814. *The Rates of Reaction of Complexes of Nickel*(II) *with Nitrogen-containing Unidentate Ligands.*

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The rates of dissociation, in an excess of acid, of nickel(II) complexes with a series of nitrogen-containing unidentate ligands have been investigated, spectrally, by the stopped-flow method. These ligands include ammonia, pyridine, aziridine, 2-aminoethyltrimethylammonium, and hydrazine. The kinetic parameters have been determined and are discussed. The rates of formation of some of these and related complexes can be estimated from the known stability constants and checked (roughly) experimentally. Some comments on the mechanism of the formation reaction are offered, and the importance of the dissociative process in determining the stability of nickel(II) complexes is further established.

ALTHOUGH there have been a number of investigations of the kinetics of reactions of complexes of cobalt(III) and platinum(II), there are only meagre kinetic data for the simple complexes of bivalent metals of the first transition series. This arises mainly from the difficulty of measuring experimentally the rapid rates of formation and replacement reactions of these complexes. Bjerrum and Poulsen [1] circumvented this problem by studying reactions at —75° and —100° in methanol, although even at these temperatures the reactions of bivalent manganese, copper, and zinc were often rapid. The subject has since lain dormant until recently Eigen and his collaborators measured the rates of some very fast reactions involving simple metal complexes, using relaxation methods.[2]

The relative inertness of nickel in the titanium–zinc series has been consistently observed, for example, in the slowness of attainment of equilibrium in thermodynamic

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[1] Bjerrum and Poulsen, *Nature*, 1952, **169**, 463.

[2] For a general account see Eigen, in " Advances in the Chemistry of the Coordination Compounds," ed. Kirschner, Macmillan, New York, 1961, pp. 371 *et seq.*

studies. In addition, it can be readily understood from crystal-field theoretical considerations that a d^8-system might react relatively slowly.[3] Thus in this, and some subsequent, work we have concentrated on nickel complexes for studying the effect of ligand structure on reactivity. Even so, the techniques for measurement of rapid reactions are usually required, of the kind used previously in the study of the ethylenediamine and racemic 2,3-diaminobutane complexes.[4] The stopped-flow method has now been used to study the acid dissociation of nickel complexes with a variety of unidentate ligands (A), each containing one donor nitrogen atom: *

$$[\mathrm{Ni(A)(H_2O)}_n]^{2+} + \mathrm{H_3O^+} \longrightarrow [\mathrm{Ni(H_2O)}_{n+1}]^{2+} + \mathrm{AH^+} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The mono-complex has been examined since (*a*) it can be obtained in solution almost free from other complex species, simplifying the kinetics, (*b*) we are not concerned with *cis*- or *trans*-forms, and (*c*) the lower species generally has the slower rate.[4] Offsetting these advantages, however, are the small spectral changes associated with reaction (1).

The complexes of ammonia and pyridine have been included for comparison with the results already obtained with polyamines and polypyridines. The effect of alkyl substitution in ammonia has been studied by examining aziridine: this cyclic imine has been shown recently to form stable, soluble metal complexes,[5] whereas alkylamines do not form complexes to a significant extent with nickel in solution. The complex of $\mathrm{NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_3^+}$ has been included to show the effect of charge within the ligand on its bond rupture. Finally, the hydrazine complex has been investigated since, being almost certainly non-chelated,[6] it contains a non-co-ordinated $-\mathrm{NH_2}$ group and interesting acid effects are possible. We have also examined very briefly the rates of formation of some of these and related complexes.

EXPERIMENTAL

Materials.—*2-Aminoethyltrimethylammonium bromide hydrochloride* resulted from heating trimethyl-2-phthalimidoethylammonium bromide with 4M-hydrochloric acid for 3 hr. (Found: C, 27·2; H, 7·0. $\mathrm{C_5H_{16}BrClN_2}$ requires C, 27·2; H, 7·3%). The phthalimide had been obtained by heating 2-bromoethylphthalimide with trimethylamine in alcohol in a sealed tube at 100° for several hours.[7] Aziridine [8] and pyridine were dried and redistilled before use. Hydrazine was generated in aqueous solution from " AnalaR " hydrazine sulphate and sodium hydroxide. The mono-nickel complex of hydrazine was soluble in a sulphate, but not chloride or nitrate, medium.

Stopped-flow Apparatus.—The general procedure has already been described.[4] The apparatus used for the efficient mixing and stopping of the reactant solutions was designed by Professor Q. H. Gibson [9] and supersedes that used in a previous study.[4] It was so constructed that it could be rigidly attached to a Unicam S.P. 500 spectrophotometer, from which the cell compartment and photocell housing had been removed.[10] Perspex windows and the photomultiplier tube used (R.C.A. I.P. 28) limit, at present, our observation range from about 375 to 675 mμ; this is, however, a useful region for many of the nickel complexes we are examining. Thermostat-controlled water was circulated through the mixing and observation chambers, temperature control being within 0·1°. For temperatures near 0°, dried air was passed over the photomultiplier tube and the windows of the observation tube to prevent misting. Conventional electronic equipment was used to convert the current changes in the

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* n almost certainly equals 5; co-ordinated water will be omitted subsequently.

[3] Basolo and Pearson, " Mechanisms of Inorganic Reactions," Wiley, New York, 1958, pp. 96 *et seq.*

[4] Ahmed and Wilkins, *J.*, 1960, 2901.

[5] Jackson and Edwards, *J. Amer. Chem. Soc.*, 1961, **83**, 355.

[6] Schwarzenbach and Zobrist, *Helv. Chim. Acta*, 1952, **35**, 1291.

[7] Gabriel, *Ber.*, 1920, **53**, 1985.

[8] *Org. Synth.*, 1950, **30**, 38.

[9] Gibson, unpublished work.

[10] Spencer and Sturtevant, *J. Amer. Chem. Soc.*, 1959, **81**, 1874.

TABLE 1.

Dissociation of $[\mathrm{NiA}]^{2+}$ to nickel ions.

Dissociating species	Temp.	$[\mathrm{Ni}]_{\mathrm{total}}$ (M)	$[\mathrm{A}]_{\mathrm{total}}$ (M)	$[\mathrm{HNO_3}]$ * (M)	Wavelength (mμ)	k (sec.$^{-1}$)
$[\mathrm{Ni(NH_3)}]^{2+}$	4·8°	0·18	0·10	0·20	610	1·06
		0·18	0·10	0·20	610	1·12
		0·18	0·10	0·50	610	1·12
	5·2	0·18	0·10	0·20	610	1·03
	15·2	0·18	0·10	0·20	610	2·73
		0·18	0·10	0·20	610	2·68
		0·18	0·10	0·20	630	3·07
		0·18	0·10	0·20	630	2·94
	25·0	0·33	0·10	0·20	610	6·19
		0·18	0·10	0·20	610	6·30
		0·18	0·10	0·20	610	5·68
		0·18	0·10	0·20 †	610	5·55
		0·18	0·20	0·50	610	6·30 ‡
		0·18	0·20	pH = 3·0 §	610	9·90
$[\mathrm{Ni(C_5H_5N)}]^{2+}$	6·3	0·20	0·10	0·20	600	7·37
		0·20	0·10	0·20	450 ¶	6·03
		0·20	0·10	0·50	600	6·67
		0·20	0·10	0·50	600	6·67
	15·2	0·20	0·10	0·50	600	16·5
		0·20	0·10	0·50	600	15·7
		0·20	0·10	0·20	450 ¶	14·7
	25·0	0·20	0·10	0·50	600	46·2
		0·20	0·10	0·50	600	38·5
		0·20	0·10	0·50	600	36·5
		0·20	0·10	0·50	600	40·8
$[\mathrm{Ni(C_2H_4NH)}]^{2+}$	5·8	0·20	0·10	0·50	595	0·67
	14·8	0·20	0·10	0·50	595	1·87
		0·20	0·10	0·50	595	1·90
	25·1	0·10	0·05	0·20	595	4·59
		0·10	0·05	0·50	595	4·59
		0·20	0·10	0·50	595	4·95
$[\mathrm{Ni(NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_3)}]^{3+}$	10·5	0·20	0·10	0·50	650	9·8
		0·20	0·10	0·50	650	9·6
		0·20	0·10	0·50	650	10·4
	25·0	0·20	0·10	0·50	650	42·0
		0·20	0·10	0·50	650	37·8
$[\mathrm{Ni(N_2H_4)}]^{2+}$	15·4	0·10	0·05	0·20	600	1·25
		0·10	0·05	0·20	600	1·30
		0·10	0·05	0·50	600	1·25
	25·0	0·10	0·05	0·50	600	3·47
		0·10	0·05	0·20	600	3·47
		0·10	0·05	0·10	600	3·27
		0·20	0·10	0·20	445 ¶	4·10
	34·0	0·10	0·05	0·20	560	9·76
		0·10	0·05	0·20	600	9·76

* Acidity at commencement. † With 2·0M-sodium nitrate. ‡ Using later portion of curve after the bis-complex reacted. § Sodium acetate–acetic acid buffer. ¶ Indicator method.

TABLE 2.

Kinetic data, $k = A \exp(-E/\boldsymbol{R}T)$, for dissociation of $[\mathrm{NiA}]^{2+}$ in nitric acid at 25°.

Species	k (sec.$^{-1}$)	E (kcal. mole^{-1})	$\log A$ (sec.$^{-1}$)
$[\mathrm{Ni(NH_3)}]^{2+}$	5·8	14·3	11·2
$[\mathrm{Ni(C_5H_5N)}]^{2+}$	38·5	16·3	13·6
$[\mathrm{Ni(C_2H_4NH)}]^{2+}$	5·0	17·2	13·3
$[\mathrm{Ni(NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_3)}]^{3+}$	40·0	16·0	13·3
$[\mathrm{Ni(N_2H_4)}]^{2+}$	3·6	18·9	14·5

photomultiplier detector into an oscilloscope trace. It was very convenient to have a display oscilloscope with 17″ tube (Airmec type 279) in series with a double-beam oscilloscope (Telequipment type D31) with attached camera. This served as a useful monitor since with the bright orange persistent phosphor it was easy to establish the reproducibility of runs and to detect flaws in the behaviour of the apparatus.[11] The rate constant for the dehydration of carbonic acid was determined spectrophotometrically, $k = 21{\cdot}2$ sec.$^{-1}$ at 22·8° ± 0·1°, compared with the value of 20·9 sec.$^{-1}$ estimated from the literature.[12]

Kinetic Runs.—(*a*) *Dissociation.* The main method utilised the slight spectral changes occurring in reaction (1). In the region which concerned us, an absorption maximum at ~650 mμ was found for all but the hydrazine complex where the peak of higher intensity was shifted to ~615 mμ ($\varepsilon_M \sim 4{\cdot}6$), indicating a stronger crystal field for this ligand. Bjerrum[13] has previously measured the spectra of all the nickel ammonia complexes up to the highest formed, namely, $[Ni(NH_3)_6]^{2+}$. The optical-density changes for reaction (1) in the 580—650 mμ region amounted to about 0·10—0·15 (0·05 with pyridine) with the concentrations used (0·2M-nickel, 0·1M-amine). It can be estimated that about 70—80% of the ligand was in a mono-complex and 5—10% in a bis-complex, although accurate calculations are difficult because metal and protonic stability constants either refer to conditions other than those used by us or are non-existent. Since, however, the dissociative process is of the first order and optical density changes reflect concentration changes, this lack of knowledge was unimportant. Nevertheless, the small amounts of the higher-absorbing and faster-reacting bis-complex led to an initial curvature in the usual first-order plot, which was thereafter linear up to at least three half-lives. In experiments with a higher $[Ni]_{Total} : [A]_{Total}$ ratio a similar rate was obtained without the initial curvature. Some runs were performed with 3—4-fold change of intensity of incident light without significant changes in rate, ruling out photocatalysis.

We also adopted a complementary approach which we have found useful in studying polyamine complexes. This is to follow the reduction in acidity which occurs in reaction (1) by using *p*-nitroaniline as indicator (~10^{-3}M) which with p$K \sim 1$ (ref. 14) is convenient for this acidity range. The optical density of *p*-nitroaniline solutions was determined at different acidities (nitric acid) and temperatures in a constant ionic strength of 1·0M, adjusted with sodium nitrate. Measurements were made at 445—450 mμ, which although not the peak position for the indicator base, is however where complexed and hydrated nickel have small, similar, absorption and interfere least in the estimation. The method was tested with the $[Ni\ en]^{2+}$ system: direct measurement[4,15] at 610 mμ gave $t_{\frac{1}{2}} = 4{\cdot}05$ sec., indirect measurement at 448 mμ gave $t_{\frac{1}{2}} = 3{\cdot}98$ sec., at 25°. The kinetic runs are given in Table 1 and the collected results in Table 2. The errors in the rate constants are about ±5—8% for reactions with $k \sim 5$ and ±10—15% with $k \sim 50$ sec.$^{-1}$. The errors in the energies of activation are ±1 kcal. mole^{-1} except for the two faster-reacting compounds where ±1·5 kcal. mole^{-1} is a more realistic value.

(*b*) *Formation.* This was much less thoroughly studied, only a few runs being performed. Nickel ion in aqueous or 50% v/v aqueous alcohol was added from one syringe in the stopped-flow apparatus to a solution of ligand from the other syringe. The *initial* formation rate was measured at 600 mμ for complexes of nickel with ammonia or pyridine (water) and pyridine, bipyridyl, or terpyridine (aqueous alcohol).

RESULTS AND DISCUSSION

Dissociation Rates.—The results of the present study are collected in Table 2. The ammonia complex is the only one of those examined here for which some kinetic data are available. The half-time of exchange between $[Ni(NH_3)_6]^{2+}$ and NH_3 at −50° in liquid ammonia is 0·025 second.[16] The studies of Garner and Bjerrum, however, are more relevant to our own.[17] The dissociation of 0·0058M-$[Ni(NH_3)]^{2+}$ at −25° in 2·7M-magnesium nitrate was determined by pH-stat titration of the ammonia released when the pH was adjusted to 3·1—5·8. The reaction half-time of 64 seconds, independently of pH, is longer than the value obtained by extrapolation of our results to −25·0° (15—25

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[11] Melson, Ph.D. Thesis, Sheffield, 1962, gives details of the apparatus.

[12] Dalziel, *Biochem. J.*, 1953, **55**, 79; Kern, *J. Chem. Educ.*, 1960, **37**, 14.

[13] Bjerrum, "Metal Ammine Formation in Aqueous Solution," Haase and Son, Copenhagen, 1941, p. 196.

[14] Long and Paul, *Chem. Rev.*, 1957, **57**, 1.

[15] Ahmed and Wilkins, *J.*, 1959, 3700.

[16] Sutter and Hunt, *J. Amer. Chem. Soc.*, 1960, **82**, 6420.

[17] Garner and Bjerrum, *Acta Chem. Scand.*, 1961, **15**, 2055.

seconds). The apparent discrepancy may arise from a non-linear Arrhenius plot or/and the drastic difference in the conditions of our respective experiments.

The rate of dissociation appears to be independent of acid concentration. This would be expected from the behaviour [15] of $[\text{Ni en}]^{2+}$ and is also observed with hydrolysis of chromium(III) amines over a wide range of pH.[18] The agreement between the direct and the indirect method of studying $[\text{Ni}(N_2H_4)]^{2+}$ shows that a substantial amount of the complex is not protonated (immediately) through the free NH_2 group, although of course the dissociation may proceed through kinetically active $[\text{Ni}(N_2H_5)]^{3+}$, the hydrazinium ion having recently been shown to form solid complexes.[19]

A comparison of the results for the complexes of ammonia and pyridine with those of the corresponding bidentate ligands, *viz.*, ethylenediamine [15] and bipyridyl,[20] shows that the energies of activation for the former pair are some 6—7 kcal. mole^{-1} lower than those for the latter. In addition, the ammonia complex has a distinctly lower energy and entropy of activation (the only negative value) than the other compounds listed in Table 2. Ammonia can form hydrogen bonds with surrounding water molecules more easily than can the other ligands, and this may lower the energy of activation for its replacement by water in the dissociative process. In comparing ammonia and aziridine the effect of alkyl substitution is to raise both E and A factors and give comparable rates; charge within the ligand has an accelerating effect. In a previous study of the acid decomposition of $[\text{Ni en}]^{2+}$ it was assumed that the first Ni–NH_2 bond rupture proceeded relatively slowly ($t_{\frac{1}{2}} = 4{\cdot}77$ sec. at 25°) and that the monoprotonated intermediate $[\text{Ni}(NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_3^+)]^{2+}$ decomposed rapidly.[4,15] The rapid decomposition of the trimethylammonium analogue observed in the present study strongly supports this scheme.

Formation Rates.—From the acid dissociation rate constants (assumed to pertain also to neutral solution) and the stability constants [21] the second-order rate constants for the formation of $[\text{Ni}(NH_3)]^{2+}$, $[\text{Ni}(N_2H_4)]^{2+}$, and $[\text{Ni}(C_5H_5N)]^{2+}$ can be calculated as 2·5—3·2 × 10^3 l.mole^{-1} sec.$^{-1}$ at 25°. This *order* of value has been obtained in some semi-quantitative studies on the formation of the ammonia and the pyridine complex and was estimated by extrapolation of some data for methanol solutions at low temperatures.[1] Davies and MacF. Smith [22] recently measured the second-order rate constant for the formation of $[\text{Ni}(NCS)]^{2+}$ as 4·3 × 10^3 l.mole^{-1} sec.$^{-1}$ at 20°, using the stopped-flow method. Since data on the water-exchange rates with metal aqua-ions by nuclear magnetic resonance studies have become available,[23] interest is being shown in the relation between the water exchange and the complex formation process.[2,24-26]

A lower limit for the first-order rate constant for the water-exchange reaction:

$$[\text{Ni}(H_2{}^*O)]^{2+} + H_2O \longrightarrow [\text{Ni}(H_2O)]^{2+} + H_2{}^*O$$

is 3 × 10^4 sec.$^{-1}$ (at 26°).[23,24] Since the formation rate constants quoted above are similar to one another and formation is not a rapid process compared with water exchange, an S_N2 mechanism involving direct ligand entry, appears unlikely.[2] For an S_N1 mechanism:

$$[\text{Ni}(H_2O)_6] \rightleftharpoons [\text{Ni}(H_2O)_5] + H_2O \quad . \quad . \quad . \quad . \quad k_1, k_{-1}$$

$$[\text{Ni}(H_2O)_5] + A \longrightarrow [\text{Ni}(H_2O)_5A] \quad . \quad . \quad . \quad . \quad . \quad k_2$$

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[18] Jørgensen and Bjerrum, *Acta Chem. Scand.*, 1958, **12**, 1047.

[19] Prout and Powell, *J.*, 1961, 4177.

[20] Ellis, Hogg, and Wilkins, *J.*, 1959, 3308.

[21] " Stability Constants, Parts I and II," the Chemical Society, London, 1957, 1958.

[22] Davies and MacF. Smith, *Proc. Chem. Soc.*, 1961, 380.

[23] Connick, in " Advances in the Chemistry of the Coordination Compounds," ed. Kirschner, Macmillan, New York, 1961, pp. 15 *et seq.*

[24] Connick and Stover, *J. Phys. Chem.*, 1961, **65**, 2075.

[25] Basolo and Pearson in " Advances in Inorganic Chemistry and Radiochemistry," ed. Emeléus and Sharpe, Academic Press Inc., New York, 1961, Vol. III, chapter 1.

[26] Wilkins, *Quart. Rev.*, 1962, in the press.

the rate of formation of $[Ni(H_2O)_5A]$ is given by

$$k_1k_2[Ni(H_2O)_6][A]/(k_{-1}[H_2O] + k_2[A])$$

When $k_{-1}[H_2O] \gg k_2[A]$, second-order kinetics are observed with a second-order rate constant $= k_1k_2/k_{-1}[H_2O]$. Since this composite value is similar for various ligands A and comparable to the lower-limit second-order constant for water exchange ($6k_1/[H_2O] = 6 \times 3 \times 10^4/55{\cdot}5 \sim 3 \times 10^3$ l.mole^{-1} sec.$^{-1}$), $k_2/k_{-1} \approx 1$ and thus all neutral ligands, water included, and even anions such as SCN^-, have similar affinity for the five-co-ordinated intermediate. It also follows that the departure from the second-order form ($k_2[A] \gg k_{-1}[H_2O]$) to give first-order kinetics, convincing proof for this mechanism, will occur only at probably unattainably high ligand concentrations.

This constancy for the rate constant for formation of nickel complexes led us to examine the behaviour of multidentate ligands. The mono-complex of nickel with pyridine, bipyridyl, and terpyridine represents an interesting comparative series, especially since the kinetics of dissociation and the spectral properties have been characterised.[20,27] Our preliminary results indicate that the rates of formation of $[Ni[C_5H_5N)]^{2+}$, $[Ni(bipy)]^{2+}$, and $[Ni(terpy)]^{2+}$ in aqueous alcohol were of the same order (within a factor of 10) (apparent second-order rate constant $\sim 10^2$ l.mole^{-1} sec.$^{-1}$ at 5°). Indeed, the second-order rate constant for the formation of $[Ni(bipy)]^{2+}$ can be estimated as $\sim 1{\cdot}5 \times 10^3$ l.mole^{-1} sec.$^{-1}$ at 25° from exchange data [20] and the recently determined stability constant.[28] The reaction of nickel ion with the related ligand 1,10-phenanthroline has been investigated in acid medium [29] and if the results are extrapolated to weakly acid solution a second-order formation rate constant $1{\cdot}6 \times 10^3$ l.mole^{-1} sec.$^{-1}$ at 25° is obtained.

This series of complexes constitute a most striking example of the dissociative process, accounting for the differences in the thermodynamic stability of nickel complexes.[4,30] The first-order dissociation rate constants of the mono-complexes of pyridine, bipyridyl, and terpyridine in neutral solution at 25° are 38·5, $5{\cdot}3 \times 10^{-5}$, and $2{\cdot}7 \times 10^{-8}$ sec.$^{-1}$, respectively, and account almost completely for the marked differences in stability of the complexes.

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[27] Hogg and Wilkins, *J.*, 1962, **341**.

[28] Cabini and Landucci, *J.*, 1962, 278.

[29] Margerum, Bystroff, and Banks, *J. Amer. Chem. Soc.*, 1956, **78**, 4211.

[30] Eigen, *Z. Elektrochem.*, 1960, **64**, 115.