333. *Exchange Studies of Certain Chelate Compounds of the Transitional Metals. Part II.** *The Rate of Racemisation and Dissociation of the Tris-*(1 : 10-*phenanthroline*)*nickel*(II) *Ion.*

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The exchange of phenanthroline between the tris-(1 : 10-phenanthroline)-nickel(II) ion ($[Ni\ phen_3]^{2+}$) and uncomplexed ligand has been studied in various solvents by using [^{14}C]phenanthroline. The simple rate law: R (the exchange rate, min.$^{-1}$ mole l.$^{-1}$) $= k$[Ni phen$_3$]† where k, the exchange rate constant $= 1\cdot6 \times 10^{15} \exp(-25{,}200/\boldsymbol{R}T)$, is obeyed in aqueous solution at pH 5·7—11·7. Comparison with the racemisation rate constant already measured by others and now confirmed [$k = 1\cdot2 \times 10^{15} \exp(-24{,}900/\boldsymbol{R}T)$ min.$^{-1}$] shows that the dissociation mechanisms of exchange and racemisation of $[Ni\ phen_3]^{2+}$ are identical. This involves the complete rupture of one phenanthroline–ligand bond and the subsequent rapid racemisation of the dissociated fragment.

This dissociative path for racemisation persists in alkaline solution (pH ~13) and in solutions in methanol–water, ethanol–water, ethanol, and nitrobenzene, despite a wide variation in rates in these solvents. These results confirm and amplify the conclusions already reached for aqueous acid solution.

THERE has been an increasing interest recently in the reactions of metal complexes of 1 : 10-phenanthroline (phen), 2 : 2′-dipyridyl (dipy), and related compounds.[1] Nickel and iron, amongst other metals, form with the bidentate ligands complex ions of general formula $[MA_3]^{n+}$. These have been resolved into enantiomorphs, which racemise at rates and in conditions suitable for study of the process.

Basolo, Hayes, and Neumann [2] investigated the rates of acid dissociation and the accompanying racemisation of tris-(1 : 10-phenanthroline)nickel(II) ion, $[Ni\ phen_3]^{2+}$, and found that, within experimental error, these two rates were the same. A similar result was obtained for the tris-(2 : 2′-dipyridyl)nickel(II) ion, $[Ni\ dipy_3]^{2+}$. Independently Davies and Dwyer [3] came to a similar conclusion for the reaction between $[Ni\ phen_3]^{2+}$ and ferrous ion. There seems little doubt that for these two nickel complexes a dissociative mechanism can completely account for the racemisation in the experimental conditions. It would be interesting therefore to extend this work to neutral and alkaline aqueous solutions as well as to non-aqueous solvents. The rates of dissociation of metal ammine complexes can be markedly affected by pH changes [4] so that a change in the mechanism of racemisation might appear in neutral or alkaline solution. Although this does not appear very likely with the $[Ni\ phen_3]^{2+}$ ion whose racemisation rate is almost pH-independent, it remains a real possibility with the $[Ni\ dipy_3]^{2+}$ ion which racemises more slowly in neutral than in alkali [5] or in acid [6, 2] media. Davies and Dwyer [7] have measured the racemisation rates of $[Ni\ phen_3]^{2+}$ and $[Ni\ dipy_3]^{2+}$ in non-aqueous solvents, including alcohols, acetone, pyridine, and nitrobenzene, and suggest from the similarity of the energy of activation and *PZ*-factor that in these solutions, in contrast to water, an intramolecular mechanism

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* Part I, *J.*, 1955, 4098.

† In this and similar equations the usual enclosing brackets of the complex ion have been omitted to avoid confusion with those indicating molar concentrations.

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

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

[3] Reported by Davies, *Rev. Pure Appl. Chem.* (*Australia*), 1954, **4**, 66.

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

[5] Davies and Dwyer, *Trans. Faraday Soc.*, 1952, **48**, 244.

[6] Schweitzer and Lee, *J. Phys. Chem.*, 1952, **56**, 195.

[7] Davies and Dwyer, *Trans. Faraday Soc.*, 1954, **50**, 1325.

operates. Indeed some preliminary work by Neumann[8] suggested that in water containing 0·7 mole-fraction of methanol, $[\mathrm{Ni\,phen_3}]^{2+}$ racemised more rapidly than it dissociated. An intramolecular racemisation has been definitely established for the analogous iron(II)[9, 10] and iron(III)[11] complexes of dipyridyl and phenanthroline.

Dissociation rates of complex ions can be simply measured by isotopic ligand exchange. Provided that any direct bimolecular exchange path involving the ligand can be allowed for, the ligand-exchange rate provides a measure of the rate of the dissociation of the first ligand. Since in exchange no net reaction occurs, the nature of the intermediate species which may be present during acid dissociation need not be considered. This is particularly useful in non-aqueous solvents. Some qualitative studies of the $[\mathrm{Ni\,dipy_3}]^{2+}$–$\mathrm{Ni}^{*2+}$ exchange have been reported[12] but quantitative metal–complex-ion exchanges have attendant difficulties absent from ligand-exchange work.[13] We have therefore synthesised [^{14}C]-phenanthroline and -dipyridyl[14] and now describe in detail the exchange between phenanthroline and the $[\mathrm{Ni\,phen_3}]^{2+}$ ion in water (over a wide pH range) and, in less detail, that in ethanol, ethanol–water, methanol–water, and nitrobenzene. We conclude that, despite a wide variation in the racemisation rates in these solvents, $[\mathrm{Ni\,phen_3}]^{2+}$ racemises by a dissociative mechanism (involving *complete* removal of one phenanthroline ligand) under all the conditions which we have used.

EXPERIMENTAL

Materials.—[^{14}C]Phenanthroline hydrate was prepared by a Skraup reaction with [1-^{14}C]-glycerol as described elsewhere.[14] Drying *in vacuo* over phosphoric oxide for about 24 hr. gave anhydrous [^{14}C]phenanthroline which was used in the non-aqueous solvent experiments. Hydrated $[\mathrm{Ni\,phen_3}](\mathrm{NO_3})_2$ containing [^{14}C]phenanthroline was prepared from hydrated nickel nitrate (1 mole) and [^{14}C]phenanthroline (3·5 moles).[14] After recrystallising several times from small amounts of water the complex was dehydrated by heating at 80° for a few hr. *in vacuo* over phosphoric oxide in an Abderhalden drying pistol (Found: Ni, 8·15; 8·2. Calc. for $\mathrm{C_{36}H_{24}O_6N_8Ni}$: Ni, 8·1%). The spectrum of an aqueous solution of this material agreed with that previously reported (*e.g.*, ref. 2). Both materials could be diluted about twenty times with inactive material to obtain activities suitable for most of the work. In a few experiments, exchange was initiated by injection of the original material into a system combining inactive materials. Inactive tris-(1 : 10-phenanthroline)nickel(II) nitrate, perchlorate, and iodide were prepared by standard methods. When available, "AnalaR" chemicals were used.

In earlier experiments optically active $[\mathrm{Ni\,phen_3}](\mathrm{NO_3})_2$ was required in order to reproduce exactly the exchange conditions. Treatment of the racemate with aqueous potassium antimonyl (+)-tartrate precipitated (+)-$[\mathrm{Ni\,phen_3}]$antimonyl (+)-tartrate.[15] This was filtered and the filtrate containing (−)$[\mathrm{Ni\,phen_3}]$antimonyl (+)-tartrate freeze-dried. Acetone extracted from the residue (−)$[\mathrm{Ni\,phen_3}](\mathrm{NO_3})_2$, $[\alpha]_D$ −1461°. Optically active anhydrous $[\mathrm{Ni\,phen_3}](\mathrm{ClO_4})_2$[15] was used in the nitrobenzene experiments and the iodide[7] in the alcohol and alcohol–water solvents.

Solvents.—Nitrobenzene was stored over phosphoric oxide for four weeks and then thrice redistilled (b. p. *ca.* 100°/1—2 mm.). The water content was estimated (Karl Fischer method) to be *ca.* 80 mg. of water/l. Further drying for three days and subsequent distillation did not reduce the water content appreciably.

Purified and "dried" ethanol[16] was estimated to contain *ca.* 180 mg. of water/l. (Karl Fischer method). No great care was taken in the drying of methanol as it was only used mixed with water.

Buffer Mixtures.—Buffers containing potassium ion were avoided because of interference

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[8] Neumann, reported in ref. 7, p. 1331.

[9] Basolo, Hayes, and Neumann, *J. Amer. Chem. Soc.*, 1954, **76**, 3807.

[10] Brinzinger, Fallab, and Erlenmeyer, *Helv. Chim. Acta*, 1955, **38**, 557.

[11] Davies and Dwyer, *Trans. Faraday Soc.*, 1954, **50**, 820.

[12] Johnson and Hall, *J. Amer. Chem. Soc.*, 1948, **70**, 2344.

[13] Stranks and Wilkins, *Chem. Rev.*, in the press.

[14] Ellis, Wilkins, and Williams, *J.*, 1956, 3975.

[15] Dwyer and Gyarfas, *J. Proc. Roy. Soc. New South Wales*, 1949, **83**, 232.

[16] Adickes, Brunnert, and Lücker, *Ber.*, 1930, **63**, *B*, 2753.

by precipitation of potassium perchlorate in the separation procedure. In the 5·6—7·0 pH range, NaH_2PO_4–Na_2HPO_4 mixtures were used; for measurements at pH 9·6—9·7, sodium barbiturate–HCl or sodium borate–HCl buffers were used. Sodium hydroxide solutions were prepared from conductivity water and rinsed sodium hydroxide pellets. pH was measured with a Pye " Universal " pH meter and millivoltmeter.

Counting Procedure.—This was essentially as described in Part I.

Exchange Experiments.—Since anions which precipitate $[\text{Ni phen}_3]^{2+}$, *e.g.*, $PdCl_4^{2-}$ or ClO_4^-, tend to precipitate phenanthroline, it was necessary to separate the free phenanthroline from the complex, which was substantially complete after two extractions with benzene. The complex remaining in the aqueous solution was precipitated as the sparingly soluble $[\text{Ni phen}_3](ClO_4)_2,3H_2O$ [2, 15] by adding sodium perchlorate. The phenanthroline in the benzene extract was converted into $[\text{Ni phen}_3](ClO_4)_2$ so that direct comparison of the activities was possible. (This was not absolutely necessary but it was a fairly simple means of obtaining the phenanthroline in reproducible form.) In a typical run solid phenanthroline (0·1—0·2 g.) was added to the buffer or alkaline solution (60—120 c.c.) and kept overnight at 45° to dissolve. A weighed quantity of the radioactive nickel complex (0·1—0·3 g.) was added and dissolved by vigorous shaking. This rarely took longer than 1 min. In several runs an aliquot part (10—20 c.c.) was immediately taken (zero-time) and further aliquot parts removed after various times. A final portion was allowed to reach exchange equilibrium (usually 24 hr.). Each aliquot portion was quickly shaken with benzene (1 × 25 c.c. and 2 × 15 c.c.), and nickel nitrate solution (8·5 mg., 5 c.c.) added to the combined benzene extracts. The benzene was almost evaporated and the aqueous solution of the complex remaining separated from the benzene layer. Sodium perchlorate added to this aqueous solution and to the original solution after removal of the phenanthroline precipitated the complex perchlorate, which was washed twice with small amounts of water and dried in a vacuum desiccator overnight (P_2O_5). It was then washed with ethyl acetate to complete removal of sodium perchlorate, dried in an oven at about 80°, and prepared for counting as previously described.[4] In one run (No. 11, Table 1) active phenanthroline and inactive complex were used and a similar result was obtained to that by the

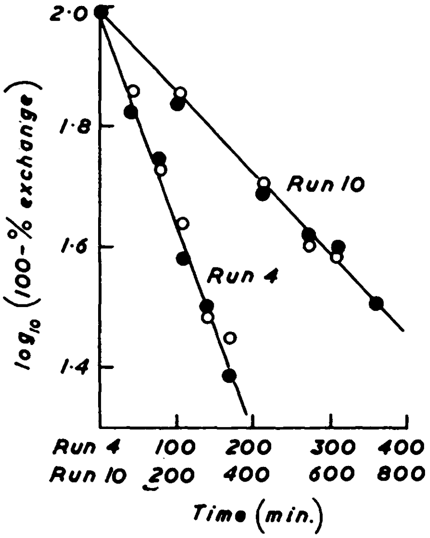
TABLE 1. *Exchange of* $[\text{Ni phen}_3]^{2+}$ *with phenanthroline under various conditions.*

Run No.	Solvent and conditions	Temp.	[Complex] (mmole l.$^{-1}$)	[Phen] (mmole l.$^{-1}$)	$t_{\frac{1}{2}(\text{exch})}$ (min.)	10^5R (min.$^{-1}$ mole l.$^{-1}$)	$10^4k_{(\text{exch})}$ (min.$^{-1}$)	$10^4k_{(\text{rac})}$ min.$^{-1}$
1	pH = 7·0	45·1°	3·05	11·10	118	2·95	96·7	93·6
2	pH = 7·0 [a]	45·1	3·15	11·31	127	2·81	89·5	
3	pH = 7·0 [a]	45·1	3·04	11·26	129	2·70	89·0	
4	pH = 7·0 [a]	45·1	5·92	11·41	86	5·60	94·6	
5	pH = 7·0 [a]	45·1	1·59	11·54	144	1·62	102·0	
6	pH = 7·0 [a]	45·1	3·28	21·48	151	3·09	94·5	
7	pH = 7·0 [a]	45·1	2·13	5·98	100	2·14	100·5	
8 [b]	pH = 7·0 [a]	45·1	3·27	6·02	90	2·88	88·0	
9	pH = 7·0 [a]	45·0	3·60	13·16	127	3·24	90·0	91·2
10	pH = 7·0 [a]	35·0	3·19	13·10	435	0·88	27·6	
11	pH = 7·0 [a]	35·0	3·12	11·43	430	0·83	26·6	
12	pH = 7·0 [a]	55·0	3·34	11·50	35	10·70	302·0	
13	pH = 9·7 [c]	45·0	2·96	13·37	149	2·51	78·9	77·0
14	pH = 9·6 [d]	44·9	3·16	13·76	130	3·00	95·0	
15	pH = 5·7 [a]	45·0	3·23	12·88	129	2·98	92·3	
16	0·01M-NaOH	44·9	3·18	11·60	121	2·83	94·0	92·4
17	pH = 13·4	45·0	3·23	11·55	55	6·59	204·0	
18	pH = 13·3	45·0	3·21	11·59	58	6·83	212·7	112·0
19	0·087M-NaOH	45·0	2·85	9·64	99	3·18	111·2	
20	0·097M-NaOH	45·0	2·82	9·27	96	3·19	113·0	110·8
21	0·129M-NaOH	45·0	2·82	9·74	90	3·49	123·0	
22	Nitrobenzene	45·3	6·86	1·52	940	0·104	1·52	1·57
23	Nitrobenzene	45·3	5·37	1·95	1760	0·069	1·28	1·34
24	Ethanol	45·3	5·92	2·14	82	1·62	27·4	29·5
25	Ethanol–water [e]	45·3	5·82	2·07	25·5	5·04	86·5	86·0
26	Methanol–water [e]	45·3	5·80	1·97	20·5	5·97	102·5	92·5

[a] Phosphate buffer, $\mu = 0·36$. [b] Diffuse light. [c] Barbiturate buffer, $\mu = 0·36$. [d] Borate buffer, $\mu = 0·36$. [e] Mole-fraction : Alcohol, 0·3, water 0·7.

more usual method. In the experiments in nitrobenzene, separation was easily affected by addition of benzene which precipitated the complex perchlorate, from which traces of phenanthroline could be removed by washing with several portions of benzene. In the experiments in ethanol, ethanol–water, and methanol–water, the complex was precipitated by ether. In all cases, very small " zero-time " exchange values confirmed the effectiveness of the separation procedures.

Racemisation Experiments.—These were all performed at 45°, a complex concentration of about 10^{-3}M being used. In the work on aqueous solutions some parallel racemisation and exchange runs were performed in, as far as possible, identical conditions (see Table 1). However, because of difficulty in reproducing results, especially in nitrobenzene, the racemisation and exchange rates in alcohol and in nitrobenzene were measured in the same run, *i.e.*, with optically active complex and radioactive phenanthroline. A decimetre polarimeter tube and a Hilger polarimeter (sodium D line) were used for all measurements, and in all kinetic work the temperature was maintained constant within ±0·03°.



Results from: ○ complex activities, ● phenanthroline activities.

Calculation of Results.—Log [1 − (fraction of racemisation)] was plotted against time, and the racemisation half-life, $t_{\frac{1}{2}(\mathrm{rac})}$, read off directly from the linear plot. The racemisation rate constant $k_{\mathrm{rac}} = 0{\cdot}693/t_{\frac{1}{2}(\mathrm{rac})}$ was then calculated; in this form the value can be related directly to the dissociative rate constants obtained from the exchange results.[2,3] The exchange rate, R, is given by:

$$R = \frac{0{\cdot}693}{t_{\frac{1}{2}(\mathrm{exch})}} \cdot \frac{3[\mathrm{complex}][\mathrm{phen}]}{(3[\mathrm{complex}] + [\mathrm{phen}])}$$

where $t_{\frac{1}{2}(\mathrm{exch})}$ is read directly from the linear log [1 − (fraction of exchange)]–time plot.[17] Some experimental plots are given in the Figure. Davidson and Sullivan [18] have discussed the choice of the optimum times of exchange so that errors in the estimated exchange rates may be minimised. It is assumed, justifiably, that most of the error resides in the radio-assay of the separated exchange reactants. Where 3[complex]/[phen] lies between 2 and 0·5, as in nearly all our experiments, the best separation time to use is 1·4 × $t_{\frac{1}{2}(\mathrm{exch})}$ or 60% exchange. In all our runs therefore at least three values were obtained between one and two half-lives and, when necessary, more weight was given to these points when constructing the graph. In most runs, the reported $t_{\frac{1}{2}(\mathrm{exch})}$ is the mean of two values, one obtained from counting the separated complex activity, and the other from examining the separated phenanthroline (as a solid complex). Usually the specific activity, at equilibrium, of the two separated reactants agreed within the experimental error of sample preparation of about 4%. In some of the later experiments however the equilibrium specific activities of both reactants were consistently 5—10% less than that calculated from the known specific activity of the originally active complex and the equivalents of phenanthroline in the complex and that added in the free state. This was due to water in the nickel complex, which caused the concentration of active complex ion to be less than that estimated from the weight added. Such difficulties did not arise if the exchange was carried out as follows: a standard solution of nickel nitrate was mixed with excess of phenanthroline (6 : 1 mole ratio) and, when formation of $[\mathrm{Ni\,phen}_3]^{2+}$ was complete, exchange was initiated by the addition of a small amount of the original complex (p.1764). Close agreement of experimental and theoretical equilibrium specific activities was then obtained. This is by far the best approach, and will be adopted, when applicable, in subsequent studies.

Species present in the Exchange Runs.—Except in run 15 (Table 1), at least 99% of the

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[17] Wahl and Bonner, " Radioactivity Applied to Chemistry," Chapman and Hall, Ltd., London, 1951, pp. 7 *et seq.*

[18] Davidson and Sullivan, *J. Amer. Chem. Soc.*, 1949, **71**, 739.

phenanthroline was present as the free base ($pK = 4{\cdot}96$ [19]). In run 15 the molarity of phenanthroline recorded represented the sum [phen] + [phen H$^+$]. In runs 2—12, which were used to determine concentration dependence and the energy of activation, the ionic strength was maintained at the arbitrary value of 0·36M, which included buffer and added sodium nitrate. In all the experiments in aqueous solution it can be shown by calculation that $[\mathrm{Ni\ phen_3}]^{2+}$ is the predominant complex ion present, the advantageous circumstance that excess of free phenanthroline is always present being borne in mind ($\log K_1 = 8{\cdot}6$; $\log K_2 = 8{\cdot}1$; $\log K_3 = 7{\cdot}6$ from spectrophotometric data [20]). The similar spectra of the exchange mixture in aqueous alkaline, nitrobenzene, and alcohol as well as in neutral aqueous solutions indicated that the trisphenanthroline nickel ion was the predominant species in all the exchange runs. Cryoscopic molecular-weight determinations of $[\mathrm{Ni\ phen_3}](\mathrm{ClO_4})_2$ in nitrobenzene indicated that it was substantially ionised. This was supported by conductivity measurements in the same solvent (molecular conductivity of a 3×10^{-3}M solution = 57 mhos). Run 9 (Table 1) showed that no new nickel species of different exchangeability were formed in aqueous solution during an exchange experiment: inactive complex and inactive phenanthroline were mixed in aqueous solution and kept for about 24 hr.; exchange was then initiated by injecting a small amount of the original (active) complex. A very similar rate constant was obtained to that resulting from an exchange reaction carried out without previous "ageing."

RESULTS and DISCUSSION

TABLE 2. · *Exchange and racemisation results for* $[\mathrm{Ni\ phen_3}]^{2+}$ *in various solvents at* 45°.

Solvent	$10^4k_{(\mathrm{exch})}$ (min.$^{-1}$)	$10^4k_{(\mathrm{rac})}$ (min.$^{-1}$) this work	$10^4k_{(\mathrm{rac})}$(min.$^{-1}$) extrap. from previous workers' results
Water: pH = 7 *	95 *	91	89,[5] 93 [2]
pH = 13	113	111	—
Ethanol	27	29	31 [7]
0·7 Mole-fraction of ethanol	87	86	87 [7]
0·7 Mole-fraction of methanol	102	93	—
Nitrobenzene	1·24	1·34	11·3 [7]
	1·52	1·57	11·3 [7]

* At 35·0°, $10^4k_{(\mathrm{exch})} = 27$ and $10^4k_{(\mathrm{rac})} = 31$ (ref. 2).

Aqueous Solution.—The results of the exchange study are recorded in Table 1 and a summary of them and a comparison with racemisation rates given in Table 2. It having been established that phosphate buffers and ionic strength had little effect on the exchange rate (runs 1 and 2), the conditions chosen to study the variations of *R* with the concentrations of the exchanging species were pH 7·0 and ionic strength 0·36 M (runs 2—9) at 45·1°. As expected the results indicated a first-order dependence of *R* on the concentration of $[\mathrm{Ni\ phen_3}]^{2+}$ and a zero-order dependence on the concentration of phenanthroline. This is also shown by the reasonable constancy of the rate-constant, *k*, in the equation $R = k[\mathrm{Ni\ phen_3}^{2+}]$. From additional exchange rates at 35° and 55° the energy of activation and the *PZ* factor were estimated as 25·2 kcal./mole and $1{\cdot}6 \times 10^{15}$ min.$^{-1}$ respectively. Comparison with the corresponding quantities for the racemisation (24·9[5] and 25·0[2] kcal./mole and $1{\cdot}2 \times 10^{15}$ [5]), in addition to the results in Table 2, prove that the same path accommodates both processes, *viz.*, removal of one phenanthroline molecule:

$$[\mathrm{Ni\ phen_3}]^{2+} \rightleftharpoons [\mathrm{Ni\ phen_2}]^{2+} + \mathrm{phen} \qquad (A)$$

or

$$[\mathrm{Ni\ phen_3}]^{2+} + 2\mathrm{H_2O} \rightleftharpoons [\mathrm{Ni\ phen_2(H_2O)_2}]^{2+} + \mathrm{phen} \qquad (B)$$

It is then necessary only that the intermediate (*A*) or (*B*) racemises rapidly compared with the rate of re-formation [2, 11] of $[\mathrm{Ni\ phen_3}]^{2+}$.

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[19] Kolthoff, Lee, and Leussing, *J. Amer. Chem. Soc.*, 1948, **70**, 2348.

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

No variation of the exchange-rate constant with hydrogen-ion concentration was observed from pH 5·7 to 11·7 (runs 14—16) although a slight but definite enhancement of rate was observed in 0·1M-sodium hydroxide (runs 19—21). Once again comparison with the rate of racemisation under the latter conditions indicated that the two rate constants were similar (Table 2). Thus the results of Basolo, Hayes, and Neumann[2] are confirmed and amplified over a wide pH range.

Two points in connection with the aqueous exchange study are worth mention. Both the exchange and racemisation rate were unexpectedly lowered at pH 9·7 when a sodium barbiturate–hydrochloric acid buffer mixture was used (run 13). Davies and Dwyer[21] found that the racemisation of $[\text{Ni phen}_3]I_2$ was considerably retarded by the presence of large anions and cations, whether optically active or not. Thus, for example, k_{rac} at 25° in water ($= 6{\cdot}70 \times 10^{-4}$ min.$^{-1}$) was reduced to $3{\cdot}26 \times 10^{-4}$ min.$^{-1}$ in the presence of 2% of ammonium naphthalene-1-sulphonate, an effect rather more pronounced than our own, which was observed with an M/15 or approximately 1% buffer solution. The suggestion[21] that considerable inhibition of ligand dissociation is caused by the presence of clusters of large ions appears reasonable in view of the close agreement of the two lowered rates.

We obtained, using one sodium hydroxide solution sample (runs 16 and 17), a marked enhancement of the exchange rate without a parallel change in the racemisation rate, using the same hydroxide solution but different reaction vessels. Subsequent work with use of fresh alkali solutions (runs 19—21 are only representative examples) never revealed this effect again; we ascribe it to catalytic impurities. Adamson and Basolo[22] noted in the hydrolysis of $[Co(NH_3)_5Cl]^{2+}$ and $[Co(NH_3)_5Br]^{2+}$ that unless very pure sodium hydroxide was used irreproducible and generally high rates resulted. Exchange of [^{14}C]dipyridyl with $[\text{Ni dipy}_3]^{2+}$ in water gave a dissociative rate constant $k = 14{\cdot}6 \times 10^{-2}$ min.$^{-1}$ at 25° and an energy of activation = 22·8 kcal./mole.[23] When these values are compared with racemisation values, $14{\cdot}0 \times 10^{-2}$ min.$^{-1}$,[24] and 21·8,[2] 21·9,[6] and 24·0[23] kcal./mole, respectively, it can be seen that, despite the dependence of rates on pH, dissociation accounts for the racemisation of this ion also.

Non-aqueous Solution.—No attempt was made to study fully the exchange behaviour of $[\text{Ni phen}_3]^{2+}$ in other solvents, our purpose being to compare dissociation (as shown by exchange) and racemisation rates directly. In the racemisation runs in ethanol and alcohol–water close agreement with published racemisation rates was obtained and the dissociative exchange rate constant (runs 24—26) calculated from the assumed rate law, $R = k[\text{Ni phen}_3{}^{2+}]$, showed that in all these solutions a dissociative process accounted, once again, for the racemisation. (Dr. Neumann[25] has kindly supplied us with his results in 70 mole % of methanol and although preliminary work indicated a real difference between the racemisation and acid dissociation rates there were inherent difficulties in obtaining accurate rate constants and the work was abandoned.)

Some difficulty was encountered with nitrobenzene. Our racemisation rates were some ten-fold slower than those of Davies and Dwyer.[7] This rate was enhanced by added phenanthroline or water and then became somewhat irreproducible. We therefore carried out our exchange and racemisation experiments *under the same experimental conditions* and despite some variation in the rates (cf. runs 22 and 23) the rate constants were identical within experimental error. Even in nitrobenzene then, despite the unsatisfactory quantitative features of the experiments the dissociative mechanism persists. The dissociation process in aqueous solution undoubtedly involves participation of water molecules. One of the difficulties in discussing this process in " anhydrous " solvents is connected with the presence of water which Karl Fischer determination indicated as about 0·01M (in alcohol) and 0·005M (in nitrobenzene). This means that water is present in

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[21] Davies and Dwyer, *Trans. Faraday Soc.*, 1954, **50**, 24.
[22] Adamson and Basolo, *Acta Chem. Scand.*, 1955, **9**, 1261.
[23] Wilkins and Ellis, unpublished work.
[24] Davies and Dwyer, *Trans. Faraday Soc.*, 1953, **49**, 180.
[25] Neumann, personal communication.

concentrations comparable with the exchange reactants so that a similar dissociation process to that which takes place in aqueous solution cannot be ruled out. Only very dry solvents and special precautions to exclude moisture during the measurements could resolve this ambiguity.

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