751. *Factors influencing the Rates of Dissociation of Metal Complexes. Part I. The Mechanism of Dissociation of Mono(ethylenediamine)-nickel(II) Ion.**

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The rate of dissociation of $[\mathrm{Ni\,en(H_2O)_4}]^{2+}$ into nickel ion and ligand has been examined in aqueous solution at 0° over a wide range of pH. The rate increases about twenty-fold from pH 7·3 to 4, then remains constant until pH 1·5, and increases again at higher acid concentration. These rates are estimated from (*a*) $^{63}\mathrm{Ni}^{2+}$ exchange experiments (in the pH region where no net chemical reaction occurs), (*b*) the rate of consumption of acid added to maintain constant pH as amine is liberated from the dissociating complex (pH 5 to 2), and (*c*) spectrophotometry (at acidities greater than 0·01M).

The complex acid-dependence can be explained in terms of a rate-determining step (rate constant k_2) involving the first bond rupture of the bidentate ligand measured by the constant rate in weakly acid solution. A comparison of $^{63}\mathrm{Ni}^{2+}$ and $^{3}\mathrm{H_2O}$ exchange studies with the complex, at chemical equilibrium, in neutral solution also yields a value for k_2 and the agreement from the independent approaches is good. The enhanced rate in highly acid solution results from proton-aided rupture of the first bond, the contribution being directly proportional to C_{H^+}. In a dilute solution of $[\mathrm{Ni\,en(H_2O)_4}]^{2+}$ in 2M-perchlorate, $k_2 = 10^{16} \exp(-20{,}500/\boldsymbol{R}T)$ min.$^{-1}$. The significance of the results is discussed.

ALTHOUGH there is considerable information about the successive stability constants for many organic chelate systems [1] there are, unfortunately, many fewer data on the formation and dissociation † rates of metal complexes and of the many factors influencing these rates. Further, the study of the mechanism of dissociation of simple chelates has not led to completely satisfactory results.[2a] In an attempt to remedy some of these deficiencies, the present work was commenced.

Our earlier studies of ethylenediamine exchange and acid dissociation of $[\mathrm{Ni\,en_3}]^{2+}$ in water,[3] as well as the dissociation studies in methanol at low temperatures,[4] indicated that the dissociation of $[\mathrm{Ni\,en}]^{2+}$ should be measurable at 0°. The mono-complex is the simplest to investigate and interpret, since we are not concerned then with multiple ligand dissociation. The rate behaviour over a wide range of pH should give insight into the detailed mechanism of chelate dissociation and if, in addition, we study the exchange of amine hydrogen with water using the now readily available tritium (^{3}H) isotope we might differentiate any stages of co-ordinated and free amine groups during the stepwise dissociation. We were encouraged in the latter respect by the work of Carter, Odell, and Llewellyn,[2b] who showed from $\mathrm{H_2{}^{18}O}$ exchange that one oxalate group of $[\mathrm{Cr(oxal)_3}]^{3-}$ must open and close at one end many times before complete rupture, although the quantitative interpretation of their results was complicated.

EXPERIMENTAL

Materials.—Nickel perchlorate solutions were obtained by dissolving well-washed freshly precipitated nickel hydroxide (obtained from " AnalaR " nickel nitrate and sodium hydroxide)

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* Presented in part at the International Conference on Co-ordination Chemistry, London, April 1959.

† The terms aquation and hydrolysis have also been used with the same connotation.

[1] " Stability Constants," Part I, Organic Ligands, The Chemical Society, London, 1957.

[2] Basolo and Pearson, " Mechanisms of Inorganic Reactions," Wiley, New York, 1958, (*a*) p. 152 *et seq.*, (*b*) p. 272.

[3] Popplewell and Wilkins, *J.*, 1955, 4098.

[4] Bjerrum, Poulsen, and Poulsen, " Proceedings of the Symposium on Co-ordination Chemistry " Danish Chemical Society, 1954, p. 51.

in the minimum of " AnalaR " perchloric acid. The solution was standardised by complexometric analysis.[5] Ethylenediamine nitrate and perchlorate were prepared from distilled ethylenediamine. $^{63}\mathrm{Ni(NO_3)_2}$ solution was obtained as described previously,[6] and tritiated water purchased from A.E.R.E., Harwell. The following nickel complexes were prepared:

$[\mathrm{Ni\ en(H_2O)_4}](\mathrm{NO_3})_2$. Nickel nitrate hexahydrate (15 g.) was dissolved in water (5 c.c.). and ethylenediamine hydrate (1 g.) added. The warm solution was cooled in ice, and the pale blue crystals of the *mono-complex* were filtered off, washed with a small amount of ice-cold water, then acetone, and finally air-dried (yield 3·0 g.) (Found: C, 7·45; H, 5·05; Ni, 18·8; H_2O, 23·2. $\mathrm{C_2H_{16}N_4NiO_{10}}$ requires C, 7·6; H, 5·1; Ni, 18·7; H_2O, 22·9%). The tritium-labelled compound was prepared on about 1/5th of this scale by using ethylendiamine hydrate in ^3H_2O.

$[\mathrm{Ni\ en(H_2O)_4}][\mathrm{C_{10}H_6(SO_3)_2}],2\mathrm{H_2O}$.[7] This was precipitated when a saturated solution of disodium naphthalene-1,5-disulphonate was added to a solution containing the $[\mathrm{Ni\ en}]^{2+}$ ion (Found: en, 11·6; Ni, 11·4; H_2O, 21·6. Calc. for $\mathrm{C_{12}H_{26}O_{12}N_2S_2Ni}$: en, 11·7; Ni, 11·5; H_2O, 21·1%). The substance turns green when heated at 60° over phosphoric oxide for several hours.[7]

Exchange Runs.—(a) *Nickel exchange*. The separation of $[\mathrm{Ni\ en}]^{2+}$ from Ni^{2+} proved difficult. Many anions were tried but the only satisfactory one proved to be naphthalene-1,5-disulphonate, which precipitated the complex, free from nickel ion, when the concentration of the former exceeded 0·04M. Nickel ion (0·12—0·20M) and ethylenediamine salt (0·04—0·08M) were mixed, pH was adjusted, neutral salt added, if required, and the solution settled to thermal equilibrium. Exchange was initiated by adding $^{63}\mathrm{Ni}^{2+}$. At various times exchange was quenched by adding an ice-cold saturated solution of disodium naphthalene-1,5-disulphonate to the mixture, shaking vigorously, and then scratching hard with a sharp glass rod. A blue precipitate of the mono-complex, $[\mathrm{Ni\ en(H_2O)_4}][\mathrm{C_{10}H_6(SO_3)_2}],2\mathrm{H_2O}$, appeared, usually within

TABLE 1. *Dissociation of* $[\mathrm{Ni\ en}]^{2+}$ *to nickel ions in nitrate medium.*

Run no.	pH	[complex] (mmole l.$^{-1}$)	[nickel] (mmole l.$^{-1}$)	$t_{1/2}$ (min.)	10^3R Ni (min.$^{-1}$ mole l.$^{-1}$)	10^2k_{Ni} (min.$^{-1}$)
		(*a*) pH range 7·3—5·7 ($^{63}\mathrm{Ni}^{2+}$ exchange studies) at 0·2°				
1	7·3	80·0	120·0	10·0	3·3	4·15
2	7·1	80·0	120·0	8·5	3·9	4·9
3	6·8	80·0	120·0	4·9	6·8	8·5
4[a]	6·8	80·0	120·0	4·8	6·9	8·6
5[a]	6·8	80·0	200·0	5·7	7·0	8·75
6[a]	6·8	40·0	120·0	6·3	3·3	8·25
7[b]	6·8	40·0	120·0	6·1	3·4	8·5
8	6·2	69·0	131·0	4·0	7·5	11·3
9	5·7	54·7	145·3	2·1	10·5	23·7
		(*b*) pH range 5·0—2·1 (H^+ consumption) at 0·2°.				
10	4·9	80·0	200·0	1·28	—	54
11	4·0	80·0	200·0	1·08	—	64
12	3·0	100·0	200·0	1·03	—	67
13	2·1	80·0	120·0	1·03	—	67
		(*c*) pH 1·0 (spectral) at 0·6°.				
14	1·0	100·0	200·0	1·00	—	69
		(*d*) ^3H_2O exchange studies at 0·6°.				
					10^3R_{H}	10^2k_2
15	7·1	100·0	200·0	1·75	158	74
16	6·7	153·0	200·0	1·43	297	88
17[c]	6·7	80·0	200·0	1·53	145	82
18	6·2	80·0	200·0	1·50	148	81
19	1·5	80·0[d]	200·0	<5% in 1 min.		—

[a] Ionic strength = 1·0M-nitrate. [b] Ionic strength = 2·0M, in perchlorate medium. [c] ^3H_2O being used. [d] Complex concentration at commencement of run.

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[5] Schwarzenbach, " Complexometric Titrations," transl. by Irving, Methuen, London, 1957.

[6] Wilkins and Williams, *J.*, 1957, 4514.

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

10—20 sec., otherwise the point was abandoned, and the point of " clouding " was taken as the exchange time. The precipitate was quickly centrifuged, washed twice with cold water, and dissolved in dilute hydrochloric acid, and nickel was precipitated with dimethylglyoxime and ammonia. ^{63}Ni assay was as described previously.[6] Only a very small " zero-time " exchange was obtained by this procedure (Fig. 1, Curve *A*). The results are in Table 1(*a*). Spectral analysis of Run 3 showed that the mono-species predominated with maxima at 372, 625, and 980 mμ (Ballhausen [8a] reports 370, 640, and 980 mμ), and inflection point at *ca.* 730 mμ.[8b] This was verified from the known stability data.[1] Runs 3—7 indicated that Rate = k_{Ni}[complex], even though it was strongly pH-dependent, and that at pH = 6·8 the value of k_{Ni} did not vary in 0·76M and 1·0M-nitrate and 2.0M-perchlorate. The rate data are not accurate for Runs 8 and 9 because of relatively large zero-time exchange. This arises from complex dissociation (*ca.* 15 and 30% respectively from spectral data) at these pH.

(b) *Hydrogen exchange.* Basically the method was similar to (a). The equilibrium of $[\text{Ni en}]^{2+}$ and Ni^{2+} was set up and exchange initiated by the addition of the tritiated nickel complex. The separated complex naphthalenedisulphonate was washed with cold water (no heterogeneous exchange occurs at this stage), then alcohol and ether, air-dried, and radio-assayed as described below. In one run (No. 17) $^{1}\text{H}^{3}\text{HO}$ was added to the exchange mixture, and the increase in activity of the precipitated complex measured. This will not start from zero because of the presence of tritiated water in the solid. It is necessary in this case to use the precipitant in $^{1}\text{H}^{3}\text{HO}$ of similar specific activity to that in the exchange mixture, this being much easier than mixing known volumes, accurately, of reactants and precipitants at these temperatures and exchange speeds. In order to follow an exchange completely the following detailed procedure was adopted in one run (No. 16) with the experimental results shown (see also Fig. 1, Curve *B*): $[\text{Ni *en(*H}_2\text{O)}_4](\text{NO}_3)_2$, prepared as described earlier, and naphthalenedisulphonate added to filtrate gave $[\text{Ni *en(*H}_2\text{O)}_4]$ naphthalenedisulphonate,2*H_2O, which gave 3460 counts/min. Therefore $[\text{Ni *en(*H}_2\text{O)}_4]$ naphthalenedisulphonate,2H_2O gives 2595 counts/min. Then $[\text{Ni *en(*H}_2\text{O)}_4](\text{NO}_3)_2$ (30 mg.) was added to Ni^{2+} (1·0 c.c., 0·2M, pH ~6) and the complex was precipitated with saturated naphthalenedisulphonate solution (1·0 c.c.), all solutions being pre-cooled to 0°. This procedure was repeated for each exchange point and at the end of the exchange. The value at zero time was 837 counts/min. Thus all the hydrogen in the water of $[\text{Ni *en(*H}_2\text{O)}_4](\text{NO}_2)_2$ has exchanged immediately ($1/3 \times 2595 = 865$). The remaining slower process with only a small zero-time exchange is due to exchange of amine-hydrogen, the final equilibrium value being 37 counts/min. It is difficult to calculate an equilibrium value since there will almost certainly be an isotope effect and the precipitated complex contains both types of hydrogen, amine, and water and the specific activites of these will differ.

There being no isotope effect on the rate R_{H} (see below), $R_{\text{H}} = (0{\cdot}693/t_{\frac{1}{2}}) \times 4[\text{complex}]$. In both nickel and hydrogen exchanges reasonably good first-order exchange plots were obtained (Fig. 1).

(c) *Tritium assay.* All measurements were made with dry samples, in a Packard (U.S.A.) gas-flow proportional counter, methane or (less satisfactorily) argon–methane being used. The solid was spread over a cylindrical depression in a thick aluminium disc and firmly " matted " by steady pressure at the end of a cylindrical rod placed over the sample.[3] It was found unnecessary to incorporate graphite in the sample [9] to obtain reproducibility in count rate. " Infinite thickness " is easily reached with 0·6 mg. cm.$^{-2}$ or more.[10] The important quantity in exchange reactions is relative specific activity, and this is measured by relative count rates, since the other factors which affect the latter (geometry, back-scattering, etc.) are constant. The same amount, approximately, of material ($\geqslant$0·6 mg. cm.$^{-2}$) was used in each sample since the count rate was a little sensitive to sample height. Reproducibility of counting was about ±5%. The background varied from 20 to 30 counts/min.

H^{+}-*Consumption Experiments.*—As the complex dissociates, the free amine liberated increases the pH value. Constant pH can be maintained by controlled addition of acid, the rate of which measures $d[\text{Ni en}^{2+}]/dt$. In early experiments we used a Radiometer titrator (Copenhagen), acid being added from a micro-syringe by means of an electronic relay, and the rate

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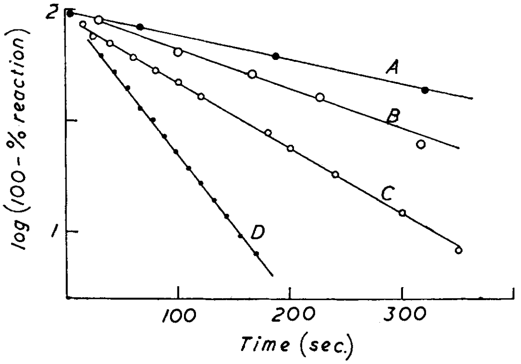
[8] (*a*) Ballhausen, *Dansk. Mat. Fys. Medd.*, 1955, **29**, No. 8; (*b*) Jörgensen, *Acta Chem. Scand.*, 1956, **10**, 887.

[9] Banks, Crawhall, and Smyth, *Biochem. J.*, 1956, **64**, 411.

[10] Rydberg, *Acta Chem. Scand.*, 1958, **12**, 399.

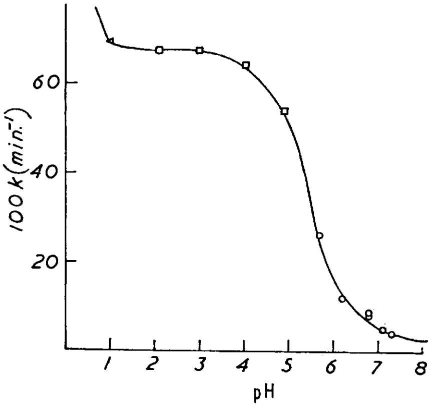
of acid consumption recorded automatically.[11] Although this arrangement was convenient we found that the apparatus did not always respond quickly to pH changes because of the relatively fast dissociation rates studied in this and similar work. We therefore replaced the automatic features by a manual Morse key which operated a solenoid valve attached to the burette. With the key in the " on " position the burette valve was opened and a small controlled volume of acid was admitted to the well-stirred reaction solution, the tip of the burette extended to a fine jet being below the surface of the solution. With this arrangement there was no difficulty in holding the pH within 0·05 unit as the dissociation proceeded or in observing the burette reading, so that half-lives as short as 30 sec. could be accurately measured. In the runs at higher concentrations of reactants for comparison with the exchange runs [Table 1(*b*)] about 15 c.c. of solution were used and 1M-nitric acid as added acid. In the perchlorate runs [Table 2(*a*)], 2M-sodium perchlorate (75—100 c.c.) at the required pH was cooled to 0°, a pre-cooled solution of the complex (2 c.c. of 0·1M-complex, 0·2M-nickel, at pH 6·8) rapidly added, and the rate of addition of acid (0·1 or 1·0M-perchloric acid in 2M-perchlorate) recorded as the pH was maintained constant. A typical experimental curve is shown in Fig. 1, Curve *C*, which shows a slight initial curvature observed in some runs owing to the presence of a small amount of the bis-species ($t_{\frac{1}{2}} \sim 5$ sec.) which dissociates more rapidly than the mono-species. The consumption of acid corresponded to that calculated for two amine groups. Runs 20, 21, 23 (with 31) show that the rate constant is independent of the concentrations of complex, products, and perchlorate.

FIG. 1. *Typical first-order curves.*



A, ^{63}Ni exchange (Run 4).
B, ^{3}H exchange (Run 16).
C, H$^+$-consumption (Run 24).
D, Spectral (Run 38).
The time-ordinate is doubled for *B*.

FIG. 2. *Variation of first-order rate constant for* [Ni en]$^{2+}$ $\longrightarrow$ Ni^{2+} *change with* pH. [Ni en^{2+}] = 40—80 mM, [Ni^{2+}] = 120—200 mM, μ = 0·8—1·0M-NO$_3^-$.



○ ^{63}Ni exchange. □ H$^+$-consumption. △ Spectral.

Spectrophotometry.—The spectra of (Ni en]$^{2+}$ and Ni^{2+} (cf. ref. 8) show their greatest absorption difference around 900 mμ, and we used this wavelength to follow the change. In one case, we found an identical rate when we used instead 550 mμ. At 422 mμ, an isosbestic point, no absorption change occurred during the dissociation. Because of the rapid dissociation in excess of acid, it was necessary to study the reaction at ice-water temperature. A Perspex container was constructed which could fit, in a reproducible position, into the cell compartment of a Unicam SP.600 spectrophotometer. The container was divided into a central portion which contained the reaction solution and interrupted the light path (45 mm.) of the spectrophotometer. This central portion was surrounded by ice-water on both sides as well as underneath. A Perspex lid fitted tightly over the container. " Misting " on the cell face was avoided by passing cold dry air through the spectrophotometer compartment for about 1 hr.

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[11] For a discussion see Jacobsen, Leonis, Linderstrøm-Lang, and Otteson, in " Methods of Biochemical Analysis," ed. Glick, Interscience, New York, 1954, Vol. 4, pp. 171 *et seq.* This method has been used extensively in biochemistry, but this work is apparently one of the first applications to complex ion kinetics.

before, as well as during, the run. The procedure for a measurement was as follows: (i) Pre-cooled distilled water (*ca.* 15 c.c.) was placed in the central portion of the Perspex cell and optical balance obtained in " check " position. (ii) The water was removed and replaced by the reaction solution (10 c.c., *ca.* 0·02M-complex, 0·04M-nickel, ionic strength 2·0M-perchlorate) pre-cooled to 0·3°. Pre-cooled perchloric acid (with added sodium perchlorate, ionic strength 2·0M) was added (5 c.c.) and the cell and compartment lids were quickly replaced. " Misting " cleared within 15 sec. and optical densities could be read within 20 sec. of mixing.

TABLE 2. *Dissociation of* [Ni en]$^{2+}$ *to nickel ions in perchlorate medium of ionic strength* = 2·0M.

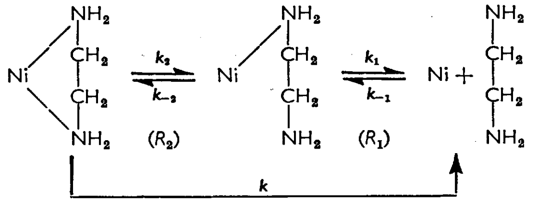
Run no.	Temp.	pH	[complex] (mmole l.$^{-1}$)	[nickel] (mmole l.$^{-1}$)	$t_{\frac{1}{2}}$ (min.)	10^2k_2 (min.$^{-1}$)
		(*a*) pH range 5·6—3·5 (H$^+$ consumption).				
20 [a]	0·2	5·5	0·8	2·0	1·80	38·5
21	0·3	5·4	3·3	5·0	1·82	38·1
22	0·3	5·2	2·6	3·9	1·75	39·6
23 [b]	0·3	4·0	3·3	—	1·68	41·2
24	0·3	3·5	2·6	3·9	1·75	39·6
25	2·25	4·0	2·9	4·3	1·35	51·4
26	2·25	4·0	2·9	4·3	1·33	52·1
27	4·3	4·0	2·9	4·3	1·03	67·3
28	4·3	4·0	2·9	4·3	1·03	67·3
29	6·1	4·0	2·9	4·3	0·82	84·5
		(*b*) 0·05—3·0M-HClO$_4$ (spectral, 0·6°).				
	[acid]					
30	0·03		13·3	20·0	1·85	37·5
31 [c]	0·10		100	200	1·67	41·5
32	0·33		26·7	40·0	1·52	45·7
33	0·68		26·6	40·0	1·23	56·3
34	1·08		26·7	40·0	1·07	65·0
35 [b]	1·50		30·0	—	0·88	78·7
36 [b]	1·50		30·0	—	1·05	66·0
37	1·58		26·7	40·0	0·90	77·0
38 [e]	2·08		26·7	40·0	0·77	90·3
39 [e]	3·15		26·7	40·0	0·67	104·0

[a] Ionic strength = 8·4mM. [b] [Ni en $(H_2O)_4$]$(NO_3)_2$ being used. [c] Reaction followed at 550 mμ; all others at 900 mμ. [d] Reaction in 85% D_2O. [e] Ionic strength >2·0M.

With this arrangement it was not easy to reach temperatures below 0·6° but the temperature stability was good, rising by less than 0·1° in 30 min. The optical density at the completion of the reaction was always small. After 30 min. the " check " with water still balanced. The linearity of the first-order plots over four or five half-lives is shown in Fig. 1, Curve *D*. Results were reproducible. Runs 14 and 31 show that with the concentration of complex at or above 0·1M, perchlorate has less accelerating effect than a nitrate (or chloride) medium.

DISCUSSION

Fig. 2 shows the variation with pH of the rate constant for *overall* dissociation (*k*) of [Ni en]$^{2+}$. The equilibria involved in this process can be represented as shown (co-ordinated water and charges have been omitted for convenience):



We shall refer to the species containing unidentate ethylenediamine as the intermediate in the subsequent discussion. In neutral solution and in acid solution, the equilibrium will lie to the left and to the right respectively. It is convenient to discuss the dissociative behaviour in terms of three regions.

Neutral Region.—The nickel-exchange rate (R_{Ni}) is markedly pH-dependent. This result can be understood from the above scheme. With the system at chemical equilibrium [12,13]

$$R_{\text{Ni}} = R_2R_1/(R_2 + R_1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If we denote the concentration of $[\text{Ni en}]^{2+}$ by a and that of the intermediate by b then

$$R_{\text{Ni}} = \frac{(k_2a)(k_1b)}{k_2a + k_1b}$$

and since

$$k_{-2}b = k_2a,\ R_{\text{Ni}} = \frac{k_2k_1a}{k_{-2} + k_1} = k_{\text{Ni}}a$$

This agrees with the observed first-order dependence on complex and lack of dependence on nickel-ion concentrations. Further there is also present, in amounts dependent on pH, a protonated form of the intermediate which will disrupt completely with its characteristic rate constant, but which is assumed to ring-close very lowly. This situation can be accommodated by expressing k_1 in the form $k_1 = k_1^{\circ} + k_1^{\text{H}}[\text{H}^+]$. For reasons which we shall see k_2 can be assumed to be acid-independent in this pH region. Therefore

$$k_{\text{Ni}} = \frac{k_2(k_1^{\circ} + k_1^{\text{H}}[\text{H}^+])}{k_{-2} + k_1^{\circ} + k_1^{\text{H}}[\text{H}^+]} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

From this it can be easily shown that

$$\frac{1}{(k_2 - k_{\text{Ni}})} = \frac{k_{-2} + k_1^{\circ}}{k_2k_{-2}} + \frac{k_1^{\text{H}}[\text{H}^+]}{k_2k_{-2}}$$

The linear plot of $1/(k_2 - k_{\text{Ni}})$ against $[\text{H}^+]$ is shown in Fig. 3. The value of k_2 can be obtained as described below. Extrapolation to $[\text{H}^+] = 0$ gives $k_{\text{Ni}} = 0{\cdot}033$ min.$^{-1}$, indicated by the limiting rate in Fig. 2 and reached at pH = 8. The onset of base catalysis may occur at this stage. It is not possible to perform nickel exchange above pH 7·4.

A comparison of nickel and hydrogen exchange rates at the same pH proves very fruitful. We must first establish that with our conditions, no *direct* hydrogen exchange occurs between the co-ordinated amine and water, as has been observed with certain ammines of cobalt(III), palladium(II), and platinum(II).[14,15,16] Our evidence is this: (i) we observe a constant hydrogen-exchange rate over a ten-fold change in hydrogen-ion concentration, whereas we should expect the rate to be a function of pH on any direct mechanism, *i.e.*, inversely proportional to $[\text{H}^+]$ on the basis of formation through a metal amide: [14,15,16]

$$\text{OH}^- + -\text{M(NH}_3)^{x+} \rightleftharpoons -\text{M(NH}_2)^{(x-1)+} + \text{H}_2\text{O}$$

(ii) we have obtained different rates of hydrogen exchange for other amines (to be described in subsequent papers) the values for which can be easily accommodated into our scheme but which would not otherwise be easily understood.

We assume then that on bond rupture, as an $-\text{NH}_2$ group is freed, rapid exchange between this and water occurs. We have confirmed that there is rapid ligand–water exchange at these pH. Tritium exchange (R_{H}) therefore is analogous to ligand exchange for the system

$$\text{MA}_4 \underset{}{\overset{(R_2)}{\rightleftharpoons}} \text{MA}_2 + \text{A}_2 \overset{(R_1)}{\rightleftharpoons} \text{M} + 2\text{A}_2$$

for which [12]

$$R_{\text{H}} = \frac{2R_2\ (2R_2 + 4R_1)}{2(R_2 + R_1)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

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[12] Wilkins and Williams, *J. Inorg. Nuclear Chem.*, 1958, **6**, 52.

[13] Taube, *Chem. Rev.*, 1952, **50**, 78.

[14] Anderson, Briscoe, and Spoor, *J.*, 1943, 361.

[15] Anderson, Briscoe, Cobb, and Spoor, *J.*, 1943, 367.

[16] Block and Gold, *J.*, 1959, 966.

Combining (1) and (2) we have

$$R_H = 2R_2 + 2R_{Ni} = 2k_2[\text{Ni en}^{2+}] + 2R_{Ni}$$

We have measured R_H and R_{Ni} at different acidities [Tables 1(*a*) and (*d*)]. The contribution of R_{Ni} towards R_H varies with pH but is always small. This and the constancy of R_H indicates that hydrogen exchange takes place mainly through one-ended bond rupture and that the rate of the latter process is acid-independent in this pH range. Since N–H bond breaking and making (for exchange) is not involved in the rate-determining step (k_2), no hydrogen-isotope effect on the rate would be expected. Further, in most exchanges there is a low concentration of labelled reactant, with which conditions the isotope effect does not enter into the rate equation.[17] For the exchange experiments we must use relatively high reactant concentrations and then $k_2 = 0{\cdot}80 \pm 0{\cdot}12$ min.$^{-1}$ (0·6°).

Weakly Acid Region.—An independent method of obtaining k_2 is from the data on the dependence of k on pH. It can be easily shown from eqn. (2) that, at high enough acidities, a limiting rate for k will be obtained and that this value can be equated to k_2. We observed such a limiting rate [Table 1(*b*) and (*c*) and Fig. 2] and with the reactant concentrations used in the exchange runs we observed $k_2 = 0{\cdot}69 \pm 0{\cdot}03$ min.$^{-1}$ at 0·2°. This is in good agreement with the value from exchange data, the difficulties in obtaining really accurate results for the rapid exchanges being considered. As a corollary to this there should be very slow or no exchange between water and the complex in this limiting region since rupture of one bond and amine exchanges *always* lead to complete and irreversible dissociation. Thus the specific activity of the tritiated amine remains constant at pH 1·5 for nearly one minute (Run 19) which is the longest time the experiment can be carried out because of concomitant loss of complex by dissociation. In this time at pH 6·8 the specific activity of the complex would have fallen by nearly one-half.

FIG. 3.

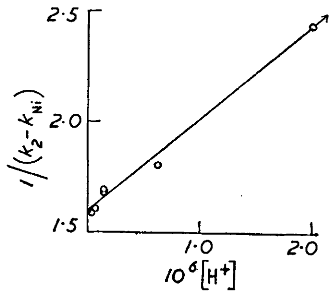
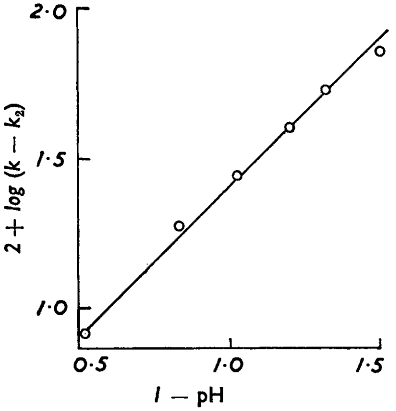


FIG. 4.



We investigated rates in this region also at much lower concentrations of reactants than that above and at constant ionic strength. We used a perchlorate medium since we had observed that chloride and even nitrate enhanced rates. The results are shown in Table 2(*a*). We used these conditions to determine the Arrhenius parameters and found that, for k_2, $E = 20{\cdot}5 \pm 0{\cdot}4$ kcal. mole^{-1} and log $PZ = 16{\cdot}0$ min.$^{-1}$. We also used these reactant concentrations for the determination of k_2 for a variety of amine complexes[18].

We used the hydrogen-ion consumption rate at constant pH as a measure of the dissociation rate in this region. The observation of a first-order rate for over 90% of the reaction, in addition to a final acid consumption corresponding to *both* amino-groups in the

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[17] Harris, *Trans. Faraday Soc.*, 1951, **47**, 716.

[18] Shamsuddin Ahmed and Wilkins, unpublished work.

chelate, shows that the intermediate is unstable, and rapidly dissociates further once formed. There is close agreement between the k_2 values obtained by this method and from spectral work at relatively low acidity (Run 30).

Strongly Acid Region.—At pH value below 2, H$^+$-consumption experiments are no longer sensitive to the liberation of small quantities of amine from the complex. We therefore examined the dissociation spectrally [Table 2(*b*)]. From Fig. 4, which is a linear plot of unit slope, $R = k[\text{Ni en}^{2+}] = \{k_2 + k_2^{\text{H}}[\text{H}^+]\}[\text{Ni en}^{2+}]$ with $k_2 = 0{\cdot}375$ and $k_2^{\text{H}} = 0{\cdot}26$ min.$^{-1}$ at 0·6°.

The acid catalysis could be explained by a pre-equilibrium involving H$^+$, followed by decomposition of the proton adduct. It is difficult to formulate such a pre-equilibrium involving the amine portion of the molecule, and it is not easy to see why, if the co-ordinated water were involved, this should affect the rate of rupture of bonds. The slightly slower rate in 85% D_2O than in H_2O (runs 35 and 36) does not provide in this case much guidance on the presence of such an equilibrium.[18, 19] We favour the idea that the hydrated proton is able, in relatively high concentration, to aid bond rupture directly by competing for the nickel–nitrogen bonding electrons. In low ionic strengths it would be expected that, for charged reactants, log k_2^{H} would vary linearly with the square-root of the ionic strength. At higher ionic strengths the effect usually tails off and, since acid-catalysis is unimportant below about 0·5M-perchloric acid, little effect of ionic strength on the rate is observed.

Summary and General Points.—Our results agree with the idea of stepwise rupture of the ligand from [Ni en]$^{2+}$ during its dissociation to Ni^{2+}. Since the p*K* of the intermediate, Ni enH^{3+}, is likely to be less than that [1] of enH$_2^{2+}$ and so have a value of *ca.* 7, then at pH 7 the free nitrogen of the intermediate will exist to an important extent as the free amino-group and the tendency to re-form chelate is then greater than that of further breakage. Thus the *overall* rate of dissociation is much less than at pH 5 where, because the intermediate must be present mainly as the acid form, re-formation is much slower, dissociation depending only on the relatively fast, rate-determining, first bond rupture. The idea of a complex containing unidentate ethylenediamine is not new and has been invoked, for example, as a chemical intermediate in recent kinetic studies.[20, 21] Schläfer and Kling [21] have studied spectrophotometrically the dissociation of [Cr en$_3$]$^{3+}$ to [Cr en$_2$(H$_2$O)$_2$]$^{3+}$ and postulated the existence of a stable intermediate during the reaction which, they suggest, might be a " one-end attached " species. However, Bjerrum, Jörgensen, and Nielsen [22] maintain that Schläfer and Kling's results can be as easily explained on the basis of a *labile* intermediate of constitution [Cr en$_2$(enH)(H$_2$O)]$^{4+}$. The subsequent dissociation of [Cr en$_2$(H$_2$O)$_2$]$^{3+}$ has been studied, and stable chemical intermediates have been suggested here also.[23]

The fact that the bond-rupture rate constant k_2 is measurable indicates that the enhanced kinetic stability of chelates compared with unidentate-containing complexes (*e.g.*, in this case ammonia complexes) does not result solely from this ability to sever and re-form a single bond before complete cleavage. In fact, in our work only a factor of about twenty (ratio of the two limiting rate constants) is thus introduced. It must therefore be easier to remove an ammonia molecule from the environment of the nickel ion than an $-NH_2$ ligand when it is attached *via* another group also. In the latter case, to constitute severance in a kinetic sense it may be that the aliphatic chain must twist so that the $-NH_2$ group is rotated away from the metal atom. The k_1 step is more analogous to Ni–NH$_3$ cleavage and we know this is fast. As well as a water molecule (as we believe) opening up the first bond (k_2), in higher acidities the hydrated proton can also aid bond

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[19] Bell, " Acid–Base Catalysis," Oxford, 1941; Wiberg, *Chem. Rev.*, 1955, **55**, 713.

[20] Gehman and Fernelius, *J. Inorg. Nuclear Chem.*, 1959, **9**, 71.

[21] Schläfer and Kling, *Z. phys. Chem.* (*Leipzig*), 1958, **16**, 14.

[22] Bjerrum, Jörgensen, and Nielsen, reported at International Conference on Co-ordination Compounds, London, 1959, Paper 101.

rupture (k_2^H) although its contribution to the effect below 3M is never overwhelming. It is apparent then that acid can enhance the overall dissociation rate of $[Ni\ en]^{2+}$ in two ways: at lower acidity, by altering the form of the intermediate, and at high acidities, more directly, by increasing the value of k_2.

Our results are compared in Table 3 with those of Bjerrum, Poulsen, and Poulsen in methanol.[4] The latter are results extrapolated to 0° from measurements at much lower temperatures. Considering the experimental difficulties and the preliminary nature of the methanol work, apart from the change in medium, we feel that the agreement is quite good. Certainly the observed sequence of a gradually slowing dissociation as ligands are removed from the tris-species to the free metal ion has been confirmed in our work. The only other chelate amine systems which have been similarly studied, phenanthroline-nickel [6] and ethylenediaminechromium [21,23] show a similar characteristic.

TABLE 3. *Kinetic data for successive dissociation of* $[Ni\ en_3]^{2+}$.

Change	Rate constant (0·0°) in 0·1–0·5M-acid (sec.$^{-1}$)	
	This work	Methanol
$[Ni\ en_3]^{2+} \longrightarrow [Ni\ en_2]^{2+}$	>0·1 (ref. 3)	8·0
$[Ni\ en_2]^{2+} \longrightarrow [Ni\ en]^{2+}$	~0·1	0·6
$[Ni\ en]^{2+} \longrightarrow Ni^{2+}$	0·01	0·1

The pattern of behaviour with pH observed here has been confirmed for several similar compounds.[18] We hope to extend our approach to mono-complexes containing an unsymmetrical bidentate ligand (*e.g.*, both a primary and a tertiary amine) so that we might in this way determine the relative tendencies of the two ends to dissociation.

We thank Drs. W. C. E. Higginson and M. J. G. Williams for discussions, and the Pakistan Government for a maintenance grant.

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[23] Schläfer and Kollrack, *Z. phys. Chem.*, 1958, **18**, 348.