

# KINETICS OF THE EXCHANGE REACTION BETWEEN COPPER-CHELATES OF TRIETHYLENETETRAMINEHEXAACETIC ACID AND THE NICKEL(II) TETRAETHYLENEPENTAMINE COMPLEX

V. STARÁ and M. KOPANICA

*J. Heyrovský Institute of Physical Chemistry and Electrochemistry,  
Czechoslovak Academy of Sciences, 110 00 Prague 1*

Received July 4th, 1972

Using the concept of chain mechanism, which was proposed for the studied reaction, the acceleration effect of free ligands on the reaction rate was explained. Application of the studied reaction for the kinetic determination of small concentration of metals was suggested.

The double ligand-exchange reactions between two multidentate complexes were studied by Margerum and coworkers<sup>1-3</sup> and it has been shown that this type of reaction may proceed by a chain reaction mechanism. The exchange reaction between the copper(II) EDTA chelate and nickel(II) triethylenetetramine is initiated by trace amounts of either of these ligands and in the chain-propagation steps one multidentate ligand displaces the other from its metal complex and *vice versa*<sup>1</sup>.

Examination of the reaction between copper-triethylenetetraminehexaacetate and the nickel-tetraethylenepentamine complex showed some evidence that the effects described by Margerum<sup>1-3</sup> may play a role in the double-ligand exchange reactions of the mentioned complexes.

## EXPERIMENTAL

*Reagent and apparatus.* The solution of triethylenetetraminehexaacetic acid (TTHA, H<sub>6</sub>L) was prepared from the R. G. chemical (Dojin Pharmaceutical Laboratories, Japan) and standardized by amperometric titration with zinc solution. Tetraethylenepentamine(tetren) (Fluka A. G., Switzerland) was recrystallized five times from nitric acid solutions according to Reilley and Holloway<sup>4</sup> and the resulting NO<sub>3</sub>-salt was standardized by neutralization titrations. The solutions of nickel-tetren and copper-tetren complexes were prepared by the addition of a slight excess of the metal salt to a given quantity of tetren; the excess of the metal was precipitated by the addition of sodium hydroxide solution to pH 10.5. After separation of the precipitate, the pH was adjusted to approx. 7. The solutions of the copper-TTHA chelates were prepared by mixing known quantities of the metal and the ligand in the molar ratios 1 : 1 and 2 : 1. As buffer solution mixtures of 0.005M boric acid and sodium borate were used. Twice distilled water was used for all measurements. All other solutions were prepared from R. G. chemicals. Sodium perchlorate was used to adjust the ionic strength of all solutions. Spectrophotometric measurements were carried out using the spectrophotometer Unicam SP/800 (Unicam Instr., England) with

a thermostated cell compartment; polarographic measurements were made using the polarograph LP-60 (Laboratory Instruments, Prague) and a thermostated polarographic cell with a separated satd. calomel electrode. The pH values of the solutions examined were measured with the Radiometer pH meter PHM-25 and a glass electrode.

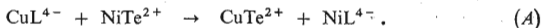
*Procedure.* The rate of the exchange reaction between the copper(II)-TTHA chelate and nickel(II)-tetren was followed by the polarographic determination of the concentration of Ni-tetren complex in dependence on time. It was found that the Ni-tetren complex yields a well developed polarographic wave in neutral and alkaline media. This wave corresponds to an irreversible electrode process; the corresponding limiting current is diffusion controlled. The half-wave potential of this wave depends on the pH of the base electrolyte; at pH 8.2,  $E_{1/2} = -0.96$  V (s.c.e.). — The determination of the concentration of Ni-tetren was carried out as follows: The solution containing the buffer, sodium perchlorate and the Ni-tetren complex was placed in the thermostated cell and dissolved oxygen was removed by bubbling nitrogen. The copper-TTHA chelate solution was then added using a syringe, passage of nitrogen was stopped, and the limiting current at a potential of  $-1.05$  V (s.c.e.) was recorded in dependence on time. — The rate of the disappearance of copper-TTHA chelate was followed spectrophotometrically. In alkaline media (pH 8–9) the copper-TTHA chelate yields an absorbance maximum<sup>5–7</sup> at 280 nm, and the copper-tetren complex at 250 nm. Due to the close values of these maxima, the measurement of the concentration of  $\text{CuL}^{4-}$  chelate was carried at a wave length of 325 nm, where the absorbance of CuTe is practically zero.

## RESULTS

### *Reactions of Cu-TTHA Chelates with NiTe Complex*

The TTHA reagent forms mono- and binuclear chelates with copper(II) ions, with the following constants<sup>8</sup>:  $\log \beta_{\text{Cu}_2\text{L}} = 32.6$  and  $\log K_{\text{CuL}}^{\text{Cu}} = 19.2$ . The mononuclear copper chelate predominates in the solution when the copper(II) ions and TTHA reagent are mixed in a 1 : 1 molar ratio and when the pH value of the resulting solution is higher than 5. When, on the other hand, the solution contains a mixture of copper(II) ions and TTHA in a molar ratio of 2 : 1, the binuclear chelate predominates only at very low pH values, where the formation of protonated binuclear chelates also occurs. These phenomena follow from the pH dependence of the conditional stability constants of copper-TTHA chelates<sup>9</sup>.

The kinetics of the reaction between Cu-TTHA chelate and  $\text{NiTe}^{2+}$  complex was studied with 1 : 1 molar mixture ( $\text{Cu}^{2+}$ -TTHA) in the pH interval 6–9; under these conditions the existence of practically only the  $\text{CuL}^{4-}$  chelate can be supposed. Preliminary polarographic measurements showed that the exchange between  $\text{CuL}^{4-}$  and  $\text{NiTe}^{2+}$  complexes can be expressed by reaction (A).

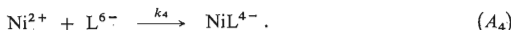
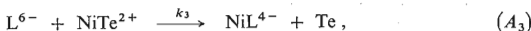
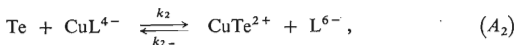
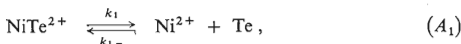


The tetren complexes of nickel(II) and copper(II) have stability constants with  $\log K$  values of 17.6 and 22.9, respectively<sup>10</sup>, and the TTHA complexes of copper(II) and nickel(II) have  $\log K_1$  values of 19.2 and 18.1, respectively<sup>8</sup>. These values indicate

that reaction (A) proceeds essentially to completion and that the reverse reaction can be neglected; the equilibrium constant of reaction (A) has the value  $\log K_E = 4.2$ . For examination of the rate of reaction (A) the concentration of the  $\text{NiTe}^{2+}$  complex was determined polarographically in dependence on time as described in the Experimental of this work. These measurements showed that reaction (A) is catalyzed by traces of either TTHA or tetren and inhibited by traces of metal ions, similar to the exchange reactions involving  $\text{EDTA}^{1-3}$ . The experimental reaction orders with respect to  $\text{NiTe}^{2+}$  and  $\text{CuL}^{4-}$  were determined using the differential method<sup>11</sup> when, in a series of experiments the concentration of one species was kept constant and the other was varied. It was found that the reactions are complex and the orders vary with the ratio of the concentration of the reactants and with pH. In the interval between pH 7.0–9.5, the order with respect to  $\text{NiTe}^{2+}$  was found to be 2.0 (polarographic measurement), the order with respect to  $\text{CuL}^{4-}$  varied from 0.7 to 1.2 (spectrophotometric measurement). The plot of  $1/[\text{NiTe}]$  vs time was linear and the intercept corresponding to zero time equaled the theoretical value (the reciprocal of the initial concentration of NiTe). These results led to formulation of the experimental rate law as

$$-(d[\text{CuL}^{4-}]/dt) = k_{L,\text{NiTe}}[\text{CuL}^{4-}][\text{NiTe}^{2+}]^2. \quad (1)$$

Due to the catalytic effect of the free ligands (TTHA or Tetren) and due to the inhibiting effect of free metal ions on the rate of reaction (A), it was proposed that the studied reaction is a chain reaction and the corresponding mechanism was assumed as follows:



In this reaction sequence, reaction (A<sub>1</sub>) is the initiating step producing small amounts of free tetren, reactions (A<sub>2</sub>) and (A<sub>3</sub>) are the chain-propagating steps and reaction (A<sub>4</sub>) is the terminating step. The step of dissociation of  $\text{NiTe}^{2+}$  is slow and thus quite satisfactory for a chain reaction of this type. If the reaction mechanism expressed by the sequence (A<sub>1</sub>)–(A<sub>4</sub>) is valid, the rate of the exchange reaction (A) is determined by the rate of the chain propagating step (A<sub>2</sub>) and is expressed by the equation

$$-(d[\text{CuL}^{4-}]/dt) = k_2[\text{CuL}^{4-}][\text{Te}] - k_{2-}[\text{CuTe}^{2+}][\text{L}^{6-}]. \quad (2)$$

The general rate equation for the exchange reaction (A) was derived by application of the steady state approximation with respect to the concentration terms  $[\text{Te}]$  and  $[\text{L}^{6-}]$ . After substitution into equation (2) the rate equation became

$$-\frac{d[\text{CuL}^{4-}]}{dt} = \frac{k_1 k_2 k_3 [\text{NiTe}^{2+}]^2 [\text{CuL}^{4-}] \{1 + k_4 [\text{Ni}^{2+}] / k_3 [\text{NiTe}^{2+}]\}}{k_2 k_4 [\text{CuL}^{4-}] + k_{1-} k_3 [\text{NiTe}^{2+}] + k_{1-} k_4 [\text{Ni}^{2+}] + k_{1-} k_{2-} [\text{CuTe}^{2+}]} \quad (3)$$

In solutions with pH above 8, the term  $k_3 [\text{NiTe}^{2+}]$  is much larger than  $k_4 [\text{Ni}^{2+}]$  (slow dissociation of the  $\text{NiTe}^{2+}$  complex in alkaline media, compared with the rate of the exchange reaction (A)). Under these conditions the term  $k_4 [\text{Ni}^{2+}]$  can be neglected, and when the reaction system contains an excess of  $\text{CuL}^{4-}$ , then the second term in the numerator and all terms in the denominator of the right hand side of equation (3), with the exception of the term,  $k_2 k_4 [\text{CuL}^{4-}]$ , can be neglected and equation (3) simplifies to

$$-(d[\text{CuL}^{4-}]/dt) = (k_1 k_3 / k_4) [\text{NiTe}^{2+}]^2. \quad (4)$$

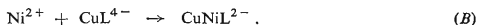
When, on the other hand, the system studied contains an excess of  $\text{NiTe}^{2+}$ , its terms in the numerator and denominator of reaction (3) are predominant and equation (3) can be simplified to give

$$-(d[\text{CuL}^{4-}]/dt) = (k_1 k_2 / k_{1-}) [\text{CuL}^{4-}] [\text{NiTe}^{2+}] = k_2 [\text{CuL}^{4-}] [\text{T}] [\text{Ni}^{2+}], \quad (5)$$

since  $k_1 / k_{1-} = [\text{Ni}^{2+}] [\text{Te}] / [\text{NiTe}^{2+}]$  (reaction  $(A_1)$ ).

Equations (4) and (5) show that, under the specified conditions, the studied reaction should be first order with respect to  $[\text{CuL}^{4-}]$  and second order with respect to  $[\text{NiTe}^{2+}]$ , as was found experimentally. As stated above, the rate of the exchange reaction (A) should be determined by the rate of step  $(A_2)$  or  $(A_3)$ . The kinetics of reaction  $(A_3)$  has already been studied<sup>7</sup> separately and it has been found that the experimental pseudo-second order rate constant (corresponding to the reaction  $\text{NiTe}^{2+} + \text{L}^6$  at 1 : 1 molar ratio of the reactants at pH 8.05) has the value  $1.5 \cdot 10^3 \text{ l mol}^{-1} \text{ s}^{-1}$ , and the rate constant of the reaction  $\text{NiTe}^{2+} + \text{CuL}^{4-}$  (at 1 : 1 molar ratio of the reactants and pH 8.0) has the value  $6.0 \cdot 10^3 \text{ l mol}^{-1} \text{ s}^{-1}$ . These data support the suggested mechanisms of the studied reaction.

It should also be mentioned here that several possible reaction steps have been omitted from the presented reaction scheme ( $A_1$ )–( $A_4$ ). In the system containing TTHA chelate and free metal ions the formation of a mixed binuclear chelate may occur as indicated by the reaction



In the system studied, the formation of  $\text{CuNiL}^{2-}$  is, however, suppressed by low concentration of free  $\text{Ni}^{2+}$  ions, compared with the concentration of  $\text{CuL}^{4-}$ . Similarly, the possibility of the formation of the  $\text{CuTe}^{2+}$  complex, by a direct reaction between  $\text{Cu}^{2+}$  ions and tetren, was discounted due to the low concentration of free  $\text{Cu}^{2+}$  ions.

Essentially identical results were obtained when, in reaction ( $A$ ), the  $\text{CuL}^{4-}$  chelate was replaced by a 2 : 1 molar mixture of  $\text{Cu}^{2+}$  ions and TTHA. This agrees very well with the theoretical proposal that the binuclear copper chelate is formed only at low pH values, as stated above.

### Analytical Applications of the Reaction between Cu-TTHA Chelate and Ni-Tetren Complex

As stated in the previous section, the rate of the exchange reaction ( $A$ ) is governed by the rate of reaction steps ( $A_2$ ) and ( $A_3$ ). Shortly after mixing the reactants (under steady state conditions) the rates of steps ( $A_2$ ) and ( $A_3$ ) must be equal and the following equation should be valid:

$$k_3[\text{L}][\text{NiTe}] = k_2[\text{Te}][\text{CuL}] \quad (6)$$

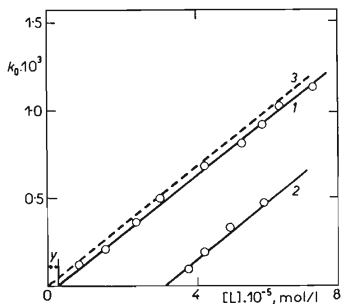


FIG. 1

Dependence of the Rate Constant  $k_0$  on the Amount of TTHA

$[\text{CuL}^{4-}] = [\text{NiTe}^{2+}] = 9.0 \cdot 10^{-5}$  mol.  $l^{-1}$ , pH 8.2,  $\mu = 0.1$ ; 22°C. 1 experimental calibration curve; 2 as line 1, the system contains also  $2.96 \cdot 10^{-5}$  mol  $l^{-1}$   $\text{Cd}^{2+}$ , 3 Theoretical line.

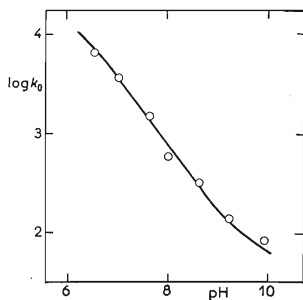


FIG. 2

Dependence of the log Value of Experimental Rate Constant  $k_0$  on pH

$[\text{CuL}^{4-}] = [\text{NiTe}^{2+}] = 5.10 \cdot 10^{-5}$  mol  $l^{-1}$ ,  $\mu = 0.1$ , 22°C.

where the charges of the ions are omitted since they vary with pH. When a given amount of TTHA is added to the system the rate of step ( $A_3$ ) will increase, resulting in an increase in the tetren concentration and throughout the chain mechanism (reaction ( $A_2$ ) and ( $A_3$ )) the rates of reactions ( $A_2$ ) and ( $A_3$ ) (which are identical) will also increase proportionately. When the reactants are mixed in 1 : 1 molar ratio, the rate of the disappearance of  $\text{NiTe}^{2+}$  can be expressed by the equation

$$- (d[\text{NiTe}^{2+}]/dt) = k_0[\text{NiTe}^{2+}]^2, \quad (7)$$

where  $k_0$  is the pseudo-second order rate constant, experimentally determined from the slope of the dependence  $1/[\text{NiTe}^{2+}]$  vs time. The constant  $k_0$  is defined by the equation

$$k_0 = k_3[L]. \quad (8)$$

Equation (8) indicates the linear dependence of the experimental rate constant  $k_0$  on the concentration of free TTHA in the system. The experimentally found dependence of  $k_0$  vs concentration of TTHA added is presented in Fig. 1, line 1, which verifies the results of the theoretical treatment. The distance  $y$  on the ordinate in Fig. 1 determines the amount of metal impurities in the solution analyzed. The metal impurities must first be complexed by TTHA before the acceleration effect of the ligand can be observed. The theoretical line (line 3, Fig. 1) is obtained only when no impurities are present. If the reaction system also contains a small amount of a metal ion which forms complexes with TTHA, equation (8) has the form

$$k_0 = k_3([L] - [\text{Me}^{n+}]), \quad (9a)$$

which suggests the analytical utilization of the exchange reaction ( $A$ ) for the determination of metals forming complexes with TTHA. As illustrated by Fig. 1 lines 1 and 2, a metal can be determined either by a kinetic titration (the reaction mixture plus the sample solution is titrated with TTHA and when all the metal is complexed by the reagent, the rate of the exchange will increase), or using a fixed time procedure<sup>12</sup>. If the reactants are mixed in equal molar amounts in the concentration range  $10^{-5}$  mol l<sup>-1</sup> at pH 8.0, the fixed time 10 min is satisfactory for construction of the calibration line ( $\Delta[\text{NiTe}^{2+}]$  vs [TTHA]) and for the determination of metals in the concentration range  $10^{-5}$  mol l<sup>-1</sup>. For analyses based on the measurement of the rate of reaction ( $A$ ), rapid formation of stable TTHA chelates is very important, even under conditions when the metal to be determined is present in very small concentrations. At present, no quantitative data are available connected with the rate of the formation of TTHA chelates. The analyses of various metal ions ( $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Th}^{3+}$ ,  $\text{La}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ) in concentrations of about  $10^{-5}$  mol l<sup>-1</sup>, carried out using the presented method, gave results with an average error of  $\pm 7\%$ . These results show that the formation of the chelates of the mentioned metals is rapid enough to permit their determination based on the measurement of the rate

of reaction (A). Two factors limit the sensitivity of the analytical procedure based on the kinetic measurement of reaction (A). The first is the amount of metal impurities in the reaction mixture. The present experiments (as shown for example, in Fig. 1, line 1) indicate an impurity concentration level of approx.  $10^{-7} \text{ mol l}^{-1}$ . The second factor is the sensitivity of the measurement itself, *i.e.* the sensitivity of the polarographic method. Using standard equipment and when the total volume of the analyzed solution is 10 ml, Ni-tetren can be determined at a minimum concentration of 1 to  $10 \cdot 10^{-5} \text{ mol l}^{-1}$ . Application of more sensitive instrumentation (A. C. polarography for example) enables determinations of various metals at the concentration level  $10^{-6} \text{ mol l}^{-1}$ .

Further purification of all reaction components would be rather difficult and does not seem to be worthwhile considering the minimum increase in accuracy which would result. The specificity of the proposed method is poor; the stability of the TTHA chelates depends, however, strongly on pH. The dependence of the values of the conditional stability constants of TTHA chelates on pH was summarized by Harju and Ringbom<sup>9</sup>. These data suggest that variation of the pH of the analyzed solution may suppress the formation of the complex of one metal ion and simultaneously favour formation of some other complex. Fig. 2 illustrates that the experimental rate constant  $k_0$  can be determined polarographically in the pH interval from pH 6–11, and thus analysis can also be carried out in this pH range. More detailed data will be published in a separate paper.

#### REFERENCES

1. Olson D. C., Margerum D. W.: *J. Am. Chem. Soc.* 85, 297 (1963).
2. Margerum D. W., Carr J. D.: *J. Am. Chem. Soc.* 88, 1639 (1966).
3. Carr J. D., Margerum D. W.: *J. Am. Chem. Soc.* 88, 1645 (1966).
4. Reilly C. N., Holloway J. H.: *J. Am. Chem. Soc.* 80, 2971 (1958).
5. Neubauer L., Kopanica M.: *This Journal* 36, 1121 (1971).
6. Kopanica M., Stará V.: *This Journal* 37, 80 (1972).
7. Stará V., Kopanica M.: *This Journal* 37, 3545 (1972).
8. Harju L.: *Anal. Chim. Acta* 50, 457 (1970).
9. Harju L., Ringbom A.: *Anal. Chim. Acta* 49, 221 (1970).
10. Sillén L. G., Martell A. E.: *Stability Constants of Metal-Ion Complexes*, p. 576. The Chem. Soc., London 1964.
11. Laidler K. J.: *Chemical Kinetics*, p. 15. McGraw-Hill, New York 1950.
12. Mark H. B., Rehnitz G. A.: *Kinetics in Analytical Chemistry*, p. 28. Interscience, New York 1968.

Translated by the author (M. K.).