Acknowledgments.—We wish to express our appreciation to R. W. Cogley for carrying out some of the experimental work. The analytical work was carried out at our Center by Mrs. Charlotte Gottschalk of the Physics Division.

LANCASTER, PENNSYLVANIA

[CONTRIBUTION FROM THE DOW CHEMICAL COMPANY]

Exchange Properties of the Tetracyanonickelate Ion with Certain Amino Acid Complexes of Nickel(II)[1-3]

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RECEIVED APRIL 17, 1958

The manner in which nickel in the tetracyanonickelate ion, $Ni(CN)_4^{-2}$, exchanges with nickel in each of four amino acid complexes of the metal has been studied employing radioactive nickel tracer. Poor correlation is exhibited between exchange rate and charge of the amino acid complex. In exchanges between strong and weaker complexes, the specific nature of the weaker complexing agent affects the exchange rate more than does the charge of the resulting complex. Reactions are first order in respect to each of the exchanging species, suggesting as the most probable reaction mechanism a direct transfer of nickel atoms resulting from bimolecular collision. Exchange rate, activation energy and entropy of activation were calculated for each exchange.

Introduction

Long has reported[4] a good correlation between the rate of exchange of nickel between two nickel complexes and the respective charges of the complexes involved, more rapid exchanges taking place between species of opposite charge than between species of like charge. In the work reported here the manner in which nickel tied up in the tetracyanonickelate ion exchanges with that associated with four amino acid complexes of the metal was studied. Since simple amino acid complexes of nickel can be obtained as cationic, anionic or neutral species, depending upon the particular amino acid used, these complexes are useful in studying the effect of the charge borne by the weaker complex upon the rate of exchange of its nickel with that of the tetracyanonickelate ion.

Experimental

Radionickel.—In each of the exchange reactions one of the nickel complexes, usually the amino acid complex, was made up using nickel containing a little radioactive nickel-63. One of the complexes was isolated at the end of the exchange period and its nickel electroplated on a copper planchette. Determination of the change in specific activity of the nickel associated with this complex provided a convenient measure of the extent of exchange. Radionickel used in these experiments was obtained from the United States Atomic Energy Commission, Oak Ridge, Tennessee. Cobalt activity present in the original metal was removed by repeated dimethylglyoxime precipitation of the nickel using "cold" cobalt carrier.

Counting Infinitely Thick Radionickel Plates.—The electroplated nickel was "infinitely thick" in respect to the weak Ni^{63} β-radiation. The unavoidable presence of long-lived Ni^{59}, whose decay is accompanied by the emission of X-rays, causes the counting rate for nickel of a given specific activity to increase with thickness even beyond infinite thickness. To determine accurately the specific activity of the plated nickel it was necessary to keep the weight of these plates nearly constant.

Preparation of Nickel Complexes. Potassium Tetracyanonickelate.—This compound was prepared from nickel of natural isotopic composition using the procedure described in "Inorganic Syntheses."[5] Analysis of crystals of this salt for nickel gave 23.8% by both the dimethylglyoxime precipitation method[6] and by titration with Versene.[7] The theoretical amount of nickel in $K_2Ni(CN)_4 \cdot H_2O$ is 22.7%. In the analysis for cyanide, weighed, acidified samples were steam distilled and the hydrocyanic acid caught in 0.1 N sodium hydroxide solution. The cyanide was titrated with standard silver nitrate solution according to the method described by Kolthoff and Sandell.[8] The average value obtained was 41.7%. The molar ratio of nickel to cyanide is therefore 1.00/3.96 which is within the experimental error of the theoretical value of 1.00/4.00. A standard solution of potassium tetracyanonickelate was prepared.

Amino Acid Complexes.—The amino acid complex solutions were prepared by adding to the required amount of a standard solution of hot nickel sulfate an amount of amino acid calculated to form a 2:1 complex of all of the nickel present. The pH of the solution was raised to 9 by the addition of sodium hydroxide solution. The absence of nickel hydroxide precipitate in these solutions, even on long standing, precludes the presence of uncomplexed nickel. In the kinetic study, nickel did tend to precipitate from the more dilute solutions. To prevent this, twice the theoretical amount of glycine was employed in the tetracyanonickelate–nickel glycinate series and three times the theoretical amount of glutamic acid was used in the tetracyanonickelate–nickel glutamate series. Thus the amino acid was present in known and constant excess.

Nickel Versenate.—A standard nickel Versenate solution was prepared by adding to a known amount of cold nickel sulfate in solution a calculated amount of recrystallized disodium Versenate.

Tris-ethylenediamine-Nickel.—A solution of this complex was prepared using a measured quantity of standard hot nickel sulfate solution and a slight excess of redistilled ethylenediamine. The pH of the solution was raised to 9 by the addition of sodium hydroxide solution.

Nickel Tetramine.—This complex was prepared using a measured quantity of standard hot nickel sulfate solution and excess ammonium hydroxide.

Procedure Used in Exchange Experiments.—The exchange reactions were carried out in reaction vessels having the shape of an inverted "V" with a ground glass stoppered opening at the apex. Each of the two complex solutions, at twice the desired final concentration, was placed in one

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(1) Presented in part before the Division of Physical and Inorganic Chemistry at the Sept., 1957, Meeting of the American Chemical Society at New York, N. Y.

(2) From a thesis of R. C. Calkins presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin (Sept., 1953).

(3) This work was assisted in part by the Research Committee of the Graduate School from funds supplied by the Wisconsin Alumni Research Foundation.

(4) F. A. Long, THIS JOURNAL, **73**, 537 (1951).

(5) W. C. Fernelius, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 227–228.

(6) F. P. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. II, 9th Ed., John Wiley and Sons, Inc., New York, N. Y., 1942, p. 193.

(7) G. Schwarzenbach, "Titration Methods Using Complexons."

(8) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis, The Macmillan Co., New York, N. Y., 1948, p. 478.

leg of the reaction vessel. The reaction vessel then was placed in a constant temperature bath for 0.5 hr. The solutions of the two complexes were mixed then by inverting and vigorously shaking the stoppered reaction vessel. At the instant of mixing (time = 0) a stopwatch was started. Aliquots of the solution were removed at intervals using a thermostated pipet and transferred to thermostated separation vessels. The separation vessels were small glass-stoppered erlenmeyer flasks having a bulbous side arm attached at the neck. The bulbous side arm held a measured quantity of 1% alcoholic dimethylglyoxime solution. At the appropriate time, the stoppered separation vessel was removed from the bath, inverted and shaken vigorously (time = t). Nickel in the amino acid complex was precipitated immediately and quantitatively whereas nickel in the extremely stable nickel cyanide complex remained in solution. As soon as possible the contents of the separation vessel was poured into an equal volume of boiling water and heated for a few minutes to coagulate the precipitate. This mixture then was chilled in an ice-bath and filtered. The filtrate containing the nickel cyanide complex plus excess dimethylglyoxime was treated with sulfuric and nitric acids to destroy the organic matter. This solution then was made ammoniacal and transferred to a Tracerlab Electroplating Cell for the plating of the radionickel. The weight of radionickel electroplated onto the copper planchette was 16.6 ± 0.3 mg. in almost all cases. Because of the extremely weak nature of the nickel-63 beta radiation the samples were counted in a windowless counter.

Calculations

Determination of the Reaction Rate.—The exchange rate for each reaction was determined from the half-time of the exchange using the expression

$$R = \frac{ab}{a+b} \times \frac{1}{\tau}$$

where a is the molar concentration of the tetracyanonickelate ion, b the molar concentration of the amino acid complex and τ the half-time of the exchange. In Table I are listed exchange rates which were obtained for the exchange of nickel between the tetracyanonickelate ion and each of the four amino acids studied.

TABLE I

EXCHANGE OF RADIONICKEL BETWEEN THE TETRACYANONICKELATE ION AND SEVERAL AMINO ACID COMPLEXES OF NICKEL

Temp., 25.1°; pH 9; 0.010 M in each complex

Amino acid	Ionic charge difference	Ionic wt. weaker complex	R, moles l.$^{-1}$ sec.$^{-1}$ × 10^5	
Ni(glycinate)$_2^0$	2	207	4.6	6.9[a]
Ni(serinate)$_2^0$	2	267	8.3	6.8[b]
Ni(glutamate)$_2^{-2}$	0	349	5.0	7.4[a]
Ni(lysinate)$_2^{+?}$	>2	341	8.1	5.9[a]

[a] In 3 M $NaClO_4$. [b] In 0.2 M $NaClO_4$

Effect of Relative Charge on Exchange Rate.—It might be expected that nickel in the negatively charged tetracyanonickelate ion would exchange most rapidly with positively charged nickel lysinate, less rapidly with neutral nickel glycinate and serinate, and least rapidly with negatively charged nickel glutamate. The fact that the exchange rates for all of the exchanges are of the same order of magnitude indicates that the charge borne by the weaker amino acid complex is not the most important factor governing the rate of exchange of nickel between the complexes.

Effect of Relative Mass of Amino Acid Complex on Exchange Rate.—It will be noted from Table I that there is no good correlation between the molecular weight of the amino acid complex and the rate of nickel exchange with the tetracyanonickelate ion. Exchanges involving the lightest and heaviest of the nickel–amino acid complexes studied, nickel glycinate and nickel glutamate, respectively, have nearly the same reaction rate.

Effect of Neutral Salt on Exchange Rate.—The effect of added neutral salt (sodium perchlorate) was determined for each exchange. It might be expected that exchanges between negatively charged tetracyanonickelate ions and neutral species, such as nickel glycinate and nickel serinate, would be affected little by the addition of salt. As indicated in Table I, the addition of salt causes the nickel glycinate exchange to be speeded slightly and the nickel serinate exchange to be slowed slightly. Exchanges involving nickel glutamate and nickel lysinate were affected in the predictable manner by the addition of neutral salt. In each case the effect is quite small.

Exchanges of Nickel between Nickel Versenate and Weaker Nickel Complexes.—The results of a similar series of exchanges between the very stable nickel Versenate complex (NiY^{-2}) and a number of weaker nickel complexes are shown in Table II. Among the amino acid complexes there was a slightly better correlation between reaction rate and the charge of the weaker complex. Negatively charged nickel Versenate exchanged most rapidly with positively charged nickel lysinate, less rapidly with neutral nickel glycinate and least rapidly with negatively charged nickel glutamate. The reaction rates of the extremes, however, differ by less than an order of magnitude, indicating once again that the charge difference between strong and weak complexes of nickel is a relatively small factor affecting the rate of exchange of nickel between the two. This is indicated further by results with the ammonia and ethylenediamine complexes. Both of these complexes are opposite in charge to the nickel Versenate ion and although the ammonia complex exchanges nickel with nickel Versenate at a relatively rapid rate, the likewise positively charged ethylenediamine complex exchanges at approximately the same rate as for the amino acid complexes.

TABLE II

EXCHANGE OF RADIONICKEL BETWEEN THE NICKEL VERSENATE ION AND SEVERAL AMINO ACID COMPLEXES OF NICKEL

Temp., 25.1°; pH, 9; 0.010 M in each complex

Amino acid	Ionic charge difference	Ionic wt. weaker complex	R, moles l.$^{-1}$ sec.$^{-1}$ × 10^5
Ni(glycinate)$_2^0$	2	207	3.8
Ni(glutamate)$_2^{-2}$	0	349	1.7
Ni(lysinate)$_2^{+?}$	>2	341	9.9
$Ni(NH_3)_4^{+2}$	4	127	8.4)
$Ni(en)_3^{+2}$	4	239	5.3)

The results of both of these series of exchanges point up the fact that more important than the charge of the weaker complex or its mass is the specific nature of the complexing agent involved—whether it be ammonia, ethylenediamine, amino acids, oxalic acid, tartaric acid, etc.

Reaction Mechanisms

To get an idea about possible reaction mechanisms for these exchange reactions, the reaction order in respect to each reactant was measured. The rate expression for these exchanges may be written

$$R = k[Ni(CN)_4^{-2}]^m\ [Ni(\text{amino acid})_2]^n$$

where m represents the dependence of the rate on the $Ni(CN)_4^{-2}$ concentration and n the dependence of the rate on the $Ni(\text{amino acid})_2$ concentration. Writing the same expression in logarithmic form

$$\log R = \log k + m \log [Ni(CN)_4^{-2}] + n \log [Ni(\text{amino acid})_2]$$

Since k is a constant at constant temperature, m can be evaluated from the slope of a plot of log $[Ni(CN)_4^{-2}]$ *versus* log R in a series of experiments in which the concentration of the amino acid complex is kept constant. n can be evaluated in a corresponding manner. Figure 1 shows such a plot for the tetracyanonickelate-nickel glycinate exchange. First-order dependence of the exchange on the tetracyanonickelate concentration is indicated by the fact that the slope of this plot is approximately one. The dotted line having a slope of 1 is included for comparison. Similarly, first-order dependence of the exchange on the nickel–amino acid complex concentration is shown in Fig. 2 by the fact that the plot of log $[Ni(\text{glycinate})_2]$ *versus* log R also has a slope of one. Second-order dependence of the entire reaction on total concentration is shown in Fig. 3 by the inverse relationship between the reciprocal of the total concentration and the half-time of the exchange. A similar series of experiments carried out for the tetracyanonickelate–nickel glutamate exchange gave identical results. The possibility of an ionization-type mechanism is ruled out in both cases by the fact that the reactions are first

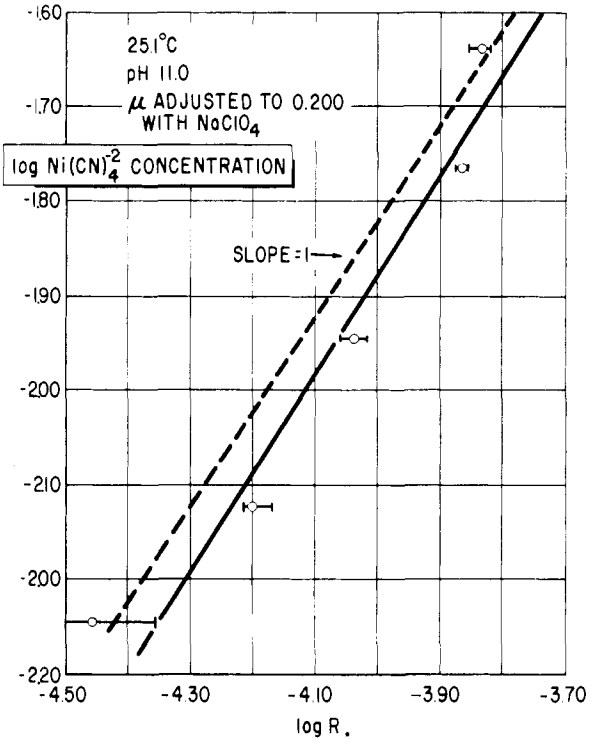

Fig. 1.—Dependence of rate of $Ni(CN)_4^{-2}$–$Ni(\text{glycinate})_2^0$ exchange on tetracyanonickelate concentration.

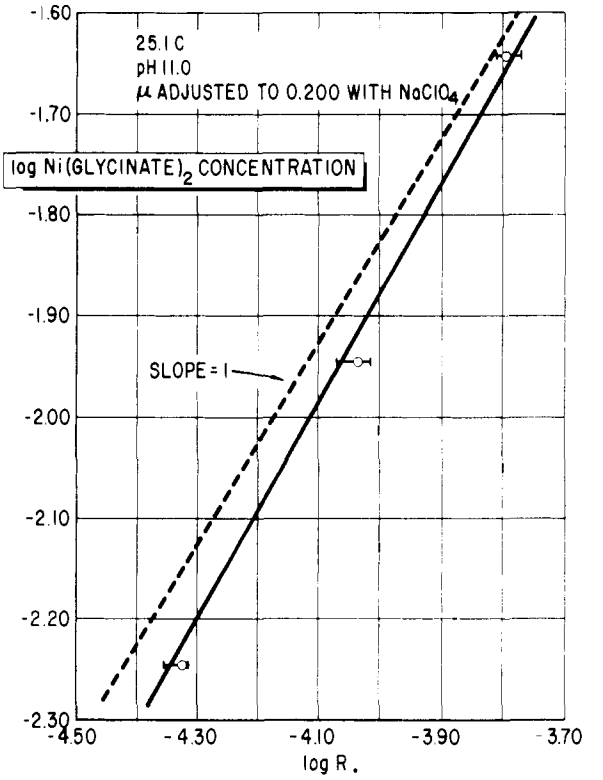

Fig. 2.—Dependence of rate of $Ni(CN)_4^{-2}$–$Ni(\text{glycinate})_2^0$ exchange on nickel glycinate concentration.

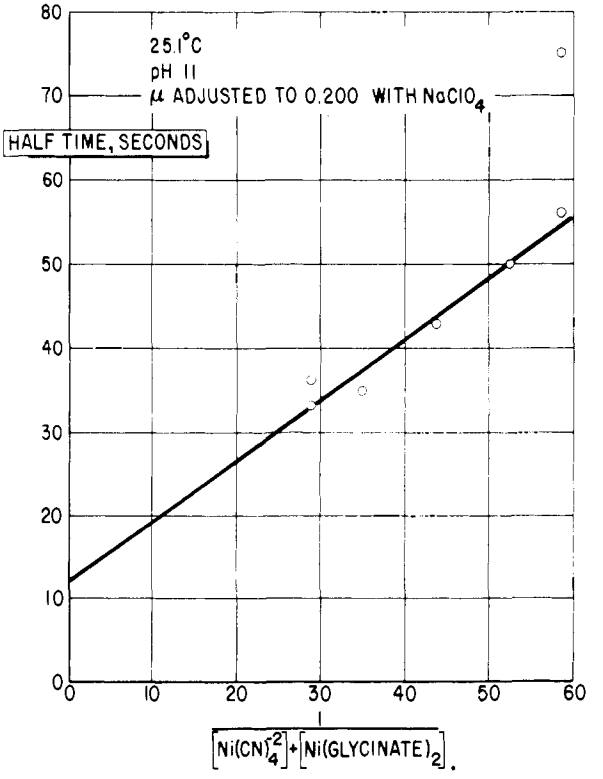

Fig. 3.—Dependence of half-time on total concentration.

order in respect to tetracyanonickelate ion and first order in respect to the amino acid complex ion. The most probable mechanism, therefore, would seem to be a direct transfer of nickel atoms resulting from bimolecular collision of the two species.

Kinetics of the Tetracyanonickelate–Nickel Amino Acid Complex Exchanges

Activation Energy and Frequency Factor.—The activation energy for each of the four tetracyanonickelate–nickel amino acid complex exchanges was evaluated using the Arrhenius expression, the logarithmic form of which is

$$\log k = \log A - \frac{E}{2.303\,R} \times \frac{1}{T}$$

The activation energy E was evaluated from the slope of a plot of log k, the specific reaction rate *versus* the reciprocal of the absolute temperature. This plot for the four exchanges is shown in Fig. 4. Exchanges were carried out at 5, 15, 25 and 45°. Reaction rates for these exchanges are quite rapid even at 25° and therefore the results obtained at 45° are given the least significance in this plot. In all of these exchanges a known excess of the theoretically required amount of amino acid was used in preparing the nickel–amino acid complex. The *p*H of each solution was 11.0 and the ionic strength adjusted to a known value by the addition of neutral salt, sodium perchlorate. Activation energies which were obtained by evaluating the slope of these plots are listed in Table III. Experimental uncertainties involved in studying such rapid reactions make it seem likely that the differences between these values are not necessarily real. Since each of the isotopic exchange reactions involves the exchange of nickel atoms between an amino acid complex and the tetracyanonickelate complex, the activation energies might be expected to be nearly the same. A value of 18.2 ± 0.8 kcal. mole^{-1} would seem to be a reasonable value for each of the exchanges and is of the right order of magnitude for such fairly rapid reactions.

TABLE III

ACTIVATION ENERGIES, ENTROPIES OF ACTIVATION AND FREQUENCY FACTORS FOR $Ni(CN)_4^{-2}$–Ni(AMINO ACID)$_2$ EXCHANGES

Exchange	E, kcal. mole^{-1}	ΔS, cal. deg. mole^{-1}	A, l. mole^{-1} sec.$^{-1}$
$Ni(glycinate)_2^0$–$Ni(CN)_4^{-2}$	17.3	−10.6	8.1×10^{10}
$Ni(serinate)_2^0$–$Ni(CN)_4^{-2}$	18.2	− 8.2	2.7×10^{11}
$Ni(glutamate)_2^{-2}$–$Ni(CN)_4^{-2}$	18.6	− 5.8	9.3×10^{11}
$Ni(lysinate)_2^{+?}$–$Ni(CN)_4^{-2}$	18.9	− 3.9	2.3×10^{11}

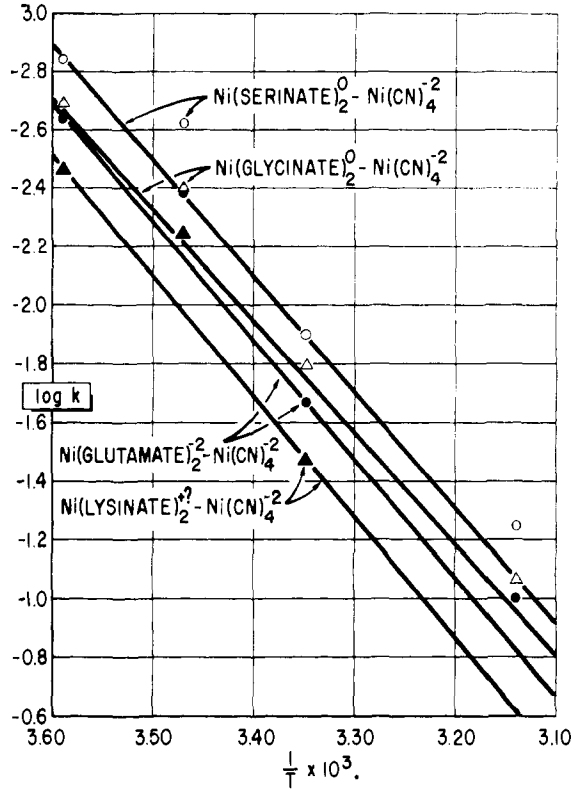

Fig. 4.—Dependence of exchange rates on temperature.

The calculated Arrhenius frequency factor A for each of these exchanges also is listed in Table III. Differences between these values may or may not be real but they do fall in the proper range for normal bimolecular reactions in solution (2.8×10^{11} within a factor of 10 or so).[9]

Entropy of Activation.—Using the more complete expression for the reaction rate and the calculated

$$k = e\frac{k_b T}{h} e^{-E/RT}\, e^{\Delta S^*/R}$$

values of the activation energies for these exchanges, the entropy of activation for each exchange could be calculated. These values also are listed in Table IV. The values range from −3.9 to −10.6 cal. deg.$^{-1}$ mole^{-1}.

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(9) E. A. Moelwyn-Hughes, "The Kinetics of Reactions in Solution," Oxford University Press, London, 1933, p. 82.