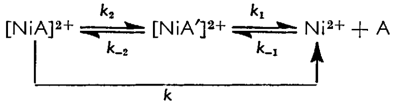
584. *Factors influencing the Rates of Dissociation of Metal Complexes. Part II.*[1] *The Dissociation of Complexes of Nickel with Various Diamines.*

By A. K. Shamsuddin Ahmed and R. G. Wilkins.

The rates of dissociation have been studied, in acid solution, of the mono-complex of nickel(II) with various aliphatic diamines, and the results compared with those previously obtained for $[Ni(en)]^{2+}$. The effects of *N*- and *C*-alkyl substitution of ethylenediamine and of the ring size of the chelate group have been investigated. Correlations of the kinetic parameters with the known thermodynamic properties of the ions have been attempted. The mode of dissociation, in neutral solution, of mono-(2-methylpyridylamine)-nickel(II) ion, containing co-ordinated primary and tertiary nitrogen, has been deduced from $^{63}Ni^{2+}$ and $^{3}H_2O$ exchange experiments.

In Part I,[1] we studied the rate of dissociation of $[Ni(en)]^{2+}$ into nickel ion and ligand, through a wide range of pH, and from this and from hydrogen-exchange data, determined the rate constant for the first bond rupture of the chelate compound (k_2). We now examine the effects of changes of the diamine (A) on the dissociation rate and, in particular, on the value of k_2 (A′ represents the diamine attached at one end):



$$\begin{tikzcd}[NiA]^{2+} \arrow[r, shift left, "k_2"] \arrow[rr, bend right, "k"'] & {[NiA']^{2+}} \arrow[l, shift left, "k_{-2}"] \arrow[r, shift left, "k_1"] & Ni^{2+} + A \arrow[l, shift left, "k_{-1}"]\end{tikzcd}$$

For simplicity of interpretation and because of their slower dissociation, the complexes with one ligand only were used (mono) and the effects, on the rate, of *N*- and *C*-alkyl * substitution of the diamine and of the ring size of the chelate compound investigated. Since the stability constants are known with the systems we have examined, we can deduce any resemblances between thermodynamic and kinetic behaviour, a relation little investigated with complex compounds.

---

* Some preliminary results on *C*-substitution are included in a previous paper.[2]

[1] Part I, Ahmed and Wilkins, *J.*, 1959, 3700.

[2] Wilkins, *J.*, 1957, 4521.

EXPERIMENTAL

Materials.—*NN'*- and *NN*-Dimethylethylenediamine and 1,3-diamino-2,2-dimethylpropane were gifts from Imperial Chemical Industries Limited, and *cis*- and *trans*-1,2-diaminocyclohexane from Geigy Chemical Company. 1,3-Diaminopropane and 2-methylpyridylamine were purchased from L. Light and Co., Ltd. *NN'*-Diethyl- and *NN'*-di-n-propyl-ethylenediamine resulted from alkylation of 2-methylimidazoline with ethyl and n-propyl bromide, respectively;[3] the mixtures with the mono-*N*-derivative were separated by fractional crystallisation. Racemic and *meso*-2,3-diaminobutane were obtained by reduction of dimethylglyoxime;[4] they were easily separated by fractional crystallisation of their dihydrochlorides from aqueous methanol. All amines were redistilled, before use, and had the b. p. in the literature. Aqueous solutions of the amines were estimated against standard acid, or prepared from weighed amounts of the perchlorate salt and alkali. Other reagents were prepared as described previously.[1]

The two nickel complexes precipitated by Reinecke's salt for exchange work reported below were analysed. (*a*) trans-1,2-*diaminocyclohexane complex* (Found: C, 18·9; H, 4·3; N, 21·1; H_2O, 12·1. $C_{14}H_{38}N_{14}Cr_2NiO_6S_8$ requires C, 18·3; H, 4·2; N, 21·4; H_2O, 11·8%); (*b*) 2-*methylpyridylamine complex* (Found: Ni, 6·6; H_2O, 8·15. $C_{14}H_{28}N_{14}Cr_2NiO_4S_8$ requires Ni, 6·7; H_2O, 8·2%). Some unaccountable difficulties were encountered with carbon and hydrogen analysis of the latter.

H^+-*Consumption and Spectrophotometric Experiments.*—The measurements were as described in Part I. The concentrations of complex and nickel used were 2—4 mM and 4—6 mM, respectively (H^+-consumption experiments) and 10—30 mM and 20—50 mM (spectrophotometry). The medium contained sodium and perchlorate ions, $\mu = 2{\cdot}0$M, unless otherwise indicated. The presence of free nickel ions in all experiments ensured that the mono-complex was the species investigated, as indicated also by spectral examination which showed characteristic mono-peak positions. A small amount of the bis-complex, easily shown to be present in the original solution as a rapid initial reaction in the first-order plot, was allowed for in determining the rate constant. In the preparation of the solution containing mono-(*cis*-1,2-diaminocyclohexane)nickel(II) ion, some bis-complex was filtered off before use. The results are shown in Table 1.

Exchange Runs.[1]—(a) *Nickel exchange.* Three amine complexes were studied. We were unable to precipitate the complex species with naphthalene-1,5-disulphonate as used with $[Ni(en)]^{2+}$. Mono-(*trans*-1,2-diaminocyclohexane)- and (2-methylpyridylamine)-nickel(II) were freed from nickel ion by addition of a saturated aqueous solution of Reinecke's salt. The pink precipitate was washed with ice-cold water, alcohol, and ether, and air-dried. With the racemic 2,3-diaminobutane complex no suitable precipitant was found, and in this case, nickel ion was preferentially precipitated with a deficiency of hydroxide. The nickel hydroxide was quickly washed with cold water, dissolved in acid, and radio-assayed as nickel dimethylglyoxime. About 20% zero-time exchange was observed and although the results were not as reproducible as usual, an indication of the exchange rate was obtained. The rate constant for dissociation was calculated from the data, on the assumption that the exchange was of first-order in complex and of zero-order in nickel-ion concentration.

(b) *Hydrogen exchange.* Since it was not possible to obtain high yields of mono-(*trans*-1,2-diaminocyclohexane)- or (2-methylpyridylamine)-nickel(II) as a solid nitrate or chloride, the method used for the ethylenediamine analogue could not be followed. The mono(diaminocyclohexane)nickel(II) ion–water exchange will be described as typical of the procedure used instead. A concentrated solution of the mono-complex in ^3H_2O (1·2 c.c., 0·15M-complex and 0·45M-nickel nitrate) was settled to 0°, and a pre-cooled dilute solution of the complex in normal water was added (60 c.c., 0·005M-complex, 0·015M-Ni^{2+}, pH = 7·0). On mixing, the original specific activity of the complex is decreased three-fold, whereas that of the water is decreased fifty-fold, so that exchange of tritium between complex and water occurs, measured by a decrease in the specific activity of the complex. At various times, an aliquot part (10 c.c.) of the mixed solution was withdrawn and added to an equal volume of a saturated solution of Reinecke's salt at 0°. The precipitate was washed, dried, and assayed in a proportional counter. It was found that incorporation of graphite in the sample, by fine mixing, increased the stability of the count.[5]

---

[3] King and McMillan, *J. Amer. Chem. Soc.*, 1946, **68**, 1774.
[4] Dickey, Fickett, and Lucas, *J. Amer. Chem. Soc.*, 1952, **74**, 944.
[5] Banks, Crawhall, and Smyth, *Biochem. J.*, 1956, **64**, 411.

TABLE 1. *Dissociation of* [NiA]$^{2+}$ *to nickel ions.*

pH	Temp.	10^3k (sec.$^{-1}$)	log K_1
1,2-Diaminoethane (en) [a]			
4·0	0·3°	6·6	7·92 [6]
Racemic 2,3-diaminobutane (*rac*-bn)			
6·8 [b]	0·3	0·16	8·30 [7]
4·3 [c]	0·3	1·23	
4·3 [d]	0·3	0·68	
4·3	0·3	0·70	
2·2	0·3	0·72	
1·5	0·6	0·73	
[Acid]			
0·35	0·6	0·81	
0·35 [e]	0·6	0·79	
0·35	19·4	8·8	
0·35	20·8	9·8	
0·35	21·4	10·35	
0·86	0·6	0·92	
1·08	0·6	1·02	
1·58	0·6	1·27	
2·08 [d]	0·6	1·43	
3·15 [d]	0·6	1·75	
0·25	0·7	1·33	
0·25 [f]	0·7	1·27	
0·25 [f]	22·4	15·8	
0·25 [f]	23·7	17·8	
0·25 [f]	24·9	20·1	
meso-2,3-Diaminobutane			
4·8	0·3	5·8	7·37 [7]
1·5	0·6	6·2	
[Acid]			
1·0	0·6	9·9	
2·05	0·6	14·2	
cis-1,2-Diaminocyclohexane			
3·6	0·3	5·6	7·50 [8]
trans-1,2-Diaminocyclohexane (*trans*-chx)			
6·8 [b]	0·3°	0·13	8·22 [8]
4·0	0·3	1·4	
1·5 [g]	0·6	1·65	
	15·9	10·8	
	17·5	13·3	
	19·3	17·8	
[Acid]			
1·03	0·6	2·3	
NN′-Dimethylethylenediamine (diMeen)			
4·0	0·3	1·7	7·87 [6]
1·5	0·6	1·9	
NN-Dimethylethylenediamine			
4·0	0·3	38·5	—
NN′-Diethylethylenediamine			
4·0	0·3	10·3	7·42 [6]
	0·3	10·0	
	3·2	13·9	
	3·5	14·5	
	6·1	19·8	
	6·2	19·8	
NN′-Di-n-propylethylenediamine			
4·0	0·3	>200	5·87 [6]
1,3-Diaminopropane			
4·8	0·3	8·8	7·00 [9]
1·5	0·6	9·2	
[Acid]			
1·03	0·6	9·6	
2·06	0·6	9·9	
1,3-Diamino-2,2-dimethylpropane			
4·8	0·3	5·1	7·22 [9]
1·5	0·6	5·2	
[Acid]			
1·03	0·6	5·9	
2·06	0·6	6·5	

[a] Ref. 4. [b] From exchange results. [c] $\mu = 2{\cdot}0$M, with added sodium nitrate. [d] No added $NaClO_4$. [e] Followed at 600 mμ; all others at 900 mμ. [f] $\mu = 0{\cdot}525$M, nitrate medium for comparison with other bn complexes, see following paper. [g] $\mu = 1{\cdot}0$M, with added sodium perchlorate.

TABLE 2. *Exchange results with* [NiA]$^{2+}$ *at* 0·3° ± 0·1°.

	Run no.	pH	[Complex] (mmole l.$^{-1}$)	[Nickel] (mmole l.$^{-1}$)	$t_{\frac{1}{2}}$ (exch) (sec.)	10^6R (exch) (sec.$^{-1}$ mole l.$^{-1}$)
Racemic 1,2-diaminobutane	1	6·8	80·0	120·0	2580(Ni)	12·9
trans-1,2-Diaminocyclohexane	2	6·8	50·0	150·0	3960(Ni)	6·6
	3	6·8	7·5	22·5	744(H)	27·9
2-Methylpyridylamine	4	5·0	100·0	300·0	9420(Ni)	5·5
	5	6·4	100·0	300·0	9480(Ni)	5·5
	6	6·1	20·0	60·0	23,400(Ni)	0·44
	7	6·8	20·0	60·0	5280(H)	5·2
	8	5·3	20·0	60·0	5460(H)	5·0

---

[6] Basolo and Murmann, *J. Amer. Chem. Soc.*, 1954, **76**, 211.

[7] Basolo, Chen, and Murmann, *J. Amer. Chem. Soc.*, 1954, **76**, 956.

[8] (*a*) Bertsch, Fernelius, and Block, *J. Phys. Chem.*, 1958, **62**, 444; (*b*) Schwarzenbach and Baur, *Helv. Chim. Acta*, 1956, **39**, 722.

[9] Hares, Fernelius, and Douglas, *J. Amer. Chem. Soc.*, 1956, **78**, 1816.

Changes in activity of the precipitate from *ca.* 1500 to 125 counts/min. and first-order exchange plots were obtained by this method. A nitrate medium was used in the *trans*-1,2-diaminocyclohexane complex studies, since perchlorate slowly precipitated the pink tris-species at 0°. The results of all exchange studies are shown in Table 2.

DISCUSSION

It was first shown with $[Ni(rac\text{-}bn)]^{2+}$ and $[Ni(trans\text{-}chx)]^{2+}$,* the least labile of the aliphatic amine complexes examined, that the general features of the dissociation of $[Ni(en)]^{2+}$ were reproduced. Their overall dissociation rate constant (k) increased about ten-fold from pH 6·8 to 5·0, remained constant until about pH = 1·5, and then increased again, linearly with C_{H^+} (Table 1). When possible, a perchlorate medium was used in all experiments, since an accelerating effect of chloride and even nitrate ion was noted. The exchange of hydrogen between water and mono-(*trans*-1,2-diaminocyclohexane)nickel ion was examined at neutral pH (Table 2). The result enabled a value of k_2 to be estimated [4] ($1{\cdot}73 \times 10^{-3}$ sec.$^{-1}$) and this compares well with that obtained from dissociation studies at pH = 3·6 ($1{\cdot}65 \times 10^{-3}$ sec.$^{-1}$) with the same concentration conditions. The experiment confirms the conclusions of the previous work with mono(ethylenediamine)nickel ion, *viz.*, that exchange of hydrogen between water and the co-ordinated amine hydrogen is indirect and is a measure of the rate of detachment of one end of the bidentate ligand, this representing the limiting rate in acid solution. Since the second acid dissociation constant of each aliphatic diamine examined is similar,[8, 9-10] the basicity of each intermediate (containing unidentate diamine) would be much the same, and thus in all cases the almost constant rate observed between pH 1·5 and 4·0 represents k_2. These, and in certain cases their associated Arrhenius parameters, will be compared for the various diamine complexes; values for k in neutral solution are more difficult to measure and also represent a composite process involving k_2, k_{-2} and k_1 and are therefore more difficult to analyse.

Rate and Stability Constants.—Little systematic investigation of a possible relation between kinetic and thermodynamic stability of co-ordination complexes has been attempted. Taft and Cook [11] recently examined the complexing of trifluorothenoylacetone with a variety of transition- and non-transition-metal ions and found no simple relation between the rate of formation and the stability constant of the mono-complex. However, for a closely related group of ligands complexing with a common metal ion, a relation might be expected, and examination of Table 1 shows that this is approximately so. The stability constants used in Table 1 are values in 0·5—1·0M-potassium nitrate at 0°. As far as possible, they are taken from comparative studies. The general decelerating effect of methyl substitution is small even when it is on nitrogen adjacent to the site of the reaction. The simple six-membered ring involving 1,3-diaminopropane is less stable than the five-membered ring involving ethylenediamine,[10] and this is accompanied by a larger rate constant for dissociation (k_2) for the former. Substitution of *gem*-dimethyl groups on the central carbon atom of 1,3-diaminopropane enhances the thermodynamic [9] and kinetic stability of the nickel complex relative to that of the unsubstituted diamine. Because of a less strained geometrical arrangement, the complexes of *trans*-1,2-diaminocyclohexane and racemic 2,3-diaminobutane are more stable than those of the corresponding geometrical isomer [7, 8] (*cis*- and *meso*-forms respectively) and it is found that their value for k_2 is decidedly lower. Finally, the parallelism is shown quite well when *NN'*-disubstituted amine complexes are considered. The thermodynamic stability sequence for the mono-complexes of nickel is [6] ethylenediamine $\sim$ *NN'*-dimethylethylenediamine $>$ *NN'*-diethylethylenediamine $\gg$ *NN'*-di-n-propylethylenediamine, and the

---

* For abbreviation of ligand names, see Tables.

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

[11] Taft and Cook, *J. Amer. Chem Soc.*. 1959, **81**, 46.

corresponding kinetic one is ethylenediamine < *NN'*-dimethylethylenediamine > *NN'*-diethylethylenediamine $\gg$ *NN'*-di-n-propylethylenediamine. The mono-nickel complex of *NN*-dimethylethylenediamine dissociates more rapidly than that of the symmetrical isomeric ligand, in agreement with its expected reduced stability.[12] It does then appear generally true that in a series the less stable compound dissociates more rapidly, this having been already noted with the proton complexes of bases, over a very much wider range of hydrolysis rate constants.[13] Unless the differences observed are fairly large, however, the relation should not be stressed since $[Ni(en)]^{2+}$ and $[Ni(diEten)]^{2+}$ show a *reversal* of relative rates of dissociation at 0° and 25°. The difference in the rates of dissociation of complexes of the isomers of butylenediamine can be made the basis of a method for their separation in a mixture.[14] There is a peculiar difference which we do not understand between the five- and six-membered rings in their dissociative behaviour towards excess of acid (Table 1). The limiting rate of dissociation of 1,3-diaminopropane and 1,3-diamino-2,3-dimethylpropane complexes is only slightly enhanced by 2·0M-acid, whereas a more than two-fold acceleration is noticed with the others examined. In the strongly acid region $k = k_2 + k_2^{H}[H^+]$; for ethylenediamine $k_2 = 0{\cdot}0063$, $k_2^{H} = 0{\cdot}0043$ sec.$^{-1}$, while for 1,3-diaminopropane, $k_2 = 0{\cdot}0093$ and $k_2^{H} = 0{\cdot}0003$ sec.$^{-1}$ at 0·6°.

Arrhenius and Thermodynamic Parameters.—Since the transition state for the dissociation process resembles the reaction products, it might be expected that there would also be a relation between the energy or entropy of activation and reaction. Unfortunately, there is much less information on enthalpies and entropies than on free energies of reactions, and even then it is much less reliable. The Arrhenius parameters, A and E in $k = A \exp(-E/\boldsymbol{R}T)$, appear in Table 3 for several complexes, the choice being dictated by ease of measurement and their possible value. The estimated errors in the E and log A terms are about ±0·5 unit. In every case, substitution on carbon or nitrogen decreased E and A terms. This behaviour is duplicated by bis- and tris-racemic 2,3-diaminobutane and ethylenediamine complexes (see following paper). The values for ΔH° and ΔS° for the dissociation of bis-(*NN'*-diethylethylenediamine)nickel(II) ion are 7·8 kcal./mole and −27 e.u. and these differ significantly from the values for the corresponding ethylenediamine compounds (16·3, −7 respectively).[6] Data for the monosubstituted compound are lacking, but must bear the same relative relation. It is interesting then that, kinetically, the dissociation of $[Ni(diEten)]^{2+}$ has markedly lower values for $E_{act.}$ and $\Delta S^\ddagger$ when compared with $[Ni(en)]^{2+}$. The dissociations of $[Ni(\textit{trans}\text{-chx})]^{2+}$ and $[Ni(tetraMeen)_2]^{2+}$ have also significantly lower entropies of reaction [7,8a] and activation [2,15] than that of the corresponding ethylenediamine complex.

TABLE 3. *Arrhenius parameters for acid dissociation of* $[NiA]^{2+}$ *in perchlorate medium.*

Species A	$E_{act.}$ (kcal. mole^{-1})	log A (sec.$^{-1}$)	Species A	$E_{act.}$ (kcal. mole^{-1})	log A (sec.$^{-1}$)
Ethylenediamine	20·5	14·2	Racemic 2,3-diaminobutane ...	19·4	12·4
NN'-Diethylethylenediamine	17·1	11·8	*trans*-1,2-Diaminocyclohexane	19·5	12·9

The Dissociation of Mono-(2-methylpyridylamine)nickel Ion.—We were interested in applying the hydrogen-exchange approach to the complex of an unsymmetrical ligand, to determine the relative tendencies of the ends of the ligand towards dissociation from the metal. The dissociation of the nickel mono-complex with *NN*-dimethylethylenediamine is fast, and accurate exchange studies would be very difficult. For this reason we selected 2-methylpyridylamine as the ligand, in which there is a primary aliphatic amine and a tertiary nitrogen atom present in a heterocyclic nucleus and thus might be expected to

---

[12] Irving and Griffiths, *J.*, 1954, 213.
[13] Bell, *Quart. Rev.*, 1959, **13**, 169.
[14] Ahmed, Ph.D. Thesis, Sheffield, 1960.
[15] Ahmed and Wilkins, *Proc. Chem. Soc.*, 1959, 399.

form a more stable complex. In addition, this compound has some of the characteristics of the mono(ethylenediamine)nickel and mono(dipyridyl)nickel ions, both studied previously.[4,16] The sequence of formation constants for the nickel–2-methylpyridylamine system resembles that of the ethylenediamine complexes.[17] The rate of dissociation of the species depends on pH in a complicated manner,[14] but some conclusions about the rate of the $(C_5H_5N)CH_2{\cdot}NH_2$–Ni bond rupture can be made from the exchange data in Table 2. The dissociation of the ligand, from $^{63}Ni^{2+}$ exchange, is independent of pH from 5·0 to 6·4 and, as might be expected, the neutral exchange rate constant (k), $2{\cdot}2 \times 10^{-5}$ sec.$^{-1}$, is intermediate between those of ethylenediamine ($1{\cdot}4 \times 10^{-3}$ sec.$^{-1}$) and dipyridyl ($1{\cdot}5 \times 10^{-6}$ sec.$^{-1}$) at 0·3°. The exchange of hydrogen between the complex and water is also independent of pH between 5·3 and 6·8, and it is unlikely then that any direct exchange path operates, but probable that only on rupture of the metal–aliphatic amine bond does exchange occur. We are thus able to place limits on the rate constant for this process (k_2) for if, in the complete dissociation process, the metal–tertiary nitrogen bond is always severed in the second stage, then $R^{\mathrm{H}}_{\mathrm{exch}} = 2k_2[\text{complex}]$ and, in the other extreme, if the metal bond with the tertiary nitrogen atom is always broken before that with the primary amine in complete dissociation, then this rupture will also contribute a path to hydrogen exchange and $R^{\mathrm{H}}_{\mathrm{exch}} \simeq 2k_2[\text{complex}] + 2R^{\mathrm{Ni}}_{\mathrm{exch}}$. From the relative values of $R^{\mathrm{H}}_{\mathrm{exch}}$ and $R^{\mathrm{Ni}}_{\mathrm{exch}}$ (Table 2) it is apparent that at least 85% of the acts involving complete dissociation follow Ni–NH_2 bond rupture as the first step, and that $1{\cdot}3 \times 10^{-4} \geqslant k_2 \geqslant 1{\cdot}1 \times 10^{-4}$ sec.$^{-1}$ at 0·3°. We are not able from these experiments to dismiss the possibility of rapid dissociation and association of the tertiary nitrogen–metal bond but can assert that only rarely (if at all) does such dissociation lead to further, complete, dissociation of the ligand. Since we should expect the aromatic nitrogen in the chelate to be more strongly bound (kinetically) than an aliphatic nitrogen (for, after all, dipyridyl complexes are less labile than those of ethylenediamine), it is very likely that k_2 has the highest possible value. This is about 50 times less than that for the corresponding process for ethylenediamine and may arise from the following: the aromatic nitrogen atom may participate in double-bonded structures with the metal, and this π-bonding results in drainage of electrons from the metal, which enhances the stability of the Ni–NH_2 bond. Alternatively, the pyridine ring may offer steric hindrance to the rupture of the aliphatic amine–nickel bond.

We hope to examine more complicated complexes of nickel with ter- and quadri-dentate ligands, using methods of investigation which we have developed in this and the previous paper.

We thank Imperial Chemical Industries Limited and the Geigy Chemical Company for gifts of amines, Mr. R. Hogg for experimental assistance, and the Pakistan Government for a maintenance grant. We are indebted to the Microbiology Department of this University for gas-flow proportional counting facilities.

THE UNIVERSITY, SHEFFIELD.

[*Received, January* 28*th*, 1960.]

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

[17] Goldberg and Fernelius, *J. Phys. Chem.*, 1959, **63**, 1246.