen_3]^{2+}$ and $[Ni\ phen_2]^{2+}$. More recently, Margerum, Bystroff, and Banks [4] have studied spectrophotometrically the kinetics of dissociation (and formation) of $[Ni\ phen]^{2+}$ in 10^{-4}—10^{-5}-molar solutions and concentrations of hydrogen ion ranging from 0·02 to 4·5M. The results from both of these studies confirm the relation $R_2, R_1 \ll R_3$ implied in our ligand-exchange results. However, it would be interesting to determine the values of k_2 and k_1 as well as the other kinetic parameters in neutral solution in order to compare them with the values obtained for the equilibrium represented by R_3. The dissociation rate constant in neutral or weakly acid solution (which we shall see is pH-independent) refers to a process in which one phenanthroline molecule is disrupted from the complex, and the question of protonated complex species [4] probably does not arise. In addition, it will be possible to detect any direct $[Ni\ phen]^{2+}$–Ni^{2+} exchange, a type of process already encountered in several metal-exchange studies. From the measured successive stability constants for the nickel–phenanthroline system [4] it can easily be shown that with $[Ni^{2+}] \sim 5$[phen] at pH about

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* Part III, *J.*, 1957, 4456.

[1] Wilkins and Williams, *J.*, 1957, 1763.

[2] Wilkins and Williams, *J. Inorg. Nuclear Chem.*, to be published.

[3] Basolo, Hayes, and Neumann, *J. Amer. Chem. Soc.*, 1953, **75**, 5102.

[4] Margerum, Bystroff, and Banks, *ibid.*, 1956, **78**, 4211.

6—7 [Ni phen]$^{2+}$ is present at least as 98% of the phenanthroline-containing species so that exchange studies can be carried out easily in these conditions with radioactive nickel tracer.

If a small amount of $^{63}Ni^{2+}$ is added to an equilibrium mixture containing comparable amounts of [Ni phen$_2$]$^{2+}$, [Ni phen]$^{2+}$, and Ni^{2+} then by following the specific activities of the three species against time it is possible to determine k_2 and k_1, although the accuracy of k_1 attained by this procedure is not as high as that from the exchange studies involving only two species.

TABLE 1. *Exchange of* [Ni phen]$^{2+}$ *with* Ni^{2+}.

Run No.	pH	Temp.	[Ni phen]$^{2+}$ (mmole l.$^{-1}$)	[Ni^{2+}] (mmole l.$^{-1}$)	$t_{\frac{1}{2}}$ (min.)	10^5R (min.$^{-1}$ mole l.$^{-1}$)	$10^4k_{(exch)}$ (min.$^{-1}$)
1	5·5	25·0°	5·1	16·6	1120	0·24	4·72
2	6·2	45·1	5·3	16·0	61	4·52	85·2
3	6·8 [a]	45·1	5·2	16·0	62	4·38	84·3
4	5·8	45·1	2·6	8·0	67	2·03	78·1
5	5·7 [b]	45·1	4·9	14·6	37	6·87	140·2
6	—	45·1	52·0	153·0	60	44·80	86·3
7	—	45·1	26·2	179·0	72	22·00	84·0
8	—	34·9	50·4	154·0	220	11·95	23·7
9	—	34·9	21·8	210·0	301	4·54	20·8
10	1·05	25·0	45·0	145·0	310	7·65	17·0

[a] Adjusted with sodium hydroxide. [b] 0·3M-Sodium acetate–acetic acid buffer being used.

EXPERIMENTAL

Radioactive Nickel.—Nickel of high specific activity was necessary for these experiments, and this was obtained from A.E.R.E., Harwell, through the courtesy of Dr. G. B. Cook. Nickel nitrate solution [containing ^{63}Ni from irradiation of nickel metal (0·5 g.) in the Windscale pile] was purified from ^{58}Co and other possible radiochemical impurities by precipitation with dimethylglyoxime in the presence of added Fe^{3+}, Co^{2+}, Mn^{2+}, and Cr^{3+} carriers.[5] The urea is best added in small portions otherwise immediate precipitation of some of the red bulky form of nickel dimethylglyoxime (rather than the brown crystalline form) occurs. After 6 hr., nickel dimethylglyoxime was converted into nickel sulphate by heating it with concentrated sulphuric acid containing a small amount of concentrated nitric acid. This procedure was repeated until the " solution count " of the nickel solution (measured in a 20th Century Electronics solution counter) was constant. The original solution gave 40,000 counts/min.; this was reduced to a constant value of 160 counts/min. (under identical conditions) after five cycles. This solution count probably arises from very small amounts of ^{59}Ni (*K*-capture; $E =$ 1·07 Mev [6]) also produced in neutron irradiation of nickel.[5] The energy of the final sample of ^{63}nickel dimethylglyoxime was measured as $E_{max.} = 0{\cdot}055 \pm 0{\cdot}003$ Mev (0·063 Mev [7]). The relation used, $E_{max.} = 1{\cdot}92R^{0{\cdot}725}$, where $E_{max.}$ is in Mev and R is the range in aluminium in g./cm.^{2} holds well for energies down to 0·15 Mev and was assumed to hold for lower energies. There was no sign of *X*-rays after the β-particles of ^{63}Ni had been removed by aluminium or Polythene absorbers, and less than 0·2% can be *X*-rays or γ-rays which are not absorbed by aluminium (9·2 mg. cm.$^{-2}$). The organic part of nickel dimethylglyoxime was not readily decomposed except by perchloric or sulphuric acid. ^{63}Nickel nitrate solution for the exchange work was therefore prepared by decomposing ^{63}nickel dimethylglyoxime with concentrated sulphuric acid. After dilution, ^{63}nickel hydroxide was precipitated and washed several times with water to remove adsorbed sulphate. The hydroxide was finally dissolved in the minimum amount of dilute nitric acid. Small amounts of this solution (0·2—0·5 ml.) were added from a Pregl micropipette to exchange solutions for each run. The molarity of this solution was estimated colorimetrically, as the red oxidised-dimethylglyoxime complex.[8]

Counting Procedure.—Counting ^{63}Ni with a mica end-window Geiger–Müller tube is an insensitive method for detecting this weak β-particle emitter, but unfortunately we did not have a 2π-flow-counter, where the sample is incorporated within the tube. All the samples

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[5] Singer and Kurbatov, *J. Amer. Chem. Soc.*, 1954, **76**, 4739.

[6] Emmerich, Singer, and Kurbatov, *Phys. Rev.*, 1954, **94**, 113.

[7] " Chart of the Nuclides," General Electric Co., 1956.

[8] Vogel, " Quantitative Inorganic Analysis," Longmans, Green and Co., London, 1951, p. 654.

contained ^{63}Ni as nickel dimethylglyoxime and were prepared by slurrying acetone suspensions on large G.E.C. planchets (4·9 cm.^{2}). The value[9] of "infinite thickness" for ^{63}Ni is ~4 mg./cm.^{2}, and 12·0 ± 0·2 mg. mats of nickel dimethylglyoxime were used. Acetone was allowed to evaporate from the slurry at room temperature and a few minutes' heating at 110° completed the drying. Fine, even mats were obtained and the reproducibility by this method was about ±5%.

Exchange Runs and Separation Procedure.—(a) [Ni phen$_3$]$^{2+}$–[Ni phen$_2$]$^{2+}$ *exchange.* Tris-(phenanthroline)nickel(II) nitrate of high specific activity was prepared by the addition of excess of phenanthroline to a *Ni^{2+} solution of known concentration. The excess of phenanthroline was then removed by extraction with benzene, and the solution made up to known volume. A solution for exchange was prepared by mixing standard nickel nitrate solution and 1 : 10-phenanthroline in such quantities that $\bar{n}$ (the degree of formation) was approximately 2·67. With these conditions the bis- and tris-phenanthroline complexes predominate. After this solution had equilibrated at 45° for several hours a small quantity of the [*Ni phen$_3$]$^{2+}$ solution was added and aliquot portions were removed for separation at various times. The separation method involved cooling in ice–water and adding sodium oxalate solution; this precipitates the purple bisphenanthroline complex. After centrifugation, the trisphenanthroline complex was precipitated as the perchlorate. Both precipitates were decomposed (nitric and perchloric acids) and converted into nickel dimethylglyoxime.

(b) [Ni phen$_2$]$^{2+}$–[Ni phen]$^{2+}$–Ni^{2+} *exchanges.* Nickel nitrate and phenanthroline were mixed in equimolecular amounts in water. It was known from successive stability constants for the system[4] that with such quantities an equilibrium mixture in which all three species were present in comparable amounts would result and that [Ni phen$_3$]$^{2+}$ would constitute ⩽2%. Exploratory experiments discovered anionic reagents which separately precipitated the three species. Solutions containing [Ni phen$_2$]$^{2+}$ and [Ni phen]$^{2+}$ prepared from the solid complexes[15] were stable for several hours. Both ions gave precipitates with S^{2-}, N$_3^-$, CN$^-$, C$_2$O$_4^{2-}$, PdCl$_4^{2-}$, SCN$^-$, and S$_2$O$_3^{2-}$. However, S$_2$O$_3^{2-}$ precipitated the bisphenanthroline complex very much faster than the mono-complex; the separation therefore involved addition of S$_2$O$_3^{2-}$ which precipitated [Ni phen$_2$]$^{2+}$ as a yellowish-green solid. This was centrifuged and the remaining solution kept at 0° for about 5 min. to ensure complete removal of bisphenanthroline complex. During this time a little blue-green mono-compounds was occasionally precipitated; this was centrifuged off and discarded. To the resulting solution potassium thiocyanate solution was added to precipitate the mono-compound; the remainder of the procedure was as given in (c) below. Both complexes were decomposed to Ni^{2+} with nitric–perchloric acid and precipitated as nickel dimethylglyoxime. The Ni^{2+} ion remaining in solution after removal of the complexes was precipitated with dimethylglyoxime.

(c) [Ni phen]$^{2+}$–Ni^{2+} *exchanges.* Alcoholic dimethylglyoxime formed nickel dimethylglyoxime rapidly with [Ni phen]$^{2+}$ only in ammoniacal solution, and when a small amount of dimethylglyoxime was added to an equilibrated mixture of Ni^{2+} (1·0 mmole) and phenanthroline (0·20 mmole) the aquated nickel ion was preferentially attacked. This was shown by adding ^{63}Ni^{2+} to the above mixture and measuring the specific activity of the precipitated nickel dimethylglyoxime just after mixing and after warming for some hours had effected complete exchange. The values obtained, 531 counts/min./12 mg. and 434 counts/min./12 mg. [theory = 531 × (1·0—0·2)/1·0 = 425], respectively, confirmed that all the phenanthroline was bound and that the nickel–phenanthroline complex was unattacked by small amounts of dimethylglyoxime as long as uncomplexed nickel ion was present. Since for the conditions of this exchange the concentration of nickel ion substantially exceeds that of [Ni phen]$^{2+}$, following the exchange by observing the specific activities of the Ni^{2+} end was insensitive and it was difficult to detect a sharp division in the decomposition of Ni^{2+} and of [Ni phen]$^{2+}$ so that following the activity of the latter was not satisfactory. It was only towards the end of the study that the solid nickel monophenanthroline complex became available so that exchange experiments by adding highly active [^{63}Ni phen]$^{2+}$ and following the increase in Ni^{2+} ion would then have been possible. Details of a typical run are: Aqueous solutions of nickel nitrate (2—4 mmoles) and phenanthroline (0·5 mmole) were mixed, warmed for about an hour to complete formation of [Ni phen]$^{2+}$, made up to volume (10—200 c.c.), and allowed to settle to the desired temperature. ^{63}Nickel nitrate (0·05 mmole) was added and at various times, including very early and at completion of exchange (seven half-times), the [Ni phen]$^{2+}$ was precipitated as thiocyanate

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[9] Schweitzer, Stein, and Nehls, *J. Phys. Chem.*, 1952, **56**, 692.

complex. This was washed and decomposed by heating it for several hours with concentrated perchloric–nitric acid. After considerable concentration the solution was diluted with water and nickel dimethylglyoxime precipitated. " AnalaR " chemicals were used and the concentration of nickel nitrate solution was determined gravimetrically. The pH was measured by a Pye " Universal " pH meter and the spectrum was determined on a Unicam S.P. 500 spectrophotometer.

Calculation of Results.—In this and all subsequent discussion, the concentrations of Ni^{2+}, $[Ni\ phen]^{2+}$, $[Ni\ phen_2]^{2+}$, and $[Ni\ phen_3]^{2+}$ will be represented by a, b, c, and d, and of the corresponding species containing ^{63}Ni by a^*, b^*, c^*, and d^*. The counting rate (in counts/min./12 mg.) of nickel dimethylglyoxime derived from each of these species will be denoted by α, β, γ, and δ, respectively, and subscripts 0 and ∞ will refer to values at zero-time and at the completion of exchange. The amount of dimethylglyoxime used represents (virtually) " infinite thickness," taking into account the window thickness ($\sim$2 mg./cm.^{2}). The count rate therefore will be proportional to the specific activity, *i.e.* $\delta \propto d^*/d$, etc., with the proportionality constant disappearing in all the equations derived.

Exchange (a). For the equilibria represented by eqn. (1)

$$R_3 = k_3 d = \frac{0\cdot693}{t_{\frac{1}{2}}} \cdot \frac{cd}{(c + d)} \text{ and } \therefore k_3 = \frac{0\cdot693}{t_{\frac{1}{2}}} \cdot \frac{\delta_0 - \delta_\infty}{\delta_0}$$

In the one run carried out in this exchange, $\delta_0 = 996$, $\delta_\infty = 656$, and $t_{\frac{1}{2}} = 27$ min., giving a value for k_3 of $87\cdot5 \times 10^{-4}$ min.$^{-1}$ at 45·0°.

Exchange (b). For the equilibria represented by R_1 only

$$-\mathrm{d}a^*/\mathrm{d}t = R_1[(a^*/a) - (b^*/b)]$$

$$\therefore k_1 = \frac{R_1}{b} = \frac{1}{b}\left[-\frac{\mathrm{d}a^*}{\mathrm{d}t}\Big/\left(\frac{a^*}{a} - \frac{b^*}{b}\right)\right] = \frac{a}{b}\left[-\frac{\mathrm{d}\alpha}{dt}\Big/\left(\alpha - \beta\right)\right]$$

while from a consideration of that governed by R_2:

$$\frac{\mathrm{d}c^*}{\mathrm{d}t} = R_2\left(\frac{b^*}{b} - \frac{c^*}{c}\right) \therefore k_2 = \frac{R_2}{c} = -\frac{\mathrm{d}\gamma}{\mathrm{d}t}\Big/\left(\beta - \gamma\right)$$

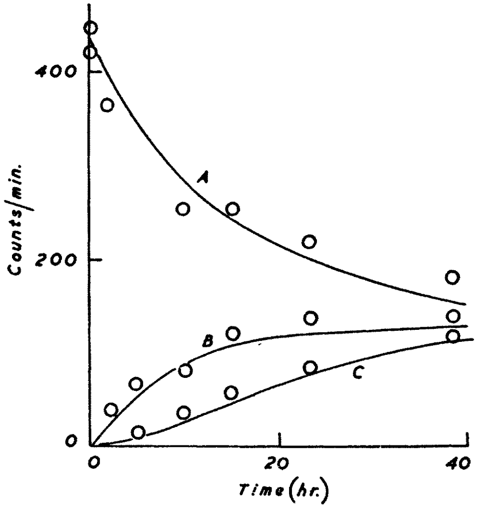
In order to estimate a value for k_1 knowledge of the composition of the system is necessary, and a large error in the determination of k_1 can thereby be introduced; the concentration of free nickel ion in the exchange mixture can be determined by several methods and this value automatically fixes the concentration of $[Ni\ phen]^{2+}$ and $[Ni\ phen_2]^{2+}$. The spectral differences in the visible region between the species are very small,[3] so that determination of the composition based thereon is unsatisfactory. The values of α_0 and α_∞ give the ratio of free to total nickel present. Comparison of α_0 with counting rates of nickel dimethylglyoxime prepared from standard amounts of radioactive nickel and inactive nickel ion also affords an estimation of Ni^{2+} ion present in the exchange solution. Finally, the weights of nickel dimethylglyoxime obtained from each species, separated as described in the exchange procedure, give an indication of their respective amounts. There was a good deal of variation in the results obtained by these methods and mean values used were Ni^{2+}, 30; [Ni phen], 42; [Ni $phen_2$], 28%. These values compare with ones obtained from mean values of the successive dissociation constants: Ni^{2+}, 28; [Ni phen], 46; [Ni $phen_2$], 23; [Ni $phen_3$], 3%. The former values were used for both runs at 25° and 45°.

Another reason for the somewhat unsatisfactory value for k_1 is that although separation of the pure bis- and mono-phenanthroline species is possible a small amount of complexed nickel is not precipitated and continues until the Ni^{2+} stage. Finally the addition of $^{63}Ni^{2+}$ itself disturbs the chemical equilibrium slightly.

Fortunately, in order to determine k_2, which is much more valuable in view of the independent method of estimating k_1, it is necessary to know at any particular time only the rate of change of count for the bis-species (*i.e.* the tangent at that point of the curve in the Figure) and the difference in count of the mono- and bis-phenanthroline species at that time. The amounts of species undergoing exchange do not enter into the expression and the difficulties described above do not arise. From the experimental points (see Figure) three curves are drawn, tangents are estimated for the Ni^{2+} and [Ni $phen_2]^{2+}$ curves at various times, and these are used to determine k_1 and k_2. The forms of the curves for [Ni phen]$^{2+}$ and [Ni $phen_2]^{2+}$ are such that a reasonably accurate value of k_2 is possible—the same is not as true for the determination of k_1 but even here comparison with values obtained by the accurate exchange (*c*) (below) is reasonable. By using the values of k_1 and k_2 and the composition of the exchange mixture theoretical curves may be drawn based on the relations: [2]

$$a^* = 129 + 58{\cdot}5 \exp(-0{\cdot}0023t) + 246 \exp(-0{\cdot}0094t)$$
$$c^* = 129 + 89{\cdot}0 \exp(-0{\cdot}0023t) - 218 \exp(-0{\cdot}0094t)$$

and the agreement with experimental points (especially for the mono- and bis-species) is good. The procedure was repeated at 45° so that an activation energy for the dissociation of the bis-compound could be obtained. Similarly shaped curves were obtained. The results obtained were (10^4k; min.$^{-1}$): at 25°, $k_1 = 6{\cdot}0$, $k_2 = 10{\cdot}7$; and at 45°, $k_1 = 84$, $k_2 = 126$.



The specific activities of Ni^{2+}, [Ni phen]$^{2+}$, *and* [Ni $phen_2]^{2+}$ *at various times in exchange* (b).

A, Ni^{2+}. *B*, [Ni phen]$^{2+}$. *C*, [Ni $phen_2]^{2+}$.

All fractions were radioassayed as nickel dimethylglyoxime.

During the early part (up to 5 hr.) of the tracer exchange the bis-species plays little part and this is shown by an initial induction period in the Figure. The presence of [Ni $phen_2]^{2+}$ being ignored, the exchange for the first 5 hr. is very similar to exchange (*c*) and by using the values for the specific activity of [Ni phen]$^{2+}$ and plotting $\log(1 - F)/t$ a straight line was obtained having $k_1 = 5{\cdot}2 \times 10^{-4}$ min.$^{-1}$, in good agreement with results of exchange (*c*) below. Allowance must be made for the fact that the specific activity at infinite time used in this calculation will be higher than that determined experimentally by an amount calculable from the concentration of bis-species present.

Exchange (c).—A simple exchange between [Ni phen]$^{2+}$ and Ni^{2+} only is being considered here, and

$$R_1 = \frac{0{\cdot}693}{t_{\frac{1}{2}}} \cdot \frac{ab}{(a + b)}$$

By varying the concentrations of the species, but always maintaining that of [Ni^{2+}] as equal to or greater than three times that of phenanthroline, so that the presence of [Ni phen]$^{2+}$ only has to be considered,[4, 10] the rate of exchange was proved to be of first order in complex concentration and independent of the concentration of nickel ion. The exchanges therefore take place completely through dissociation and an associative path involving Ni^{2+} is unimportant. No appreciable hydrolysis of Ni^{2+} occurs below pH 8.[11] The results are given in Table 1. In Run 9 [^{63}Ni phen]$(NO_3)_2$ was added to inactive nickel ion, and the decrease in activity of the [Ni phen]$^{2+}$ fraction followed. A similar result to that obtained in other runs,

[10] Sone, Krumholz, and Stammreich, *J. Amer. Chem. Soc.*, 1955, **77**, 777.

[11] Gayer and Wootner, *ibid.*, 1952, **74**, 1436.

with the different procedure indicated above, is strong evidence that the species present in all other runs, and whose exchangeability is being examined, is the mono-phenanthroline complex. Run 10 was carried out in 0·1M-nitric acid to compare with conditions used by Margerum *et al.*[4]

Preparation of [Ni phen $(H_2O)_4](NO_3)_2$.—Phenanthroline hydrate (2·0 g.) and nickel nitrate hexahydrate (11·5 g.) were dissolved in warm water (25 c.c.) and the solution allowed to cool. The pale blue crystalline precipitate was washed with a small amount of ice-cold water (in which it was very soluble), and air dried [Found: C, 33·8; H, 3·7; Ni, 13·3; H_2O (Karl Fischer), 18·2. $C_{12}H_8O_6N_4Ni,4H_2O$ requires C, 33·2; H, 4·1; Ni, 13·5; H_2O, 16·5%]. The material when dried (P_2O_5) at 80° *in vacuo* lost the water (Found: Ni, 15·5; NO_3, 33·5; H_2O, 0·4. $C_{12}H_8O_6N_4Ni$ requires Ni, 16·2; NO_3, 34·1%). The solubility of this greenish-blue *compound* was similar to that of the perchlorate.[15] It did not give nickel dimethylglyoxime in aqueous alcohol but the red substance was rapidly precipitated on addition of ammonia. The substance gave a greenish precipitate with sodium hydroxide but this was not nickel hydroxide [15] since it dissolved in hot water and was reprecipitated on cooling. It appears to be the monophenanthrolinenickel(II) hydroxide. Rough magnetic measurements on the anhydrous compound indicated two unpaired electrons ($\mu \simeq 2·7$ B.M.).

DISCUSSION

The results of the present work, as well as data for the dissociation of [Ni $\text{phen}_3]^{2+}$ ion,[1] are collected in Table 2.

TABLE 2. *Kinetic data for the dissociation of nickel phenanthroline complexes in aqueous solution at* 25·0°.

Ion	10^4k (min.$^{-1}$)	E_{act} (kcal. mole^{-1})	$\Delta S^‡$ (e.u.)	$\Delta S_1^‡$ (e.u.)	log *PZ* (min.$^{-1}$)
[Ni $\text{phen}_3]^{2+}$	4·6	25·2	0·9	− 6·9	15·2
[Ni $\text{phen}_2]^{2+}$	10·7	23·1	−4·6	−12·5	14·0
[Ni phen$]^{2+}$	5·3	26·2	4·6	−3·2	16·0

$\Delta S^‡$ computed from value of *k* given; $\Delta S_1^‡$ obtained from value of *k* given by $R = k$ [complex] $[H_2O]$, in both cases $k = (e\boldsymbol{k}T/\boldsymbol{h}) \exp(\Delta S^‡/\boldsymbol{R}) \exp(-E_{act}/\boldsymbol{R}T)$being used.[12]

The striking feature is the similar values for the rates of dissociation and the energies of activation of the tris- and mono-phenanthroline species. Even although the bis-species dissociates with an apparently higher rate than the other two, a factor not more than two is involved and this might be high in view of the inaccuracies inherent in the determination. Certainly the rate of removal of one phenanthroline molecule from the tris-species is no slower than from the mono-, and evidently a scheme of the kind commencing with a slow bimolecular aquation of the tris-species and ending with fast spontaneous heterolysis of succeeding complex ions does not operate here.[13] From the similar values for each kinetic parameter it appears certain that the same mechanism operates throughout the sequence of changes pictured in eqn. (1). The $\Delta S_1^‡$ values may be of the order expected [14] if an S_N2 mechanism, involving participation of water, is operative but with the paucity of kinetic information on complex ions such a correlation is very speculative.

Margerum, Bystroff, and Banks [4] found that the values of k_{-2} and k_{-3} were very close to that of k_{-1} and could not readily be determined. However, rate-constant values were estimated as 10^2—10^3 l. mole^{-1} sec.$^{-1}$, and with this value in conjunction with an equilibrium constant for K_2 (8×10^{-9}), it can be easily shown that $k_2 \sim 5$—50×10^{-5} min.$^{-1}$, a value of the same order as that obtained in neutral conditions. The variation with pH of the rate constant for dissociation of [Ni phen$]^{2+}$ was expressed by the relation: [4]

$$k_1 = ([H^+] + 0·015)/(8·4 \times 10^3[H^+] + 3·6 \times 10^3) \text{ sec.}^{-1}$$

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[12] Glasstone, Laidler, and Eyring, " The Theory of Rate Processes," McGraw-Hill Book Co. Inc., New York, 1941, pp. 417, 433.

[13] (*a*) Brown, Ingold, and Nyholm, *J.*, 1953, 2674; (*b*) Brown, *Revs. Pure Appl. Chem.*, 1954, **4**, 57.

[14] See, for example, (*a*) Baxendale and George, *Trans. Faraday Soc.*, 1950, **46**, 736; (*b*) ref. 3; (*c*) Postmus and King, *J. Phys. Chem.*, 1955, **59**, 1216.

[15] Pfeiffer, Dominik, Fritzen, and Werdelmann, *Z. anorg. Chem.*, 1949, **260**, 84.

It is thus apparent that the dissociation rate will be appreciably constant in solutions more alkaline than pH 3·5. The constancy of rate constant between pH 5·7 and pH 6·8 (Table 1; Runs 2—4) agrees with this but our value ($5·3 \times 10^{-4}$ min.$^{-1}$) does not agree with that extrapolated from the formula above ($2·5 \times 10^{-4}$ min.$^{-1}$). This however is perhaps not surprising, since this relation was determined from results at fairly high acidities, and slight modification of the expression to give our value on extrapolation need not seriously disturb the experimental agreement with the acid dissociation experiments. We do not think that our use of nitrate (rather than perchlorate) would account for the increased value. An exchange at pH 1·05 was also studied (Run 10); less than 1% dissociation of the monophenanthroline compound occurred because the reactant concentration was much higher than in the acid-dissociation experiments, where at this pH about 10% dissociation will occur. The value obtained ($17·0 \times 10^{-4}$ min.$^{-1}$) agrees reasonably with that interpolated from the formula above ($15·6 \times 10^{-4}$ min.$^{-1}$). No effect of increased ionic strength was noticed in the exchange experiments (Runs 4, 6, and 7).

During the work the blue solid [Ni phen $(H_2O)_4](NO_3)_2$ was isolated simply by mixing phenanthroline with excess of nickel nitrate in concentrated aqueous solution. The pale blue solid [Ni phen $(H_2O)_4](ClO_4)_2$ has been prepared by an indirect method[15] but its existence has been questioned.[16] The complex nitrate is very soluble in water, and the visible spectra corresponded closely to that calculated from the spectra of equilibrium mixtures containing Ni_{aq}^{2+} and phenanthroline in 1 : 1 and 1 : 2 molar ratios.[3] Its ultraviolet spectra had maximum molar extinction coefficients values of $34·4 \times 10^3$ (225 mμ), $34·7 \times 10^3$ (270 mμ), and $10·7 \times 10^3$ (291·5 mμ) which compare closely with values, obtained from a mixture of 2×10^{-3}M-[Ni^{2+}] and $1·5 \times 10^{-5}$M-[phen], of $36·5 \times 10^3$ (228 mμ), $36·5 \times 10^3$ (270 mμ), and $11·0 \times 10^3$ (292 mμ).[10] As would be expected the blue aqueous solution was stable during spectrophotometry.

The results of exchange (*a*) between [Ni $phen_3]^{2+}$ and [Ni $phen_2]^{2+}$ unequivocally establish $k_3 = 87·5 \times 10^{-4}$ min.$^{-1}$ at 45·0° which compares well with $k_{(\text{ligand exch})} = 95 \times 10^{-4}$ min.$^{-1}$ at 45·1° obtained previously.[1] This agreement, in addition to the results obtained with [Ni $phen_2]^{2+}$ and [Ni phen]$^{2+}$, confirms that the condition $R_3 \gg R_2, R_1$ (eqn. 1) holds with the ligand-exchange experiments described previously. The results emphasise that in order to equate exchange rate constants with dissociative rate constants (even when the exchange mechanism is dissociative) it is necessary to have ancillary information regarding the dissociative behaviour of the lower complex ions which may be present even only in traces.

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[16] Brandt, Dwyer, and Gyarfas, *Chem. Rev.*, 1954, **54**, 959.