

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY, LAFAYETTE, INDIANA]

# Multidentate Ligand Kinetics. I. Copper(II) and Ethylenediaminetetraacetato-nickelate(II)

BY T. J. BYDALEK AND D. W. MARGERUM<sup>1</sup>

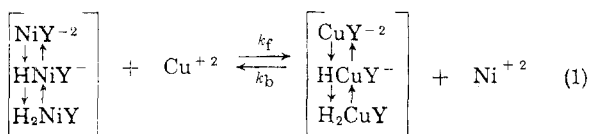
RECEIVED MAY 1, 1961

The kinetics of the substitution reaction between hydrated cupric ion and the ethylenediaminetetraacetato-nickelate(II) ion have been studied from pH 1.9 to 4.5 with ionic strength and temperature variation. Both forward and reverse rates were studied. The rate of Cu(II) substitution is 20,000 times faster than the rate of radio-nickel exchange previously measured with the same complex and is not acid catalyzed as is the radio-nickel exchange. These differences are discussed in terms of partially bonded EDTA intermediates proposed in the two systems.

## Introduction

Electrophilic substitution reactions of some of the ethylenediaminetetraacetate (EDTA),  $Y^{4-}$ , complexes have been of interest because of their sluggish behavior.<sup>2</sup> Radionickel exchange<sup>3</sup> with  $NiY^{2-}$ , the reactions<sup>4,5</sup> of  $Cu^{+2}$  with  $CdY^{2-}$ ,  $PbY^{2-}$  and  $ZnY^{2-}$  and the reaction<sup>6</sup> of  $Fe^{+3}$  with  $FeY^-$  have been examined in detail. All have complex kinetic expressions. These expressions are similar in that all the systems have rate terms expressing the direct attack of the aquo metal ion on the metal EDTA complex as well as rate terms involving the dissociation of the initial complex (acid catalyzed substitution of  $Y^{4-}$  by  $H_2O$ ) followed by reaction with the added metal ion. However, little is known about the relative effectiveness of various attacking aquo metal ions in pulling EDTA from its initial complex. In this work we find that the kinetics of the reaction of  $Cu^{+2}$  with  $NiY^{2-}$  are quite different from the kinetics reported for the reaction between  $Ni^{+2}$  and  $NiY^{2-}$ . Not only is  $Cu^{+2}$  20,000 times more effective than  $Ni^{+2}$  in its electrophilic substitution rate but the copper rate is not acid catalyzed while the direct attack of  $Ni^{+2}$  on the same complex increases rapidly with acidity. This difference in kinetic behavior is not reflected in the stability constants of the two EDTA complexes, which are nearly identical,  $10^{18.6}$  for  $NiY^{2-}$  and  $10^{18.8}$  for  $CuY^{2-}$ , both measured at 20° and in 0.1M KCl.<sup>7</sup>

The system studied is



where the acid forms of the complex are in rapid equilibria. The rate contributions of the dissociative paths increase with acidity and must be subtracted from the over-all rate to examine the effect of direct  $Cu^{+2}$  attack on Ni-EDTA or  $Ni^{+2}$  attack on Cu-EDTA. The desired rate is

- (1) Correspondence to be addressed to this author.
- (2) D. W. Margerum, *J. Phys. Chem.*, **63**, 336 (1959).
- (3) C. M. Cook, Jr., and F. A. Long, *J. Am. Chem. Soc.*, **80**, 33 (1958).
- (4) G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, **35**, 485 (1952).
- (5) N. Tanaka, K. Kato and R. Tamamushi, *Bull. Chem. Soc. Japan*, (a) **31**, 283 (1958), **32**, 1376 (1959); (b) K. Kato, *ibid.*, **33**, 600 (1960).
- (6) S. Jones and F. A. Long, *J. Phys. Chem.*, **56**, 25 (1952).
- (7) G. Schwarzenbach, R. Gut and G. Anderegg, *Helv. Chim. Acta*, **37**, 937 (1954).

$$\frac{d[CuY_T]}{dt} = k_f[Cu^{+2}][NiY_T] \quad (2)$$

where  $[CuY_T]$  and  $[NiY_T]$  refer to the sum of the concentrations of all forms of the metal EDTA complex at any time.

## Experimental

The rates were studied in the absence of any buffer to avoid complexes other than the aquo ions. No difficulty was encountered in maintaining constant pH during the reaction below pH 5. Copper hydrolysis should not be appreciable below pH 5.5. Sodium perchlorate was used to adjust the ionic strength of all solutions. To avoid  $KClO_4$  interference, NaCl was substituted for KCl in the calomel electrode used for pH measurement. Nickel and copper perchlorates were prepared by dissolution of the corresponding carbonates in perchloric acid, and then by recrystallization from water. Nickel and copper were standardized gravimetrically with dimethylglyoxime and 8-hydroxyquinoline, respectively. Reagent grade EDTA ( $H_4Y$ ), which was recrystallized twice from water and dried before use, was standardized by direct titration (using murexide indicator) against both the copper and nickel solutions. The values agreed to within 0.3 to 0.4% and showed that  $H_4Y$  can be used as a primary standard. Solutions of  $Na_2NiY$  were prepared from equimolar quantities of nickel perchlorate and EDTA. The pH of this solution was adjusted to 5.5 with sodium hydroxide. Solutions of  $Na_2CuY$  were prepared by adding excess copper perchlorate to EDTA and precipitating the excess as  $Cu(OH)_2$  before adjusting the pH to 8.

Figure 1 shows the absorption spectra (Cary Model 14) of  $NiY^{2-}$  and  $Cu^{+2}$  and the changing spectra as  $CuY^{2-}$  and  $Ni^{+2}$  are formed during the reaction. The reaction was followed at the 735 mμ absorption band of  $CuY^{2-}$  in a thermostated ( $\pm 0.1^\circ$ ) cell compartment with a Beckman DU spectrophotometer. The absorbances of most species in equation 1 are appreciable and must be considered under the conditions of both the forward and reverse reactions. As the pH is varied the apparent molar absorptivities of the equilibrium mixtures of  $NiY^{2-}$ ,  $HNiY^-$  and  $H_2NiY$  and  $CuY^{2-}$ ,  $HCuY^-$  and  $H_2CuY$  change. The molar absorptivities of  $NiY^{2-}$ ,  $HNiY^-$  and  $H_2NiY$  were determined independently at selected pH values using the acid ionization values of  $K_{H_2NiY}$  and  $K_{HNiY}$  previously measured.<sup>2,8</sup> The expression

$$\epsilon_{NiY_T} = \frac{\epsilon_{NiY} + \epsilon_{HNiY} \left( \frac{[H^+]}{K_{HNiY}} \right) + \epsilon_{H_2NiY} \left( \frac{[H^+]^2}{K_{HNiY}K_{H_2NiY}} \right)}{1 + \frac{[H^+]}{K_{HNiY}} + \frac{[H^+]^2}{K_{HNiY}K_{H_2NiY}}} \quad (3)$$

was used to calculate the apparent molar absorptivity,  $\epsilon_{NiY_T}$  of the mixture of complexes at any pH. The  $CuY^{2-}$ ,  $HCuY^-$ ,  $H_2CuY$  system was treated similarly and gave the same constants for  $K_{H_2CuY}$  and  $K_{HCuY}$ . These data are summarized in Table I. Rate constants were calculated on the basis of the total concentration of the complexes at any time by using their apparent molar absorptivities at each pH.

For the forward reaction the expression

$$[CuY_T] = \frac{A - A_i}{b(\epsilon_{CuY_T} + \epsilon_{Ni} - \epsilon_{Cu} - \epsilon_{NiY_T})} \quad (4)$$

can be derived where  $[CuY_T]$  is the sum of all protonated

TABLE I

TABLE OF MOLAR ABSORPTIVITIES AT 735 m $\mu$   
At  $\mu = 1.25$  and  $25.0^\circ$   $K_{\text{H}\text{NiY}} = K_{\text{H}\text{CuY}} = 1.2 \times 10^{-3}$  and  
 $K_{\text{H}_2\text{NiY}} = K_{\text{H}_2\text{CuY}} = 2.0 \times 10^{-2}$

Species	Molar absorptivity
$\text{NiY}^{-2}$	$\epsilon_{\text{NiY}} = 2.50$
$\text{HNiY}^{-}$	$\epsilon_{\text{HNiY}} = 2.0$
$\text{H}_2\text{NiY}$	$\epsilon_{\text{H}_2\text{NiY}} < 0.3$
$\text{CuY}^{-2}$	$\epsilon_{\text{CuY}} = 104$
$\text{HCuY}^{-}$	$\epsilon_{\text{HCuY}} = 82.8$
$\text{H}_2\text{CuY}$	$\epsilon_{\text{H}_2\text{CuY}} = 7.1$

and unprotonated forms of Cu-EDTA at any time,  $b$  is the cell length (2 or 5 cm.),  $A$  is the observed absorbance corrected for any background absorbance and  $A_i$  is the initial absorbance of the reactants at zero time. Thus

$$A_i = b(\epsilon_{\text{NiY}}[\text{NiY}]_i + \epsilon_{\text{Cu}}[\text{Cu}^{+2}]_i) \quad (5)$$

where  $[\text{NiY}]_i$  and  $[\text{Cu}^{+2}]_i$  refer to the initial reactant concentrations.

Equation 4 assumes that there is no appreciable concentration of a mixed complex such as  $\text{CuNiY}$  so that the concentration of nickel(II) liberated during the course of the reaction is equal to the concentration of Cu-EDTA formed. This assumption appears valid in that the extrapolated values for the initial absorbance agree very well with the calculated values for the reactants. Furthermore, the isobestic point in Fig. 1 indicates a transition from one set of reactants in rapid equilibrium with each other to a similar set of products according to equation 1 with no indication of any build up of another species. Finally, both forward and reverse reactions gave excellent second-order plots and the ratio of the forward and reverse rate constants is in agreement with the stability constant for equation 1.

Typical plots of  $\log [\text{Cu}^{+2}]_i - [\text{CuY}]_i / [\text{NiY}]_i - [\text{CuY}]_i$  against time were made under conditions where the reverse reaction was not appreciable. The reactions were followed for at least 25% conversion to  $\text{CuY}_T$ . The rate constants were reproducible to 5% or better.

## Results

**Kinetics of the Forward Reaction.**—The reactions showed first-order dependence in both  $[\text{NiY}_T]$  and  $[\text{Cu}^{+2}]$  and gave excellent second-order plots except at higher acidities. The results in Table II are given for variation of  $[\text{H}^+]$  in runs

TABLE II  
SECOND-ORDER RATE CONSTANTS FOR COPPER ATTACK ON  
Ni-EDTA

25.0 $^\circ$ , $\mu = 1.25$				
Run no.	$[\text{H}^+] \times 10^4$	$[\text{NiY}_T]_i \times 10^3$	$[\text{Cu}^{+2}]_i \times 10^3$	$k_t$ (l. mole $^{-1}$ min. $^{-1}$ )
1	1.12	2.29	4.40	1.00
2	3.98	2.29	4.40	1.00
3	12.6	2.29	4.40	1.02
4	79.4	2.29	4.40	0.98
5	126	2.29	4.40	.96
6	7.08	2.29	11.0	.95
7	8.91	2.29	2.20	1.00
8	10.0	2.29	6.60	1.00
9	12.6	2.29	11.0	0.95
10	12.6	2.29	22.0	.98
11	22.4	2.29	11.0	.98
12	0.32	1.14	2.20	.98
13	7.08	7.62	6.60	1.00
Av.				0.98

1–5, variation of  $[\text{H}^+]$  and  $[\text{Cu}^{+2}]$  in runs 6–11 and variation of all three concentration parameters in runs 12 and 13. Runs 4 and 5 had appreciable first-order contribution from the acid dissociation of  $\text{NiY}_T$ . These runs were plotted as first-order over the first 5% of the reaction and the first-order acid

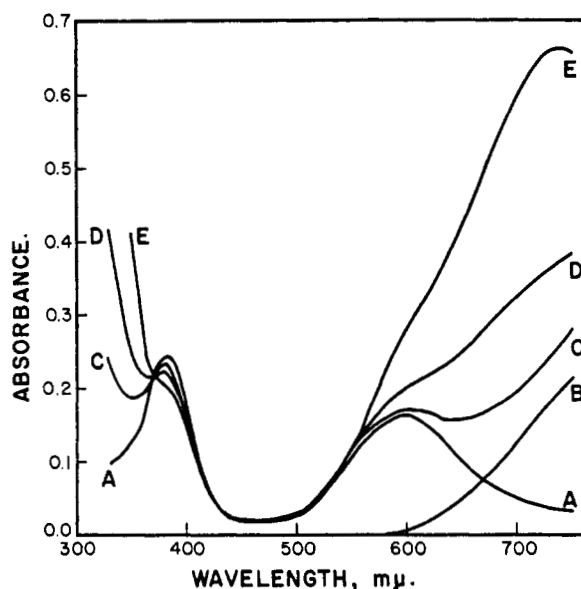


Fig. 1.—Spectra of the reaction of  $\text{NiY}^{-2}$  and  $\text{Cu}^{+2}$ :  $[\text{NiY}_T]_i = 3.81 \times 10^{-3}$ ,  $[\text{Cu}^{+2}]_i = 3.81 \times 10^{-3}$  M,  $\mu = 1.25$ ,  $\text{pH} = 3.9$ , cell length = 5 cm. and scanning speed, 1 m $\mu$ /sec.: A,  $\text{Na}_2\text{NiY}$ ; B,  $\text{Cu}(\text{ClO}_4)_2$ ; C, 1 minute after mixing; D, 20 minutes after mixing; E, 100 minutes after mixing. Times given are for start of scan at 750 m $\mu$ .

dissociation was subtracted before calculating the value of  $k_t$ . In run 4, the acid dissociation of  $\text{NiY}_T$  contributed 22% to the over-all rate and in run 5, 34%. In the other runs, the maximum contribution from the first-order dissociation of  $\text{NiY}_T$  was 3% and was neglected.

The rate also can be expressed as

$$\frac{d[\text{CuY}_T]}{dt} = k_1[\text{Cu}^{+2}][\text{NiY}^{-2}] + k_2[\text{Cu}^{+2}][\text{HNiY}^{-}] + k_3[\text{Cu}^{+2}][\text{H}_2\text{NiY}] \quad (6)$$

so that from equations 2, 6 and the definitions given

$$k_t \left( 1 + \frac{[\text{H}^+]}{K_{\text{H}\text{NiY}}} + \frac{[\text{H}^+]^2}{K_{\text{H}\text{NiY}}K_{\text{H}_2\text{NiY}}} \right) = k_1 + \frac{k_2[\text{H}^+]}{K_{\text{H}\text{NiY}}} + \frac{k_3[\text{H}^+]^2}{K_{\text{H}\text{NiY}}K_{\text{H}_2\text{NiY}}} \quad (7)$$

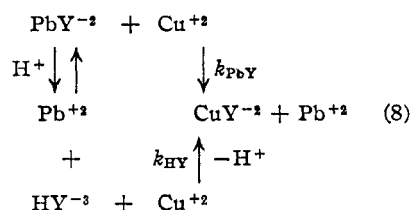
Since the value of  $k_t$  in Table II does not change with  $[\text{H}^+]$ , it follows that  $k_1$ ,  $k_2$  and  $k_3$  must all be equal and have a value identical with  $k_t$ . Copper(II) reacts at the same rate with  $\text{NiY}^{-2}$ ,  $\text{HNiY}^{-}$  and  $\text{H}_2\text{NiY}$ .

The reactions in Table II were run at an ionic strength of 1.25 in order to compare the rate constants with the previous radionickel exchange. The rate constants are only slightly affected by ionic strength in the region of high salt concentration. At  $25^\circ$  and an ionic strength of 0.44 the values of  $k_1$ ,  $k_2$  and  $k_3$  are 1.4, 1.4 and 1.2 l. mole $^{-1}$  min. $^{-1}$ , respectively. The temperature dependence of  $k_t$  between  $12^\circ$  and  $35^\circ$  was studied at  $\text{pH} 4.2$  and an ionic strength of 1.25. The  $k_2$  and  $k_3$  contributions to the rate are very small at this  $\text{pH}$ . The results follow the Arrhenius expression and give an  $E_a$  value of 18.0 kcal./mole. The values for  $\Delta H^*$  and  $\Delta S^*$  are 17.4 kcal./mole and  $-8.0$  e.u., respectively.

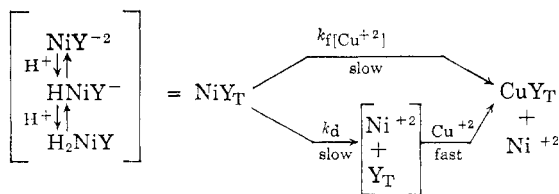
**Kinetics of the Reverse Reaction.**—The reverse reaction was studied at 25.0° and an ionic strength of 1.25. The reaction was first order in  $[\text{CuY}_T]$  and in  $[\text{Ni}^{+2}]$ . The system is consistent in that the value of  $k_b$  does not change with pH and the order of each reactant is the same, verifying the assumption of no build up of  $\text{CuNiY}$  concentration. The average value of  $k_b$  is  $6.2 \times 10^{-1} \text{ l. mole}^{-1} \text{ min.}^{-1}$ . The equilibrium constant for equation 1 calculated from the ratio of  $k_f$  to  $k_b$  is 1.58. This is in excellent agreement with the value which we obtained from equilibrium mixtures spectrophotometrically at the same ionic strength and with the value of 1.59 obtained from the ratio of the stability constants of the two complexes (which were measured in 0.1 M KCl and at 20°).

### Discussion

The general kinetic expression given in equation 6 is similar to that found in the radionickel exchange kinetics. On the other hand the reaction of  $\text{Cu}^{+2}$  with  $\text{PbY}^{-2}$  or  $\text{CdY}^{-2}$  gives different kinetics which include terms expressing an inverse dependence on  $[\text{Pb}^{+2}]$  or  $[\text{Cd}^{+2}]$ . In the  $\text{PbY}^{-2}$  and  $\text{CdY}^{-2}$  systems the dissociated forms of the complex are in rapid equilibrium with the complex relative to their rate determining reactions with  $\text{Cu}^{+2}$ . Equation 8 shows the  $\text{PbY}^{-2}$  system in simplified form.



Thus, excess  $\text{Pb}^{+2}$  will suppress the  $\text{HY}^{-3}$  in the rapid equilibrium on the left-hand side of equation 8 and therefore reduce the over-all rate of reaction with  $\text{Cu}^{+2}$ . However, with the nickel system this is not so. The rate determining step involves the loss of  $\text{Ni}^{+2}$  from  $\text{NiY}^{-2}$  and by comparison a rapid reaction with  $\text{Cu}^{+2}$ . The nickel ion released during the reaction does not suppress the rate. The proposed mechanism is



Although the two  $\text{NiY}^{-2}$  mechanisms are similar, the electrophilic action of  $\text{Cu}^{+2}$  and of  $\text{Ni}^{+2}$  on  $\text{NiY}^{-2}$  are quite different as seen from a comparison of their rate constants in Table III.

Attack of  $\text{Cu}^{+2}$  on  $\text{NiY}^{-2}$  is  $2 \times 10^4$  times faster than the attack of  $\text{Ni}^{+2}$ . The corresponding rate with  $\text{HNiY}^-$  is 35 to 47 times faster for  $\text{Cu}^{+2}$  and the estimated comparison for  $\text{H}_2\text{NiY}$  is 3 times faster for  $\text{Cu}^{+2}$ . Both the magnitude of the  $\text{Cu}^{+2}$  attack and its constancy compared to the  $\text{Ni}^{+2}$  attack are striking differences in these reactions.

TABLE III

SECOND-ORDER RATES CONSTANTS FOR  $\text{Cu}^{+2}$  AND  $\text{Ni}^{+2}$ 

NiY <sub>T</sub> species	Rate constant, l. mole <sup>-1</sup> sec. <sup>-1</sup>	Cu <sup>+2</sup>	Ni <sup>+2a</sup>	Ni <sup>+2b</sup>
NiY <sup>-2</sup>	k <sub>1</sub>	1.6 × 10 <sup>-2</sup>	8 × 10 <sup>-7</sup>	8 × 10 <sup>-7</sup>
HNiY <sup>-</sup>	k <sub>2</sub>	1.6 × 10 <sup>-2</sup>	4.5 × 10 <sup>-4</sup>	3.4 × 10 <sup>-4</sup>
H <sub>2</sub> NiY	k <sub>3</sub>	1.6 × 10 <sup>-2</sup>	.....	5.6 × 10 <sup>-3</sup>

<sup>a</sup> From ref. 3 after conversion with  $K_{\text{HNiY}}$ . <sup>b</sup> From ref. 3 using an alternative assignment of constants given in a footnote.

The electrophilic substitution must involve some reaction intermediates such as  $\text{NiYCu}$  or  $\text{NiY}^*\text{Ni}$  where two metal ions are coordinated to EDTA. Certainly, the one free acetate group in  $\text{NiY}^{-2}$  would be expected to coordinate rapidly to another metal ion and some additional stepwise breaking and making of coordinate bonds undoubtedly occurs prior to the transition state. The intermediate concentration is not appreciable in comparison with the total concentration of reactants and products but would be important kinetically. If the reaction mechanism is the same for the  $\text{Ni}^{+2}$  and  $\text{Cu}^{+2}$  attack, then some idea of their relative effectiveness can be obtained by examining the stabilities of their possible complexes arising from partial bonding to EDTA. This corresponds to an intermediate prior to the transition state which forms by partially unwrapping EDTA from nickel and coordinating it to the attacking metal ion. The transition state is then the breaking of the next EDTA bond to the original  $\text{Ni}^{+2}$ . Table IV compares the relative stability which segments of an unwrapped EDTA molecule would have with  $\text{Cu}^{+2}$  and  $\text{Ni}^{+2}$ .

TABLE IV

RELATIVE STABILITY OF  $\text{Cu}^{+2}$  AND  $\text{Ni}^{+2}$  WITH SEGMENTS OF EDTA

Extent of unwrapping	Stability constants of free group <sup>a</sup>	Cu <sup>+2</sup>	Ni <sup>+2</sup>	Relative stability Cu <sup>+2</sup> /Ni <sup>+2</sup>
One acetate	log K <sub>1</sub>	1.65	0.67	9.5
Two acetates	log β <sub>2</sub>	2.65	1.25	25
Glycinate	log K <sub>1</sub>	8.38	5.86	330
Iminodiacetate	log K <sub>1</sub>	10.55	8.26	190

The right hand column of Table IV indicates that  $\text{Cu}^{+2}$  would be expected to be a more effective electrophilic agent than  $\text{Ni}^{+2}$  if they proceeded through the same intermediate, but on an order of magnitude of 10 to 300 times only and not 20,000 as found. This difference as well as the  $[\text{H}^+]$  dependence suggests that the degree of coordination to the attacking metal ion is higher in the case of copper than in the case of nickel. This lessened degree of coordination of the electrophilic ion might be attributed to a second kinetic factor, namely, the rate of loss of  $\text{H}_2\text{O}$  from  $\text{Ni}^{+2}$ . Recent values for the rate of elimination of water molecules from the first coordination sphere<sup>9</sup> indicate that with  $\text{Ni}^{+2}$  the reaction is about 1/100 as fast as with  $\text{Cu}^{+2}$ , rather than approximately identical as first

(8) J. Bjerrum, G. Schwarzenbach and L. G. Sillén, "Stability Constants, Part I. Organic Ligands," The Chemical Society, London, 1957.

(9) R. E. Connick and E. D. Stover, Abstracts of Papers, 138th Meeting of the American Chemical Society, New York, N. Y., 1960, page 8N.

reported by Eigen.<sup>10</sup> This agrees with our experimental observation that the rate of formation of  $\text{NiY}^{-2}$  from  $\text{Ni}^{+2}$  and EDTA is much slower than the corresponding formation of  $\text{CuY}^{-2}$ . The failure of a  $\text{NiY}^*\text{Ni}$  intermediate to proceed readily with dentate transfer after a dentate cleavage from the initially bonded  $\text{Ni}^{+2}$  explains both the diminished effectiveness of  $\text{Ni}^{+2}$  and the increased importance of  $\text{H}^+$  in this reaction compared to the  $\text{Cu}^{+2}$  reaction.

The fact that  $\Delta S^*$  is  $-8$  e.u. for  $\text{Cu}^{+2}$  attack of  $\text{NiY}^{-2}$  despite the charge reduction of the transition state indicates a highly oriented transition state which still has a high coordination number for both metals. The total number of free particles cannot be increasing in the transition state which means that a  $\text{NiYCu}$  intermediate must still have six  $\text{H}_2\text{O}$  molecules coordinated to it and fair polar properties. One way this would be possible would be if the metal ions were at opposite ends of an open EDTA molecule.

A comparison of the direct reaction of  $\text{Cu}^{+2}$  with  $\text{NiY}^{-2}$ ,  $\text{CdY}^{-2}$  and  $\text{PbY}^{-2}$  would be valuable, but unfortunately strong acetate buffer was used for the

(10) M. Eigen, *Z. Elektrochem.*, **64**, 115 (1960). NOTE ADDED IN PROOF.—Since this paper was submitted Eigen has reported a second rate constant for water loss from  $\text{Cu}^{+2}$  which is 1000 times that for  $\text{Ni}^{+2}$ . M. Eigen, pp. 371-378, in S. Kirschner (Ed.), "Advances in the Chemistry of Coordination Compounds," the Macmillan Co., New York, N. Y., 1961.

other systems. The  $\text{PbY}^{-2}$  system later was corrected for acetate complexes and some comparison is possible but the corrected results are not completely satisfactory. Acetate buffer also was used in the radionickel system but apparently at sufficiently low concentrations not to interfere. If the same acetate and temperature correction used for the  $\text{PbY}^{-2} + \text{Cu}^{+2}$  reaction is applied to the  $\text{CdY}^{-2} + \text{Cu}^{+2}$  reaction, the value of  $k_1$  for  $\text{CdY}^{-2}$  is slightly greater than the  $k_1$  value for  $\text{PbY}^{-2}$ , and both are much greater than the  $k_1$  value for  $\text{NiY}^{-2}$ . Table V shows that the frequency factor ( $pZ$ ) is much

TABLE V

	$k_1$ , l. mole <sup>-1</sup> sec. <sup>-1</sup> at 25°	$pZ$	$E_a$ , kcal.	$\Delta H^*$ , kcal.	$\Delta S^*$ , e.u.
$\text{Cu}^{+2} + \text{PbY}^{-2}$	5.1	$2.7 \times 10^{15}$	20	19	10
$\text{Cu}^{+2} + \text{NiY}^{-2}$	0.016	$2.2 \times 10^{11}$	18.0	17.4	-8.0

greater for the  $\text{PbY}^{-2}$  system than for the  $\text{NiY}^{-2}$  system. In terms of the transition state theory the higher  $\Delta S^*$  indicates a more probable activated complex for  $\text{PbYCu}$  than for  $\text{NiYCu}$ . This can be interpreted as less unwrapping of EDTA from  $\text{Pb}^{+2}$  than from  $\text{Ni}^{+2}$  or more release of solvent from  $\text{PbYCu}$  than from  $\text{NiYCu}$ .

**Acknowledgment.**—The authors wish to thank the Air Force Office of Scientific Research for support of this research.

[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORIES, LOUISIANA STATE UNIVERSITY, BATON ROUGE 3, LOUISIANA]

## Iodine Complexes of Ethyl Mercaptan, Diethyl Sulfide and Diethyl Disulfide<sup>1,2</sup>

By M. GOOD, A. MAJOR, J. NAG-CHAUDHURI AND S. P. MCGLYNN

RECEIVED APRIL 1, 1961

The iodine complexes of ethyl mercaptan, diethyl sulfide and diethyl disulfide were studied in *n*-heptane and carbon tetrachloride. The results of the study have not been too surprising: diethyl sulfide is less basic than triethylamine and more basic than ethyl alcohol; it is more basic than diethyl disulfide. Reaction occurs in the system mercaptan-iodine. The results are further discussed in terms of dipole moments of the donors and the DA overlap integrals of the iodine complexes, and some arguments in favor of a geometry of the disulfide-iodine complex in which the iodine sits on the center of the  $-\text{S}-\text{S}-$  bond with the  $\text{I}-\text{I}$  axis perpendicular to the  $\text{S}-\text{S}$  axis are elaborated.

### Introduction

The interaction of the iodine molecule with various organic solvents which can behave as electron donors has been the subject of a number of research studies involved in the elucidation of the structure of molecular complexes. In particular, the complexes of iodine with several oxygen containing solvents and some nitrogen containing solvents have been studied extensively and the results obtained have agreed very well with the concept of charge transfer.<sup>3-8</sup> The organic sulfur com-

pounds have a basic character intermediate between the organic oxygen and organic nitrogen compounds and should, therefore, be of interest both experimentally and theoretically with respect to the properties of their molecular iodine complexes. This paper describes the results obtained from a comprehensive spectrophotometric study of the complexes formed between three such sulfur compounds (ethyl mercaptan, diethyl sulfide and diethyl disulfide) and molecular iodine.

### Experimental

**A. Purification of Materials.** 1. Iodine.—Baker and Adamson reagent grade iodine was sublimed under partial vacuum of dry nitrogen and stored in a desiccator until used. 2. Carbon Tetrachloride.—Merck reagent grade material was shaken for several hours with saturated potassium hydroxide solution, separated, washed with distilled water, then shaken with concentrated sulfuric acid and again separated and washed. This treatment was repeated three times. This carbon tetrachloride was washed free of acid with distilled water, shaken with anhydrous U.S.P. grade calcium chloride and stored over fresh calcium chloride in brown bottles. Immediately before use the carbon tetra-

(1) This work was supported by a Research Corporation Grant and a National Science Foundation Grant G-7390 to the Louisiana State University.

(2) Abstracted from M.S. Thesis, Antoine Major, The Louisiana State University, 1956.

(3) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **75**, 3561 (1957).

(4) P. A. D. de Maine, *J. Chem. Phys.*, **26**, 1192 (1957).

(5) R. S. Mulliken, *J. Am. Chem. Soc.*, **72**, 600 (1950).

(6) R. S. Mulliken and C. Reid, *ibid.*, **76**, 3869 (1954).

(7) S. Nagakura, *ibid.*, **80**, 520 (1958).

(8) A. I. Popov and W. A. Deskin, *ibid.*, **80**, 2076 (1958).