ature[24] to their U-forms. Yet this conversion has been assumed in explaining the "bidentate" linkage in the nitrogen tetroxide–dioxanate complex of the AB type.[25] It is interesting to note that triphenylmethyl bromide forms a one-to-one crystalline addition compound with stannic bromide.[26]

A close examination of the thermometric titration curves for dioxane reveals that the slope is perceptibly, but not measurably, different from zero after the change at the molar base to acid ratio of one; and that it fails to become zero at a ratio of two. The same is true for morpholine, but the slope is slightly greater. It must be emphasized that these are not heats of dilution, which are much smaller. Rather, these slopes must be associated with the slow, heterogeneous conversion of the AB complexes to the AB_2 type. The heats of conversion are extremely small—less than 10% of the ΔH^0 values—but that for morpholine is larger than the one for dioxane. This is to be expected, because if both oxygens were bonded to tin in the AB complex, the formation of AB_2 would require the breaking of one oxygen–tin bond with the formation of another oxygen–tin bond, and the energy change involved should be close to zero. On the other hand, the conversion of AB to AB_2, for morpholine, involves the rupture of an oxygen–tin bond with the formation of a nitrogen–tin bond, resulting in the evolution of energy, because nitrogen is a better electron donor than oxygen. A comparison of the ΔH^0 value given here for dioxane, Table I, with that of Zenchelsky, *et al.*,[5] obtained for nearly equimolar mixtures of stannic chloride and dioxane in benzene, shows that the heat of conversion is no greater than two hundred calories per mole of product. This is less than the experimental error of the ΔH^0 values.

The conductance studies of the stannic chloride–tetrahydrofuran system show that the soluble complex does consist of ion pairs, as would be expected.[26,27] They further show that the precipitate is ionic and that it dissolves in the presence of excess base to form ion pairs in solution. Since no marked change in slope of the conductance curve is observed after dissolution of the precipitate begins, and up to a base to acid ratio of five, it would appear that only one new species is formed. The species in solution before precipitation is evidently $(C_4H_8O)_2SnCl_3^+$, Cl^- while that after dissolution begins may be $(C_4H_2O)_3SnCl_3^+$, Cl^-.[28]

The ΔF^0 values calculated for the pyridine and tetrahydrofuran complexes (Table I) are in the order expected. Nitrogen is the stronger electron donor; and, moreover, the pyridine reaction involves the additional step of crystallization. However, a direct comparison of the strengths of the two bases is impossible. To do so would require knowing the concentration of undissociated complex in equilibrium with reactants and precipitate. Yet this method will permit a comparison of base strengths when the reactions involved are homogeneous. The observed entropy changes are large but not unreasonable for a case where one molecule is formed from three.

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[CONTRIBUTION FROM ARGONNE NATIONAL LABORATORY AND DUQUESNE UNIVERSITY]

Ion-exchange and Solvent-extraction Studies on Co(II) and Zn(II) Complexes of Some Organic Acids[1]

BY JACK SCHUBERT, EDMUND L. LIND, WILLIAM M. WESTFALL, RAYMOND PFLEGER AND NORMAN C. LI

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The stability of the Co(II) and Zn(II) complexes of bioxalate, oxalate, citrate and glycolate have been determined by the use of Co-60 and Zn-65 in conjunction with the methods of ion exchange and solvent extraction. It is demonstrated that both the stability of the glycolate complexes and the ion-exchange distribution coefficients of the tracer metals decrease with increase in ionic strength. An important assumption in the use of ion-exchange method for complex study is that the uptake of the complex itself by the cation exchanger is nil or very small relative to the uncomplexed cation. This is demonstrated directly for Mg(II) complex of oxalate by means of oxalate labeled with C-14. In ion-exchange experiments the uptake of Co(II) and Zn(II) in the presence of imidazole is higher than in the absence of imidazole, while in corresponding solvent-extraction experiments, the opposite is true. These results indicate that the +2 imidazole complexes themselves are taken up by the cation exchanger and show that the ion-exchange and solvent-extraction experiments complement each other in the study of metal complexes.

Introduction

Recently Li, *et al.*,[2] obtained the formation constants of uranyl complexes of glycolic and oxalic acids, using the methods of ion exchange and solvent extraction. They showed that even in 1 and 2 *M* $HClO_4$, uranyl complex with $H_2C_2O_4$ does not

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exist; only $HC_2O_4^-$ is the ligand. It is of interest to continue this study with other metal ions, and this paper presents the results on the Co(II) and Zn(II) complexes of glycolic, oxalic and citric acids.

An important assumption in the use of the ion-exchange method for the determination of complex formation constants is that the uptake of the complex itself relative to the uncomplexed cation is very small. This has been demonstrated experimentally for the first time by Li, *et al.*,[2] for some metal complexes by means of acetate labeled with tritium and with C-14. We have continued the study of this problem by using oxalic acid labeled with C-14 and by comparing ion-exchange results with solvent-extraction results of imidazole complexes.

Experimental

Materials.—High activity (>10 μc./μg.) Co-60 and carrier-free Zn-65 were obtained from Oak Ridge National Laboratory in the form of cobaltous and zinc chloride, respectively, each in HCl solution. Oxalic acid labeled with C-14 was purchased from Nuclear-Chicago Corp., Chicago, Ill.

The cation exchanger, "Dowex-50," a sulfonated polystyrene resin (Dow Chemical Co., Midland, Mich.) was used. The capacity of this type of resin is independent of *p*H over a wide *p*H range. All chemicals were of C.P. quality.

Procedure.—The conditioning of the "Dowex-50" resin and the ion-exchange technique employed have been described previously.[2,3] The flasks were agitated at 25 ± 0.1°. After a 3 hr. shaking period a measured volume of supernate was removed from each flask for radiochemical analysis.

In solvent-extraction experiments, the aqueous phase normally was prepared to contain (a) Zn-65 or Co-60 in concentrations of the order of 10^{-6} *M*, (b) complexing agent in varying concentrations and (c) acetate buffer and NaCl or $NaClO_4$ to maintain *p*H at 5.50 and ionic strength at 0.15. The chloroform phase, containing 0.005 and 0.03 *M* 8-hydroxyquinoline for Co and Zn complexes, respectively, previously was equilibrated with a 0.15 *M* acetate–NaCl buffer, *p*H 5.50, by overnight shaking. Equal volumes of aqueous and chloroform phases were then placed in glass-stoppered erlenmeyer flasks and shaken at 25° for 4 hr. At the end of the shaking period, aliquots from the aqueous phases were taken for counting. In experiments where per cent. radioactivity in the chloroform phase is less than 20%, aliquots for counting were taken from the chloroform phase. The precision attained in distribution coefficients in both ion-exchange and solvent-extraction experiments was generally better than ±5%.

Co-60 or Zn-65 were counted directly as liquid samples in a NaI(Tl) scintillation counter. In some experiments the two isotopes were present together in the same solutions and were then counted simultaneously by γ-ray spectrometry, using a pulse-height analyzer.[4] Solutions containing infinitely thin samples of C-14 were assayed using a Nuclear-Chicago D-47 flow counter.

Results and Discussion

(A) Co(II) and Zn(II) Complexes of Oxalic Acid System.—Ion-exchange and solvent-extraction experiments were conducted in $HClO_4$ solutions of varying concentrations, in order to determine the formation constants of Co(II) and Zn(II) complexes of oxalic acid systems. In these experiments the cation exchanger always was washed and equilibrated with the $HClO_4$ solutions. Some representative results are given in Table I.

TABLE I

ION-EXCHANGE EXPERIMENTS WITH Co(II) AND Zn(II) COMPLEXES OF BIOXALATE ($HC_2O_4^-$)

$(HC_2O_4^-) = (HA^-) \times 10^2$	$1/K_d{}^a$	$\frac{(K_d{}^0/K_d) - 1}{(HA^-)}$
	(a) 0.16 *M* $HClO_4$, Co-60	
0	0.51	
1.06	0.78	50.0
2.04	1.17	63.1
3.45	1.82	74.5
4.71	2.56	85.5
5.92	3.49	98.7
	(b) 0.16 *M* $HClO_4$, Zn-65	
0	0.55	
1.08	0.92	62.9
2.04	1.41	77.6
3.52	2.17	84.6
4.62	3.34	111.2
5.69	4.47	126.6

$^a\ \frac{1}{K_d} = \frac{\%\text{ tracer in aqueous phase}}{\%\text{ tracer in resin phase}} \times \frac{\text{mg. resin.}}{\text{ml. soln.}}$

In 0.16 *M* $HClO_4$, if we assume that the possible complexes are $MHC_2O_4^+$ and $M(HC_2O_4)_2$, equation 1 is derived, readily[2,3]

$$y = \frac{(K_d{}^0/K_d) - 1}{(HA^-)} = k_1' + k_1'k_2'(HA^-) \qquad (1)$$

where $k_1' = (M(HA)_i)/(M(HA)_{i-1})\ (HA^-)$, and $(HA^-) = (HC_2O_4^-)$. The values of k_1' and $k_1'k_2'$ may be obtained from the intercept and slope of a y *vs.* (HA^-) plot. The data of Table I, when plotted in this manner, yield straight lines, from which the values of the formation constants have been calculated and are summarized in Table III.

In 1 *M* $HClO_4$, the values of $1/K_d{}^0$ are 22 and 19, respectively, for Zn-65 and Co-60, and the distribution coefficients are essentially constant in the range of oxalic acid concentrations from 0 to 0.8 *M*. Obviously no complex formation takes place.

Ion-exchange experiments at *p*H about 5.5 were carried out in order to determine the formation constants of complexes where the oxalate ion, A^{--}, is the ligand. The results are listed in Table II.

In order to obtain the formation constants of oxalate complexes, equation 1 is applied as described with (A^{--}) in place of (HA^-). The formation constants are summarized in Table III.

The formation constants of the oxalate complexes are in good agreement with the values listed by Bjerrum, *et al.*,[5] taking into consideration that the latter values are for zero ionic strength. Recently, Fomin, *et al.*,[6] obtained values by ion-exchange methods which are from 0.1 to 0.8 log unit higher than our values; however, differences in their temperatures, ionic strength and other conditions of their experiments account for the discrepancies. No value for any of the bioxalate complexes has been reported.

In the use of ion-exchange method for calculation of complex formation constants, it always has been

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(6) (a) V. V. Fomin and V. V. Sin'kovskii, *Zhur. Neorg. Khim.*, **1**, 2316 (1956); *C. A.*, **51**, 7928*h* (1957); (b) G. A. Knyazev, V. V. Fomin and O. I. Zakharov-Nartsissov, *Zhur. Neorg. Khim.*, **1**, 342 (1956); *C. A.*, **51**, 6418*i* (1957).

TABLE II

EXPERIMENTS WITH Co(II) AND Zn(II) COMPLEXES OF OXALATE

$\mu = 0.16$, $t = 25°$, pH ~ 5.5

$(C_2O_4^{--}) = (A^{--}) \times 10^3$	$1/K_d$	$\frac{(K_d^0/K_d) - 1 \times 10^{-3}}{(A^{--})}$
(a) Ion-exchange, Co-60 (no buffer)		
0	1.74	
0.25	4.19	5.59
.50	6.85	5.84
1.00	12.81	6.33
2.00	27.7	7.43
(b) Ion-exchange, Zn-65 (no buffer)		
0	1.83	
0.10	3.25	7.70
.25	5.45	7.88
.50	9.70	8.57
1.00	18.76	9.22
2.00	42.61	11.11
(c) Solvent-extraction, Zn-65 (acetate buffer)		
0.80	2.16	8.81
1.20	3.27	9.29
1.60	4.97	10.94
2.00	6.58	11.73
4.00	18.19	16.66

TABLE III

SUMMARY OF FORMATION CONSTANTS[a] OF Co(II) AND Zn(II) COMPLEXES OF BIOXALATE (HA^-) AND OXALATE (A^{--})

25°, $\mu = 0.16$

Formation constant	Log formation constant	
	Co(II)	Zn(II)
k_1'	1.66	1.72
k_2'	1.25	1.40
$k_1'k_2'$	2.91	3.12
k_1	3.72	3.88 (3.85)[b]
k_2	2.31	2.35 (2.52)[b]
k_1k_2	6.03	6.23 (6.37)[b]

[a] The formation constants are defined by these reactions: $M^{++} + HA^- = MHA^+$, k_1'; $MHA^+ + HA^- = M(HA)_2$, k_2'; $M^{++} + 2HA^- = M(HA)_2$, $k_1'k_2'$; $M^{++} + A^= = MA$, k_1; $MA + A^= = MA_2^=$, k_2; $M^{++} + 2\,A^= = MA_2^=$, k_1k_2. Unless otherwise stated, the values are calculated from ion-exchange data. [b] Solvent-extraction value from Table II.

assumed tacitly that the complex itself is not taken up by the resin to any appreciable extent. In order to test this assumption experimentally for the oxalate complex, we have carried out ion-exchange experiments in which resin is shaken with solutions of 0.01 *M* sodium oxalate (labeled with C-14), both in the presence and absence of 0.01 *M* $MgCl_2$(non-radioactive). It was necessary to use $MgCl_2$ rather than $ZnCl_2$ or $CoCl_2$ because at concentrations of 0.01 *M* the oxalates of Co(II) and Zn(II) are insoluble. After equilibration, the aqueous and resin phases were tested for the C-14 activity. It was found invariably that practically all the activity was in the aqueous phase, regardless of whether metal ion was present or not. For the oxalate complex, therefore, the complex itself is not taken up by the resin.

(B) **Co(II) and Zn(II) Complexes of Citrate and Glycolate.**—Numerous ion-exchange experiments were carried out in order to determine the formation constants of the Co(II) and Zn(II) complexes of citrate and glycolate. Table IV summarizes the results obtained in this investigation, together with those available in the literature. The decrease in log k_1 with increase in ionic strength is as would be expected from changes in activity coefficients.[7]

TABLE IV

ION-EXCHANGE RESULTS OF CITRATE AND GLYCOLATE COMPLEXES, 25°

Unless otherwise stated, $\mu = 0.16$

Complex	log k_1	log k_1, as reported in lit. (pH titration)
Co(II) glycolate	1.76 ($\mu = 0.05$)	
	1.60	1.62[2]
	1.51 ($\mu = 0.23$)	
Zn(II) glycolate	1.99 ($\mu = 0.05$)	
	1.89	
	1.81 ($\mu = 0.23$)	1.92 ($\mu = 0.2$)[8]
Zn(II) citrate	4.71[a]	
	4.64[b]	

[a] Sodium diethyl barbiturate, 0.01 *M*, was used as buffer, pH 7.2. [b] Solvent-extraction method was used; the organic phase was chloroform containing 8-hydroxyquinoline.

Recently Korshunov, *et al.*,[9] report for the Zn(II) citrate complex log $k_1 = 3.55$. This value appears to be too small in comparison with corresponding values for Zn(II) oxalate and with those of other citrate complexes. However, the conditions of their experiment were such that no valid comparison of their data with ours can be made. For example, they made their measurement at pH of 8.45—a region where hydrolysis of Zn(II) occurs. We can rule out polymerization or hydrolysis of the Zn(II) and Co(II) cations in our experiments from at least two pieces of evidence. Polymerization is unlikely[10] because in all instances the extrapolated values of K_d^0 agreed with those measured directly. We investigated the possibility of hydrolysis, that is, formation of $Zn(OH)^+$ and $Co(OH)^+$, by measurement of k_d^0 for Zn(II) and Co(II), respectively, as a function of increasing ionic strength provided by additions of $NaClO_4$ or NaCl. Consider the reversible exchange reaction of a divalent cation, M^{++}, with the sodium form of the cation exchanger, NaR

$$M^{++} + 2NaR = MR_2 + 2Na \qquad (2)$$

When $(Na^+) >> (MR_2)$ and $(NaR) >> (MR_2)$ it follows that if M^{++} is indeed doubly charged, at least in the range of (Na^+) of 0.05–0.2 *M*, $K_d^0\ (Na^+)^2$ remains essentially constant. This is what we observed for both Co(II) and Zn(II); the numerical values for $K_d^0\ (Na^+)^2$ averaged 0.017 and 0.018, respectively.

In some experiments we have purposely added non-radioactive $CoCl_2$ to the tracer amount of Co-60, keeping (Na^+) constant at 0.15 *M*. When the $CoCl_2$ concentration reached 0.001 *M*, the distribution coefficients K_d were about 9% smaller than the corresponding values for solutions con-

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taining the tracer only, as expected.[11] When corrections are made for the increase in (Na^+) and decrease in (NaR) in equation 2 because of the presence of macro concentration of Co, the values of K_d, cor. become equal to the corresponding K_d for tracer only.

(C) Co(II) and Zn(II) Complexes of Imidazole.—Li, *et al.*,[3] mention that in ion-exchange experiments with Co-60 complex of imidazole, the values of $1/K_d$ for imidazole concentrations varying from 0.01–0.80 *M* were always smaller than the value of $1/K_d^0$. We have repeated the ion-exchange experiments for the zinc complex of imidazole at μ = 0.16 and *p*H 7.1 and have found that for imidazole concentrations varying from 0.01–0.40 *M*, $1/K_d$ remains practically constant at only 8% of the value of $1/K_d^0$. The zinc–imidazole complex with a double positive charge, like the Co–imidazole complex, must therefore also have been taken up by the cation exchanger as is the uncomplexed cation. The greater affinity of the larger imidazole complex relative to the uncomplexed cation of the same charge presumably is caused by van der Waals forces.[12]

Direct visual evidence of the uptake of an imidazole complex ion by "Dowex-50" cation exchanger was obtained. A solution of Cu(II)–imidazole complex ion was passed through a column of a special light-colored sample of resin ("Dowex-50 W"), and a dark blue band of the complex ion was observed at the top of the resin bed. The complex is decomposed by the passage of dilute hydrochloric acid through the resin, whereupon the imidazole is washed away, leaving an olive green band of uncomplexed Cu(II). Similar observations have been reported for other positively charged metal complexes as, for example the uptake of the ammonia complexes of Cu(II), Ni(II) and Zn(II) by a cation exchanger.[13]

Solvent-extraction experiments with imidazole complexes should behave normally in that the value of $1/K_d$ should increase with increasing concentration of imidazole and should always be greater than $1/K_d^0$. This is brought out by the data of Table V.

TABLE V

SOLVENT-EXTRACTION EXPERIMENT ON Co(II) COMPLEX OF IMIDAZOLE

*p*H 5.45, μ = 0.15, 25°

Total imidazole, *T*, *M*	(Imidazole)[a]	$1/K_d$	$\frac{(K_d^0/K_d) - 1}{(\text{imidazole})}$ [b]
0.032	0.00067	1.58	168
.048	.00101	1.62	137
.064	.00134	1.78	191
.080	.00168	1.84	174
		Av.	168

[a] In calculating (imidazole) from *T* and *p*H of 5.45, *p*H of imidazole is taken to be 7.12. [b] A plot of $1/K_d$ *vs.* (imidazole) is linear and the extrapolated value of $1/K_d^0$ is 1.42.

The average value for log k_1 of the Co(II)–imidazole complex is calculated to be 2.23. This is a reasonable value for the formation constant of Co–imidazole complex, inasmuch as log K_1 of Co(II) complex of NH_3 is 2.0.[14,15]

A solvent-extraction experiment on the Zn(II)–imidazole complex also shows that $1/K_d$ is greater than $1/K_d^0$ and increases when the concentration of imidazole increases. The value of log k_1 for Zn–imidazole complex is calculated to be 2.6, in good agreement with the value log k_1 = 2.58 reported by Edsall, *et al.*[15] The imidazole complexes therefore furnish excellent examples of how ion-exchange and solvent-extraction experiments can complement each other in the study of metal complexes.

LEMONT, ILLINOIS

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[CONTRIBUTION FROM THE INORGANIC CHEMISTRY BRANCH, RESEARCH DEPARTMENT, U. S. NAVAL ORDNANCE TEST STATION]

The Thermal Decomposition of Liquid Nitric Acid. II[1]

BY H. F. CORDES, N. R. FETTER AND J. A. HAPPE

RECEIVED MARCH 8, 1958

The thermal decomposition of liquid nitric acid has been studied at 55, 65 and 75°. The rate of decomposition can be expressed in terms of the water produced by the decomposition. $-d(HNO_3)/dt = (HNO_3)^2/[f_0^0 + S(H_2O)]$. "Activation energies" have been determined for f_0^0 and *S*. They are −38.7 and −27.8 kcal., respectively. The rate expression shows dependence upon the addition of some inorganic materials to the acid. The ionic mechanism, previously proposed for the decomposition, is discussed and found to be inadequate to explain the effects of the additives. An alternative free radical mechanism is proposed. This mechanism is found to be more satisfactory than the ionic mechanism and furnishes a correlation between the liquid phase and gas phase decompositions.

Introduction

Previous papers have reported on the thermal decomposition of liquid nitric acid.[2,3] These papers raised questions about the mechanism of the decomposition. It was felt that some further information might be obtained from a detailed study of the effect of several additives on the decomposition rate, and the present work was undertaken with this view in mind. One of the previous articles[2] contained some information about the effect of several

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