BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN   VOL. 40   1159—1162 (1967)

Isotopic Exchange Reaction between Bis(α-benzildioximato)nickel(II) and Nickel Ions in Pyridine and Pyridine-Water Solutions

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(Received September 27, 1966)

The rate of isotopic exchange reaction between bis(α-benzildioximato)nickel(II) and nickel ions in pyridine greatly increases in the presence of water. When the water content in pyridine is lower than 3 M, the reaction takes place according to the rate equation:

$$\text{Rate} = k_1(\text{complex}) + k_2(\text{complex})(\text{Ni}^{2+})(\text{H}_2\text{O})$$

For the catalyzed step, a mechanism is proposed.

The studies of Hall *et al.* on some bis(dioximato)-nickel(II) complexes have shown that the rates of isotopic exchange between these complexes and nickel ions are all slow in pyridine,[1,2] but the reported values are only qualitative and neither the solvent effects nor the reaction orders of the reagents have yet been described.

We found that the reaction rate is greatly accelerated in the presence of such substances as water and nitromethane. Since this catalytic phenomenon had not been investigated, it was decided in this case to study the kinetics of these systems in detail. This paper will report the results obtained for the isotopic exchange reaction between bis-(α-benzildioximato)nickel(II) and nickel(II) ions in the presence of water.

Experimental

Radioactive Nickel. The radioactive nickel was obtained from the New England Nuclear Corporation in the form of nickel chloride. It was a mixture of ^{63}Ni and ^{59}Ni. Its radiochemical purity was 99%, and so no further purification was carried out. The specific activity was 1.3 m Ci per mg Ni.

Preparation of the Complex. Bis(α-benzildioximato)nickel(II) was prepared by the reaction of nickel acetate with 2 equivalents of α-benzildioxime in boiling ethanol. The product, an orange precipitation, was filtered, dried, and recrystallized from chloroform.

Found: C, 62.75; H, 4.34; N, 10.95%. Calcd for $(C_{14}H_{11}N_2O_2)_2Ni$: C, 62.60; H, 4.10; N, 10.43%.

Solvent. The water-pyridine solvent mixtures were prepared for each run as needed, using distilled water and reagent-grade anhydrous pyridine. The concentration of water was determined before and after each experimental run by volumetric titration with Karl Fischer's reagent. It was shown that the concentration of water in pyridine remained constant during the experiment. Because of the decreasing solubility of the nickel complex in the solvent mixture with an increase in the ratio of water to pyridine, the water concentration of solvent was limited below 3 M.

Preparation of Nickel Chloride Solution Labelled with Radioactive Nickel. After a few drops of tracer solution had been added to a calculated amount of a nickel chloride solution, the solution mixture was evaporated to dryness on a water bath. The yellow product thus obtained was further dried in a desiccator with silica gel. Anhydrous nickel chloride was dissolved in pyridine or a pyridine-water solvent mixture and diluted to a desired concentration. In each run lithium chloride was added to the nickel chloride solution, so that the ionic strength of reaction mixture was adjusted to 1.5×10^{-2} M.

Exchange Procedure. To carry out a kinetic run, a bis(α-benzildioximato)nickel solution and a nickel chloride solution of known concentration were prepared in stoppered flasks and then placed in a thermostat-bath for a time sufficient for temperature equilibrium to be reached. The separate solutions were then mixed. The moment of mixing was taken as the time-zero. After suitable intervals, 10 m*l* aliquot portions were withdrawn and run into a separation funnel containing 10 m*l* each of water and chloroform. After being shaken for 2 min, the two layers were separated. The aqueous layer was evaporated on a water bath, and the residue was dissolved in hydrochloric acid. Nickel ions were precipitated by adding an alcoholic dimethylglyoxime solution according to the standard gravimetric method. The precipitate was filtered with a filterstick, washed with hot water, and finally with an ethanol water mixture (1 : 1) and dried at 100—120°C. As ^{63}Ni and ^{59}Ni give a very soft radiation, the radioactivity of the nickel sample was counted in a gas-flow counter.

Treatment of Data. The isotopic exchange reaction rate was calculated using Mckay's equation:

$$R = (0.693/t_{1/2})\cdot ab/(a+b)$$

where a and b are the concentrations of the nickel complex and nickel ions in the reacting solution, and where R is the rate of the exchange of nickel atoms. The

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1) N. F. Hall and. B. R. Willeford, Jr., *J. Am. Chem Soc.*, **73**, 5419 (1951).

2) J. E. Johnson and N. F. Hall, *ibid.*, **70**, 2344 (1948).

half-time of exchange, $t_{1/2}$ was obtained graphically from the slope of the plot of $\log(1-F)$ against the time, where F is the fraction of exchange at the time. R was calculated from t, a, and b. Plots of $(1-F)$ *vs.* the time showed the precision of $t_{1/2}$ to be 5%. No zero time exchange was observed.

Results and Discussion

Rate Laws for Exchange in Absolute Pyridine. As it was very difficult to obtain an absolute pyridine solution, the reaction rates in absolute pyridine were estimated graphically by extrapolation to a water concentration of zero by the use of Fig. 3, and the studies of the effects of the reactant concentration were carried out in a solution with water content of less than 0.006 M. The experimental results, given in Fig. 1 and Fig. 2 indicate a monomolecular-type reaction,

$$R = k_1(\text{complex}) \tag{1}$$

The values of the rate constant, k_1, at several temperatures are summarized in Table 1. The slopes of the linear semi-logarithmic plots of the values for the rate constant, k_1, against the reciprocal values of the absolute temperature were graphically evaluated. The experimental activation energy as calculated for this slope is 20.0 kcal per mole. The data are well represented by the rate law:

$$R = 2.5 \times 10^{13} \exp(-20000/\boldsymbol{R}T)(\text{complex}) \tag{2}$$

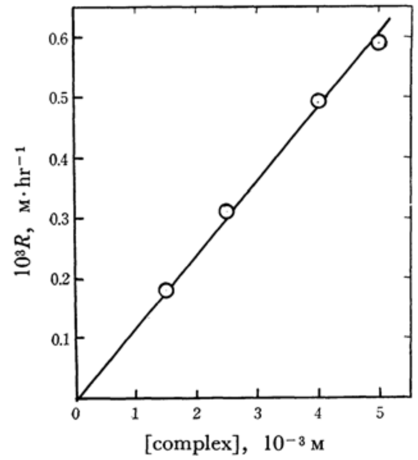

Fig. 1. Rates of reaction R in absolute pyridine at 30.0°C as a function of the concentration of the complex at a constant nickel ion concentration (5×10^{-3} M).

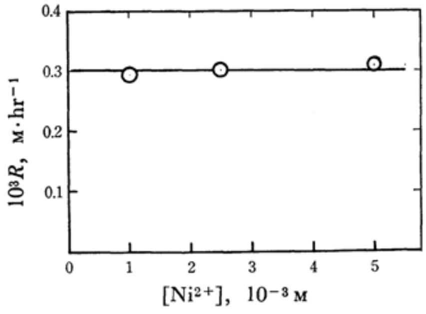

Fig. 2. Rates of reaction R in absolute pyridine at 30.0°C as a function of the concentration of nickel ion at a constant complex concentration (2.5×10^{-3} M). $\mu=1.5\times10^{-2}$ M with LiCl

TABLE 1. TTE VALUES OF THE RATE CONSTANT k_1 AND k_2 IN ABSOLUTE PYRIDINE AT SEVERAL TEMPERATURES

Temp., °C	k_1, hr^{-1}	k_2, M$^{-2}\cdot$hr^{-2}
15.3	0.022	6.4
25.0	0.068	16.8
30.0	0.117	26.0
40.0	0.336	47.6

Rate Laws for Exchange in Pyridine-water Solvents. The results of exchange experiments at 30.0°C in pyridine-water solvents mixtures are summarized in Figs. 3, 4, and 5. The data in Fig. 3 show that the rates of the exchange reaction are increased almost linearly by the addition of H_2O at constant concentrations of the complex and nickel ions.

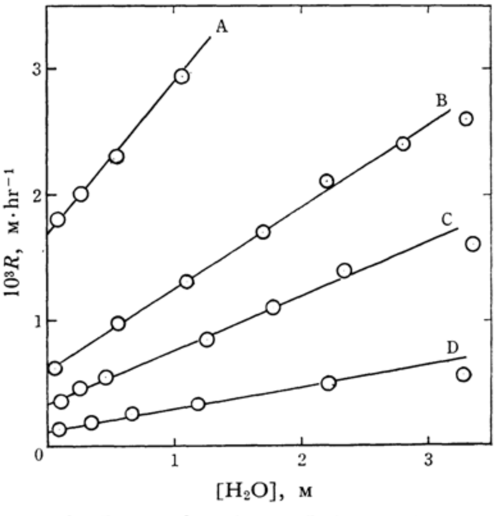

Fig. 3. Rates of exchange R in pyridine as a function of the concentration of water at 40.0°C (A), 30.0°C (B), 25.0°C (C) and 15.3°C (D). [complex]=[Ni^{2+}]=5×10^{-3} M.

Consistent with Figs. 4 and 5, the results are also in good agreement with the two-term rate expression at the water concentration 1.1 M:

$$R = k_1(\text{complex}) + k_2(\text{complex})(\text{Ni}^{2+})(\text{H}_2\text{O}) \tag{3}$$

where k_2 is the rate constant for the water-calalyzed reaction path. The average values for the rate constant k_2 at several temperatures are graphically

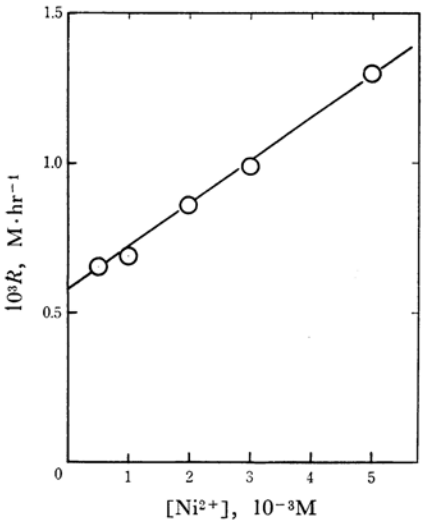

Fig. 4. Rates of reaction R in pyridine-water solvent mixture as a function of the concentration of nickel ion at constant complex concentration (5×10^{-3} M). [H_2O]=1.1 M; $\mu=1.5\times10^{-2}$ M with LiCl.

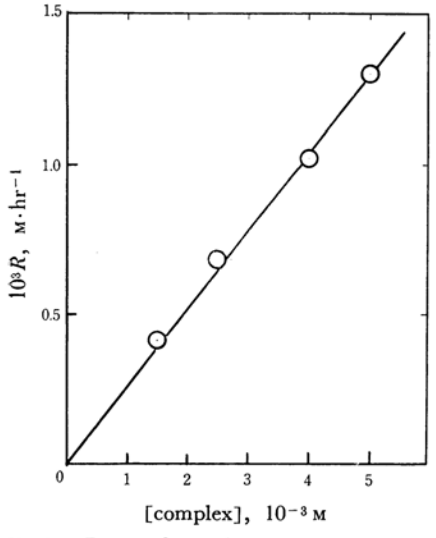

Fig. 5. Rates of reaction R in pyridine-water solvent mixture as a function of the concentration of complex at constant nickel ion concentration. [H_2O]=1.1 M.

obtained from Fig. 3. The results are summarized in Table 1.

It is considered that, in addition, the term k_1' (complex)(Ni^{2+}) may exist, but k_1' must be very small or zero. It was impossible to measure it.

From the slopes of the linear semi-logarithmic plot of the values for k_2 against the reciprocal of the absolute temperature, the Arrhenius parameters were calculated. The over-all rate law is represented as:

$$R = 2.5 \times 10^{13}\exp(-20000/\boldsymbol{R}T)(\text{complex}) + 3.9\times10^{11}\exp(-14000/\boldsymbol{R}T)(\text{complex})\cdot(\text{Ni}^{2+})(\text{H}_2\text{O}) \quad (4)$$

The two-term rate law found is consistent with the two reaction mechanisms. Thus, the first-order rate probably represents a relatively slow dissociation reaction of the metal complex, which is followed by rapid combination with incoming nickel ions.

In the absence of any real evidence, the catalyzing process can be elucidated in several ways. Considering the usual value of the activation energy, the kinetics of direct bimolecular collision is improbable. Perhaps a step-by-step dissociation of the metal chelate and simultaneous chelation of the ligand with the exchanging metal ion occurs.

One explanation can be made from the steric point of view. As large molecules of pyridine are attached above and below the plane of the square planar complex, they may block the incoming nickel ions from making a new bond with the chelating ligand. On the other hand, when the water molecule is coordinated, nickel ions can approach the nitrogen atom of the chelate ring relatively easily.

Without contradiction to the first one, another explanation of the catalyzing effect of water can also be proposed. Assuming that the coordinating property of water may weaken N–Ni bonds, the rupture of the N–Ni bonds may be accelerated by the coordinated water when the exchanging nickel ions come in and make a bond with one end of the chelate.

Spectrophotometric measurements of pyridine and pyridine-water solutions of bis(α-benzildioximato)nickel(II) were also carried out. At the

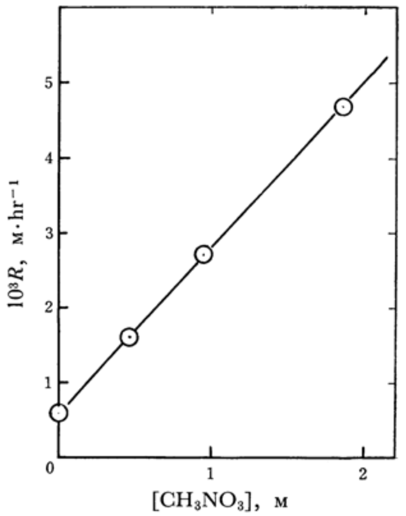

Fig. 6. Rates of the exchange R in pyridine as a function of the concentration of nitromethane at 30.0°C. [complex]=[Ni^{2+}]=5×10^{-3} M

water concentration of 3 M, the maxima of the principal bands were scarcely affected, but their intensities decreased with an increase in the water concentration. It is not obvious whether or not this effect was due to the presence of a water-coordinated complex in the solution.

We have found that the rate of this exchange reaction also increases linearly with an increase in the nitromethane content, as is shown in Fig. 6. As has previously been pointed out by Basolo,[3,4] nitromethane is known to be a good coordinating solvent to the square planar complex. Though this exchange experiment has not be completed, it is likely that the same catalytic mechanism participates in this case as in the case of the pyridine-water solvent. Exchange experiments in other solvent mixtures would decide the reaction mechanisms.

The remaining point to be explained is the deviation in rate from linearity in the region with a high water content. The simplest explanation is that another reaction mechanism appears in the region of high water content, but no measurement were carried out because of the decreased solubility of the complex in that region.

The authors are much indebted to Dr. Hideo Yamatera and Dr. Tastujirō Ishimori for their helpful suggestions and discussions.

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3) R. G. Pearson, H. B. Gray and F. Basolo, *ibid.*, **82**, 787 (1960).

4) F. Basolo and R. G. Pearson, Advances in Inorganic Chemistry and Radiochemistry, **3**, p. 47 (1960).