metal–sulfur bonding.[14] For the apparently less complicated thiocyanato system, Ni(II) does coordinate through the nitrogen,[15] in agreement with the hard acid–hard base concept.[16] A similar explanation appears reasonable for the nitrogen coordination in the mixed chelates described herein. In the present state of refinement and extension of the data, no evidence has been found for any electronic influence of the other coordinating group on the nature of the linkage isomerization in the thiopicolinamide, although the mixed chelates in which R is a sterically bulky group present some unsolved inconsistencies. Minor factors which may influence the stability of the mixed chelate include F strain interactions between the metal-bonded sulfur atom and the proton on the 6 position of the pyridine ring (stabilizing) and the loss of sulfur-metal multiple bonds in the mixed chelate (destabilizing). These effects are probably small.

The dependence of the equilibrium constants on the nature of the β-diketone ligand in the copper(II) system can be interpreted at least in part on steric grounds. Thus electron-withdrawing groups such as $-CF_3$ remove electronic charge from the metal-bonded oxygens, thus reducing their effective steric bulk either directly or by decreased solvation or by increased metal–oxygen distance with consequent increase in stability of the mixed chelate. It is interesting to note that the copper chelates C (Cu, *s*- or *t*-C_4H_9, CF_3, H, CH_3) are green solids with solution spectra showing maxima around 360 mμ. An attempt was made to correlate the equilibrium data with the λ_{max} of the lowest frequency d–d transition of the copper β-diketonates and also with the half-wave polarographic reduction potential[17] of these chelates. (Apparently these latter two physical constants correlate better with one another than with the formation constants[18] with which they are normally compared, at least for the few values obtained in the present research.) For the limited data available, as the frequency of the d–d transition increases or the half-wave potential decreases the equilibrium constant for mixed chelate formation goes through a minimum. Such a result is in qualitative agreement with the electrostatic theory of mixed chelate formation of Kida.[19]

The nickel chelate system presents an additional complication in mixed chelate formation. Bis(2,4-pentanedionato)nickel(II) and presumably other green nickel β-diketone chelates exist in solution as octahedrally-coordinated trimers (or their equivalent),[20] the equilibrium concentration of monomer being quite small. Mixed chelate formation, therefore, must proceed at the expense of one nickel oxygen bond per β-diketone ligand and the over-all equilibrium should be concentration dependent. These factors may account for our inability to isolate pure mixed nickel chelates of β-ketoesters and fluorinated β-diketones by the simple techniques introduced herein.

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(14) Several examples include: L. Cavalco, M. Nardelli, and G. Fava, "Abstracts, Seventh International Conference on Coordination Chemistry," Stockholm, Sweden, June 1962, p. 211; P. Rây and A. K. Choudhury, *J. Indian Chem. Soc.*, **27**, 673 (1950); S. N. Poddar and P. Rây, *ibid.*, **29**, 279 (1952).

(15) C. E. Schaffer, "Conference on Coordination Chemistry," London, 1959, p. 153.

(16) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).

(17) H. F. Holzclaw, Jr., A. H. Carlson, and J. P. Collman, *ibid.*, **78**, 1838 (1956).

(18) D. F. Martin and B. B. Martin, *Inorg. Chem.*, **1**, 404 (1962); L. G. Van Uitert, W. C. Fernelius, and B. E. Douglas, *J. Am. Chem. Soc.*, **75**, 2736, 457 (1953).

(19) S. Kida, *Bull. Chem. Soc. Japan*, **34**, 962 (1961).

(20) F. A. Cotton and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, **83**, 2, 818 (1961)

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A Search for Configurational Activity Effects in the Hydrolysis of the (+) and (−) Forms of the Arsenic(V)–Catechol Complex

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The rates of hydrolysis of the (+) and (−) forms of the arsenic(V) complex with catechol have been examined in solutions containing 0, 5, 10, 15, and 20% sucrose. These were determined by a method using conductance measurements which requires no assumptions to be made about the effect of one optically active species on the rotatory power of another when both are present in the same solution. Although the presence of the sucrose has a considerable effect on the rates, this effect is the same for the (+) and (−) forms, within the limits of experimental error. This system thus gives no indication of the occurrence of configurational activity effects. Some of the general factors bearing on the occurrence of such effects are delineated.

In an earlier study[1] we reported that the hydrolysis of the (+) and the (−) forms of the arsenic(V)–catechol complex proceeded at the same rates in the presence of various added optically active electrolytes. The over-all reaction here is

$$H[As(O_2R)_3(H_2O)] \rightleftharpoons R(OH)_2 + H[OAs(OR)_2]$$

where $R(OH)_2$ is catechol. These rate measurements were carried out polarimetrically. A point of conten-

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(1) J. H. Craddock and M. M. Jones, *J. Am. Chem. Soc.*, **84**, 1098 (1962).

tion which arose at that time was that the actual rotatory power of the complex might not be the same in the solutions of optically active electrolytes as it was in the pure solvent.[2] While we have checked this point for our complexes and found that it does not constitute a valid objection, it still raised a general question as to the applicability of polarimetric measurements in such studies. It became obvious that if such rate measurements could be carried out using a completely independent method which required no assumption about the rotatory power of the substrate in the presence of the optically active added species, then the entire rate aspect of configurational activity could be put on a more secure basis. For this reason we have developed a procedure using measurements of electrical conductance to obtain rate data on these systems. The general procedure is quite similar to that used in the determination of the hydrolysis rates of similar complexes in water and water–ethanol mixtures.[3]

Experimental

Arsenic(V)–Catechol Complex.—This complex was prepared, resolved, and purified as described previously.[1] The diastereoisomers were converted to their potassium salts, which were used in the kinetic studies.

Anal. Calcd. for $(+)$-K$[As(C_6H_4O_2)_3 \cdot H_2O]$: C, 47.27; H, 3.30. Found: C, 47.26; H, 2.91. $[\alpha]_D$ +501 ± 4°; lit.[4] $[\alpha]_D$ +413.4°.

Anal. Calcd. for $(-)$-K$[As(C_6H_4O_2)_3 \cdot H_2O]$: C, 47.27; H, 3.30. Found: C, 47.26; H, 2.91. $[\alpha]_D$ −501 ± 4°; lit.[4] $[\alpha]_D$ −459.9°.

Kinetic Studies.—Two standardized solutions, thermostated at the desired temperature, were used in preparing the solutions on which the rate measurements were carried out. These consisted of (1) weighed amounts of the potassium salt of the optically active arsenic complex dissolved in a sucrose solution in distilled water, and (2) standardized hydrochloric acid. The hydrolysis reaction was started by the addition of sufficient hydrochloric acid to the solution of the potassium salt to convert all of this salt to the corresponding complex acid (which was then 0.015 *M*). The solution prepared in this manner was first used to wash out a clean thermostated conductance cell (of the Jones and Bollinger type). The cell was then filled with this same solution and placed in the constant-temperature bath. Its resistance was measured at frequent intervals for a period of 2 or 3 hr. A final set of resistance values was measured after 2 or 3 days to obtain the limiting resistance value for the calculation of the rate constants.

The resistance measurements were made with a bridge whose principal components were an eight-decade resistance box (Gray Instrument Co.) and fixed resistance arms provided by a Campbell–Schackleton shielded ratio box (Leeds and Northrup Co.). The decade box had matched decades and an accuracy of ±0.025% except on the lowest decade (±0.05%). The resistance values encountered in the kinetic studies were in the region of 800–2000 ohms. The sensitivity of the amplifier–oscilloscope detector system was such that a difference of 0.1 ohm could be readily detected over this range. The temperature cited for the runs was maintained to within ±0.05° or better in all cases. A J. and J. Fric polarimeter, which could be read to ±0.01°, was used to obtain the specific rotations.

pK_a Values.—A stock solution (3×10^{-2} *M*) of the potassium salt was prepared for each enantiomeric form. Solutions of each were prepared in 0, 5, 10, 15, and 20% sucrose solutions in distilled water. The salt solutions were then titrated with 0.1000 *M* HCl using a Radiometer pHM4 pH meter, which had been previously standardized with a potassium acid phthalate buffer. From the complete titration curve the pK_a value was determined from the relationship pH = pK_a at the half-way point of the titration.

Results

The reaction studied has been shown previously to be a reversible second-order reaction.[3] The kinetics of the hydrolysis and racemization of optically active $(+)$- or $(-)$-K$[As(C_6H_4O_2)_3 \cdot H_2O]$ can be explained by the following reaction steps.

$$\underset{\text{complex anion}}{H_3O^+ + (+)\text{-}[As(O_2R)_3(H_2O)]^-} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underset{\text{complex acid}}{(+)\text{-}[As(O_2R)_2(OROH)(H_2O)]}$$

$$\underset{\text{complex acid}}{(+)\text{-}[As(O_2R)_2(OROH)(H_2O)]} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \underset{\text{inactive}}{R(OH)_2 + HOAs(O_2R)_2}$$

The rate equation for this reaction is[3]

$$-\frac{d[\text{complex}]}{dt} = k_3[\text{complex acid}] - k_4[R(OH)_2][HOAs(O_2R)_2] = (k_3/K_a)[\text{complex anion}][H^+] - k_4[R(OH)_2][HOAs(O_2R)_2]$$

The integrated rate equation for this type of reaction has been examined in detail by Frost and Pearson[5] and its application to the present system has been previously discussed in a comprehensive fashion. The integrated rate equation is

$$\ln\left[\frac{x(a - 2x_e) + ax_e}{a(x_e - x)}\right] = \left[\frac{2a(a - x_e)}{x_e}\right]kt$$

where a is the initial concentration of complex (and acid), x is the amount which has reacted in time t, and x_e is the amount which has reacted at equilibrium. Here $k = k_3/K_a$, where K_a is the dissociation constant for the complex acid.

The integrated rate equation can be changed to the form

$$\ln\left[\frac{\left(\frac{1}{R_0} - \frac{1}{R_t}\right)(C_1 - 2C_2) + C_1C_2}{C_1\left(\frac{1}{R_t} - \frac{1}{R_e}\right)}\right] = \left[\frac{2C_1(C_1 - C_2)}{C_2}\right]kt = \ln f$$

where R_0, R_t, and R_e are the resistances of the solution at times, zero, t, and equilibrium, respectively. C_1 is the initial concentration of the complex and C_2 its concentration at equilibrium. The contribution of the potassium chloride to the conductance was subtracted to determine the value due to the complex itself. This equation was programmed for the IBM 650 computer. The output consisted of a point by point k value, a least-squares k average, and the root mean square deviation. A plot of ln f *vs.* t for this run is generally a good straight line for over 80% of the course of the

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[2] N. R. Davies, private communication through F. P. Dwyer.

[3] T. H. Larkins, Jr., C. E. Martin, and M. M. Jones, *Inorg. Chem.*, **2**, 554 (1963).

[4] A. Rosenheim and W. Plato, *Ber.*, **58**, 2000 (1925).

[5] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 174, 175.

TABLE I

THE EFFECT OF SUCROSE ON THE RATE OF HYDROLYSIS OF THE (+) AND (−) ISOMERS OF THE ARSENIC(V)–CATECHOL COMPLEX[a]

Wt. % sucrose	$k \times 10^3$, l. mole^{-1} sec.$^{-1}$					
	15°		25°		30°	
	(+)	(−)	(+)	(−)	(+)	(−)
0	1.21 ± 0.10	1.27 ± 0.07	5.70 ± 0.26	5.68 ± 0.09	11.2 ± 0.2	11.5 ± 0.2
5	1.40 ± 0.05	1.44 ± 0.08	6.36 ± 0.10	6.47 ± 0.22	12.8 ± 0.2	13.0 ± 0.2
10	1.58 ± 0.06	1.63 ± 0.09	7.52 ± 0.15	7.26 ± 0.11	14.7 ± 0.3	14.8 ± 0.3
15	1.85 ± 0.09	1.91 ± 0.09	8.68 ± 0.19	8.62 ± 0.13	17.1 ± 0.4	17.1 ± 0.5
20	2.17 ± 0.06	2.18 ± 0.06	10.2 ± 0.21	10.4 ± 0.19	20.1 ± 0.7	20.7 ± 0.7

[a] Each value given is the average of at least three separate determinations of the rate constant.

reaction. The average k values and the root mean square error values are given in this paper. Table I contains the rate constants found for the hydrolysis of the arsenic complex in the presence of varying amounts of sucrose. In order to obtain k_3, the pK_a of the arsenic complex acid was determined in every concentration of sucrose used at each of the temperatures. These results are collected in Table II.

TABLE II

pK_a VALUES FOR THE ARSENIC(V)–CATECHOL COMPLEX

Wt. % sucrose	15°		25°		30°	
	(+)	(−)	(+)	(−)	(+)	(−)
0	2.19	2.19	2.11	2.14	2.13	2.16
5	2.18	2.18	2.15	2.12	2.15	2.16
10	2.18	2.17	2.14	2.13	2.15	2.16
15	2.17	2.17	2.12	2.12	2.13	2.14
20	2.16	2.16	2.15	2.11	2.14	2.15

The measured rotations of the complex in the presence of sucrose are shown in Table III.

TABLE III

SPECIFIC ROTATIONS OF THE (+) AND (−) COMPLEX ANIONS (POTASSIUM SALTS) IN THE PRESENCE OF SUCROSE AT 25°

Wt. % sucrose	(+)[b]	(−)[b]
0	+498	−503
5 (+6.75)[a]	+506	−506
10 (+13.46)[a]	+509	−510
15 (+20.06)[a]	+507	−508
20 (+26.84)[a]	+517	−517

[a] Rotation due to sucrose in a 10-cm. cell. [b] In each case the concentration was within 5% of 0.105 g./25 ml.

Discussion

The first point to be noted is based on the results presented in Table III. These show that the presence of sucrose has no effect on the specific rotation of the complexes within the limits of experimental error. They thus provide proof of the correctness of the assumptions used previously in the reduction of the polarimetrically obtained rate data.[1] Such an absence of any effect may not be found in all cases of this sort, however.

The values of k_3, the actual rate constant for the ligand loss reaction, were calculated and these are presented in Table IV. As can be seen, these show no systematic differences between the hydrolysis rates of the (+) and (−) forms in sucrose and they show no obvious trends of the sort anticipated if configurational activity effects were large in these solutions. These results confirm the polarimetric studies reported earlier from this laboratory.[1] They also reveal that the present experimental method is superior in some important ways to the optical method used previously in these studies. The most important difference is that it allows one to circumvent completely all of the questions raised by the Pfeiffer effect.[6]

The activation energies and frequency factors for all of these systems have been evaluated and these are presented in Table V.

The activation energies are all close to 27 kcal. and show no obvious differentiation between the two isomers of the sort expected if configurational activity effects were present.[7] The same may be said for the frequency factors also, though the error involved in the extrapolation to obtain A is much larger than that involved in getting E_a from the slope of the log k vs. $1/T$ plot.

The equilibrium constants for the over-all ligand loss reaction can also be obtained from the conductance data. These are summarized in Table VI. They also do not show any obvious trends of the type which would be anticipated if configurational activity effects were important in altering the over-all equilibrium conditions in these systems.

In all cases, it was found that the addition of sucrose increased the rates of hydrolysis. In previous studies, we found[3] that the addition of alcohol increased the rate of hydrolysis of this complex markedly. The gross effect of the sucrose is thus due to changes in the solvent medium caused by the addition of large amounts of a compound bearing numerous hydroxyl groups. This effect is much larger than any of the rate differences between the (+) and (−) complexes in a given solution.

From a comparison of the results we have obtained with those found for reactions in some organic systems,[8] one can conclude that water as a solvent reduces configurational activity effects, presumably because of its high dielectric constant. Since such effects are

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(6) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 285.

(7) A discussion of the typical errors of these measurements is given by S. W. Benson ["The Foundations of Chemical Thermodynamics," McGraw-Hill Book Co., New York, N. Y., 1960, pp. 86–94]. The error in E_a values is of the order of ±0.7 kcal. This leads to an error of ±0.5 in log A. We believe our results show no significant differences in E_a.

(8) W. Theilacker in "Methoden der Organischen Chemie (Houben-Weyl)," E. Miller, Ed., G. Thieme Verlag, Stuttgart, 1955, Bd. IV Tl. 2, 525 *et seq.*

TABLE IV

INTRINSIC RATE CONSTANTS FOR LIGAND LOSS ($k_3 = k_2K_3$) IN THE PRESENCE OF SUCROSE

Wt. % sucrose	$k_3 \times 10^6$ 15° (+)	15° (−)	25° (+)	25° (−)	30° (+)	30° (−)
0	7.79 ± 0.44	8.17 ± 0.43	44.2 ± 2.0	41.2 ± 0.6	82.6 ± 1.2	79.2 ± 1.1
5	9.23 ± 0.30	9.55 ± 0.54	45.1 ± 0.70	49.1 ± 1.7	90.4 ± 1.4	89.8 ± 1.4
10	10.4 ± 0.4	11.0 ± 0.6	54.5 ± 1.1	53.8 ± 0.8	104 ± 2	102 ± 2
15	12.5 ± 0.6	12.9 ± 0.6	65.9 ± 1.4	65.4 ± 1.0	127 ± 3	124 ± 4
20	15.01 ± 0.44	15.1 ± 0.4	72.5 ± 1.5	80.5 ± 1.5	145 ± 5	147 ± 6

TABLE V

ACTIVATION ENERGIES AND FREQUENCY FACTORS

Wt. % sucrose	E_a, kcal. (+)	E_a, kcal. (−)	A, sec.$^{-1}$ × 10^{-15} (+)	A, sec.$^{-1}$ × 10^{-15} (−)
0	28.1	26.9	14.8	1.95
5	26.9	26.6	2.30	1.45
10	27.5	26.9	7.53	2.88
15	27.4	27.1	8.05	4.32
20	26.8	27.1	2.94	4.88

TABLE VI

EQUILIBRIUM CONSTANTS FOR THE OVER-ALL LIGAND LOSS REACTION

Wt. % sucrose	15° (+)	15° (−)	25° (+)	25° (−)	30° (+)	30° (−)
0	3.38	3.31	2.87	2.91	2.85	2.83
5	3.40	3.23	2.94	2.86	2.81	2.78
10	3.19	3.20	2.89	3.06	2.80	2.72
15	3.09	3.04	2.80	2.63	2.70	2.73
20	2.98	2.98	2.61	2.91	2.69	2.52

presumably based on the interaction of asymmetric arrays of dipoles, such interactions would be minimal in solvents of high dielectric constant. It is also quite possible that reactions in which a proton-transfer step is rate-determining are a type where such effects will be difficult to detect. On the basis of our present work and previous studies of this reaction, the mechanism given in Figure 1 is proposed. This mechanism is consistent with the rate studies and the stoichiometry of our reaction. The rate-determining step is the decomposition of the protonated complex.

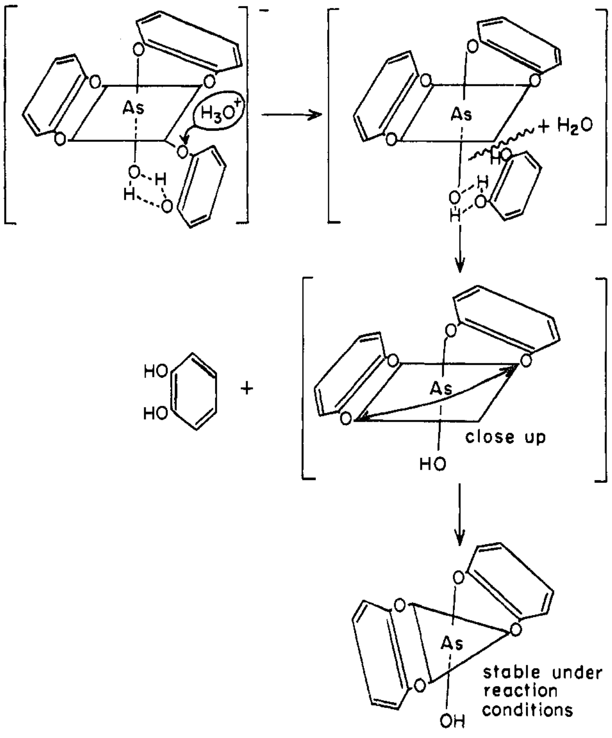

Figure 1.—Mechanism of the hydrolysis of the arsenic(V)–catechol complex.

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