The increasing complexity, without a great increase in intensity, in the visible region seems to argue that the nearly octahedral symmetry of the alkylammonium pentachloroalkoxoniobates is greatly reduced (perhaps changed to a strongly tetragonal configuration in which the $^2T_{2g}$ ground state is split to $B_2 + E$ and the ^2E_g excited state to $A_1 + B_1$, thus giving rise, in the extreme cases, to three observable transitions.

That is, the available evidence suggests that the aromatic "-inium" ions interact with the complex, possibly with the alkoxo-group oxygen, and distort the complex further toward tetragonality as well as producing the effects observed for ring C–H and alkoxo C–O stretching frequencies. It is not clear why the pyridinium and quinolinium compounds should show the same C–O frequencies.

It is also possible that the transition $b_2 \rightarrow e$ is at considerably lower energies and would appear in the near-infrared. Unfortunately we are unable to extend the reflectance measurements into that region with present equipment. In $MoOCl_5^{2-}$ that transition is reported to occur at 13,800 cm.$^{-1}$ and so might be expected at still lower frequencies in the $Nb(OR)Cl_5^-$ complexes.[13] Then the absorptions seen at about 20,000 cm.$^{-1}$ would correspond to $b_2 \rightarrow b_1$. If the latter is indeed the case, it is difficult to explain the bands in the aromatic "-inium" compounds and especially in the quinolinium case.

(13) H. B. Gray and C. R. Hare, *Inorg. Chem.*, 1, 363 (1962).

A Kinetic Study of the Dissociation of Some Arsenic(V) Complexes

By THOMAS H. LARKINS, Jr., CHARLES E. MARTIN, and MARK M. JONES

The rates and equilibrium constants for ligand dissociation have been determined for five arsenic(V) complexes with o-dihydroxyphenols. These complexes undergo a reversible hydrolytic splitting *via* the reactions

$$[(RO_2)_2As(ORO)(H_2O)]^- + H_3O^+ = H_2O + [(RO_2)_2As(OROH)(H_2O)]$$
$$[(RO_2)_2As(OROH)(H_2O)] = (RO_2)_2AsOH + R(OH)_2$$
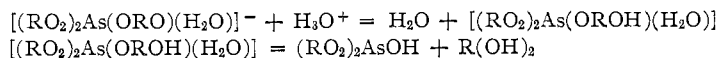
An examination of the effect of substituents on R on the rate shows that electron releasing groups facilitate the reaction. The general character of the reaction parameters indicates that the attack of a proton on the anion of the complex leads to the rate determining step and the entropies of activation are consistent with such a charge neutralization step. By carrying out pH titrations on these complexes in times short in comparison with the reaction times, the pK_a values of the parent acids were determined.

The kinetic studies which have been carried out on complexes of the non-transition elements are few in number.[1] The present work is a continuation and extension of previous studies on the hydrolysis or arsenic(V) complexes.[2] Its goal was the elucidation of details of the mechanism of the hydrolysis of arsenic(V) complexes with 1,2-dihydroxy aromatic phenols.

The complexes used in this study were those of arsenic acid with the dihydroxy aromatic phenols: catechol, 3-methylcatechol, 4-methylcatechol, 4-chlorocatechol, and pyrogallol (3-hydroxycatechol). The catechol complex was first prepared by Weinland and Heinzler,[3] and subsequently studied by others.[2,4–6] The 3-methylcatechol, 4-chlorocatechol, and 4-methylcatechol complexes were described in an earlier paper.[7] The pyrogallol complex was prepared in the course of this work.

The structure of these complexes has been the subject of some controversy. Reihlen, Sapper, and Kall[4] studied the catechol compound and assigned to it structure I, Fig. 1, in which two catechol molecules are chelated, one is monodentate, and the sixth coördination position is occupied by H$_2$O. This was based primarily on the fact that dehydration can remove only four molecules of water from the pentahydrate. Rosenheim and Plato[5] proposed structure II, Fig. 1, in which all three of the catechol molecules were chelated, although they were never able to remove more than four molecules of water without causing decomposition of the complex. We have shown earlier[7] that the corresponding 2,3-dihydroxynaphthalene complex of arsenic(V) exists as a white sesquihydrate and a tan monohydrate. The color change is reversible. The white

(1) The literature is summarized in R. G. Pearson, D. N. Edgington, and F. Basolo, *J. Am. Chem. Soc.*, 84, 3233 (1962).

(2) J. H. Craddock and M. M. Jones, *ibid.*, 83, 2839 (1961); 84, 1098 (1962).

(3) R. F. Weinland and J. Heinzler, *Ber.*, 52, 1316 (1919).

(4) H. Reihlen, A. Sapper, and G. A. Kall, *Z. anorg. allgem. Chem.*, 144, 218 (1925).

(5) A. Rosenheim and W. Plato, *Ber.*, 58, 2000 (1925).

(6) F. G. Mann and J. Watson, *J. Chem. Soc.*, 505 (1947).

(7) T. H. Larkins and M. M. Jones, *Inorg. Chem.*, 2, 142 (1963).

form gives the tan form upon heating at 65° over methanol in an Abderhalden drying apparatus at less than 1 mm. pressure. The temperature can be increased until 154–155° (atmospheric pressure) at which point the complex melts with decomposition. These findings are in agreement with the assumption that one molecule of water occupies the sixth coördination position of octahedral arsenic(V) in these complexes.

Craddock and Jones[2] studied the rate of hydrolysis of the catechol complex as a function of pH. Their work showed that the complex does not racemize in strongly basic solutions even at elevated temperatures. As the pH drops, the rate of hydrolysis becomes measurable in the region of pH values from 3, where it is slow, to about 1.2, where it is rather fast.

Experimental

Preparation of the Complex Acids.—The complex acid with catechol was prepared by the method of Weinland and Heinzler.[3] *Anal.* Calcd. for $HAs(C_6H_4O_2)_3 \cdot 5H_2O$: As, 14.91. Found: As, 15.00.

The complex with 3-methylcatechol was prepared by the method developed earlier.[7] *Anal.* Calcd. for $HAs(C_7H_6O_2)_3 \cdot 2H_2O$: C, 52.84; H, 4.86; As, 15.69. Found: C, 53.82; H, 5.10; As, 15.52.

The pure complex acids derived from 4-methylcatechol, 4-chlorocatechol, and pyrogallol could not be obtained in crystalline form. Aqueous solutions which contained 0.1000 mole of arsenic acid and 0.3000 mole of the ligand in 100 ml. were prepared. These were placed in a water bath at 35° and kept at this temperature for 1 week. At the end of this time, the complex-forming reaction was complete and suitable aliquots of these solutions were used for the kinetic runs. Several of the kinetic runs which used these solutions were repeated after an interval of 6 weeks. The same rate constants were obtained at both times.

Determination of the pK_a Values of the Complex Acids.—Weighed samples of the solid complex acids were dissolved in water and titrated with standard sodium hydroxide solution, using a Radiometer Model 4 pH meter to obtain the titration curve. For the complexes which could not be obtained as solids, suitable aliquots of the aqueous solutions described above were used. The results are presented in Table I. The temperatures used were the same as those at which the kinetic data were obtained. These pK_a values are for the reaction

$$[(RO_2)_2As(OROH)(H_2O)] + H_2O \rightleftharpoons H_3O^+ + [(RO_2)_2As(ORO)(H_2O)]^-$$
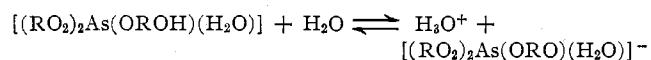
Kinetic Data.—The conductance of solutions of these complex acids was found to vary with time and this was used to follow the course of the hydrolysis reaction. The procedure for a typical kinetic run was as follows. The solvent and cell were thermostated overnight in the bath in which the reaction was to be run. The sample size was chosen so that the reaction would be about 75% complete in 1 to 2 hr. The sample was placed in a 100-ml. volumetric flask and the solvent added. The flask was shaken until the sample was completely dissolved and then the solution was used to rinse the conductance cell twice. The cell

TABLE I
pK_a VALUES FOR COMPLEX ACIDS OF ARSENIC(V)

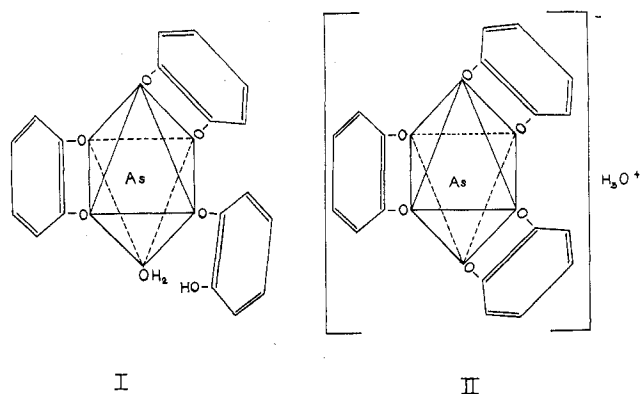| Ligand	25°	30°	35°	39.4°
Catechol	2.39	2.42	2.42	. . .
3-Methylcatechol	2.42	2.55	2.60	. . .
Pyrogallol	2.41	2.42	2.46	. . .
4-Methylcatechol	2.49	2.54	2.56	. . .
4-Chlorocatechol	. . .	2.47	2.48	2.51

Fig. 1.—Structures proposed for the complex of arsenic(V) and catechol.

then was filled and the first reading taken. The cells used were of the type described by Jones and Bollinger.[8] The bath temperature was controlled to ±0.05° of the stated values and the reported rate constants each represent an average of at least three independent experiments. Usually 2.5–3.0 min. elapsed between the time of first adding the solvent to the sample and the first resistance reading. A plot of resistance *vs.* time was extrapolated to zero time to obtain the resistance at the time of mixing. Readings were taken every minute or less for the first 10–15 min. and then less frequently until the reaction was complete. The cell was allowed to remain in the thermostated bath at least 24 hr. after an apparent equilibrium reading was obtained. An electric timer reading to 0.01 min. was used. The bridge was adjusted so that a 0.01 ohm change in the resistance at the null point would cause a 0.75–1 in. peak in the oscilloscope pattern. It was found most convenient to advance the variable resistor a constant amount, usually 2 to 5 ohms, and allow the reaction to proceed until the oscilloscope pattern reached the null point, at which time the elapsed time was recorded. We believe that this procedure is more accurate then the procedure in which we tried to obtain the resistance readings with a constant time interval. The oscilloscope was adjusted so there was less than 0.01 ohm error in the resistance and there was also a time error of no more than 0.02 min. for any given reading. Data for a typical run are presented in Table II.

Several runs were carried out with a Radiometer Model 4 pH meter by simply following the consumption of hydrogen ion in a thermostated cell.

TABLE II
DATA FOR A TYPICAL KINETIC RUN OF THE DISSOCIATION OF THE ARSENIC(V)–CATECHOL COMPLEX IN WATER: 35.0°; $C_0 = 3.56 \times 10^{-2} M$

Time, min.	Resistance, ohms
0.00	62.80
6.00	80.00
10.00	90.50
12.00	96.50
19.00	111.20
22.00	117.00
25.00	123.50
31.00	130.70
41.00	140.00
59.00	147.80
∞	153.50

Discussion

As a result of the data obtained on these hydrolytic reactions, it is possible to postulate a sequence of reac-

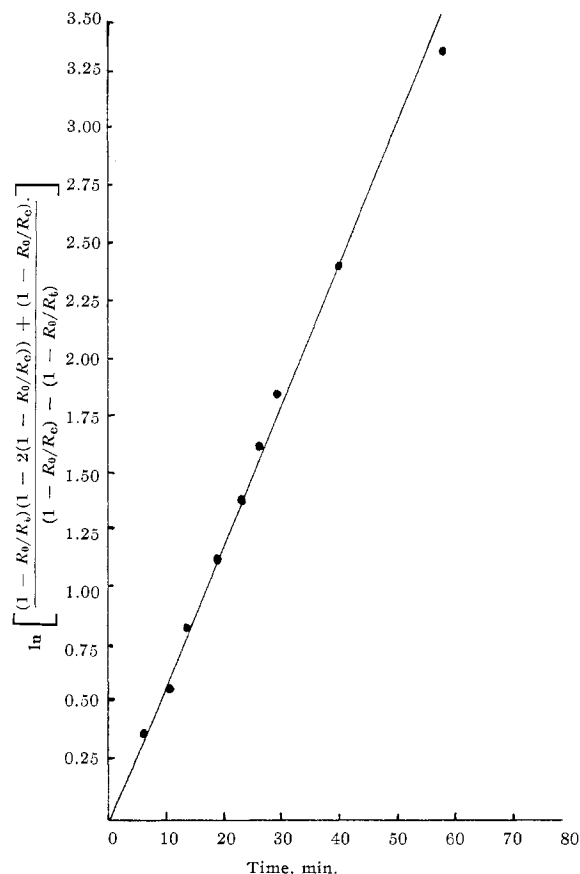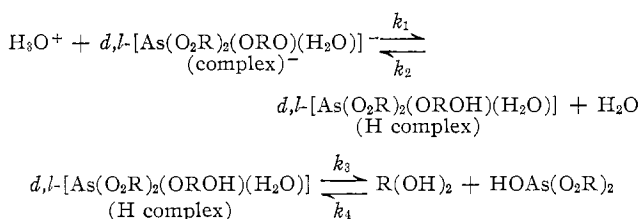(8) G. Jones and G. M. Bollinger, *J. Am. Chem. Soc.*, **53**, 411 (1931).

Fig. 2.—Typical kinetic run for the hydrolysis of the arsenic(V)–catechol complex: $T = 35°$; concentration of complex = 3.5×10^{-2} M.

tions which completely describes these systems. This sequence is given below; the specific example selected, the catechol complex, was chosen because several different types of data have been obtained for it and each fits the pattern given. This sequence is

$$H_3O^+ + d,l\text{-}[As(O_2R)_2(ORO)(H_2O)] \underset{k_2}{\overset{k_1}{\rightleftharpoons}}$$
$$\text{(complex)}^-$$

$$d,l\text{-}[As(O_2R)_2(OROH)(H_2O)] + H_2O$$
$$\text{(H complex)}$$

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

From the kinetic data it is obvious that the undissociated free acid is the species which suffers ligand loss. For this mechanism, the rate equation will have the form

$$\frac{-d[\text{H complex}]}{dt} = k_2[\text{H complex}] + k_3[\text{H complex}] -$$
$$k_1[\text{H}^+][\text{complex}^-] - k_4[R(OH)_2][HOAs(O_2R)_2]$$

Since the protonic equilibrium is very rapidly attained

$$K_1 = \frac{[\text{H complex}]}{[\text{H}^+][\text{complex}^-]} = \frac{k_1}{k_2}$$

so

$$\frac{-d[\text{H complex}]}{dt} = k_3K_1[\text{H}^+][\text{complex}^-] -$$
$$k_4[R(OH)_2][HOAs(O_2R)_2]$$

The experimental conditions were such that the con-

centration of the hydrogen ion and the complex anion were identical. The reaction is second order reversible of a type which has been examined in detail by Frost and Pearson.[9] The products are very much less ionized than the reactants and have a negligible contribution to the conductance during the major portion of the reaction. Frost and Pearson's integrated solution can be transformed into one involving the resistance of the solutions at various times by using $a = C_1R^{-1}$, $a_t = C_1R_t^{-1}$, $a_e = C_1R_e^{-1}$, and $x = a_e - a$, where a is the concentration of the complex acid and x is the amount which has been consumed in the time t. The subscript e refers to the equilibrium value. The integrated rate equation is then

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

where $k = k_3K_1$. The validity of this expression can be verified from Fig. 2, where a typical plot (data from Table II) is given for log f vs. t. The point at 41 min. corresponds to over 85% completion of the reaction.
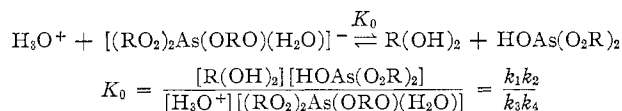
The reaction of the catechol complex also was followed using measurements of the pH change which occurred. In this case, the integrated rate equation has the form

$$\ln f = \ln\left[\frac{\Delta[\text{H}^+](a_0 - 2\Delta[\text{H}^+]_e) + a_0\Delta[\text{H}^+]_e}{a_0(\Delta[\text{H}^+]_e - \Delta[\text{H}^+])}\right] =$$
$$\left[\frac{2a_0(a_0 - \Delta[\text{H}^+]_e)}{\Delta[\text{H}^+]_e}\right] kt$$

where $k = k_3K_1$.

The rate constants obtained by this method for the catechol complex were identical with those obtained from the conductance data. The rate constants are summarized in Table III. The rate of hydrolysis of the catechol complex also was measured in a number of water–ethanol mixtures and these rate constants are presented in Table IV. Derived kinetic parameters are given in Table V and the equilibrium constants for the over-all reactions are given in Table VI. pK_a values for the water–ethanol solutions of the catechol complex are given in Table VII. These values become progressively more difficult to establish with certainty as the concentration of the alcohol is increased.

This over-all reaction is simply

$$H_3O^+ + [(RO_2)_2As(ORO)(H_2O)]^- \overset{K_0}{\rightleftharpoons} R(OH)_2 + HOAs(O_2R)_2$$

$$K_0 = \frac{[R(OH)_2][HOAs(O_2R)_2]}{[H_3O^+][(RO_2)_2As(ORO)(H_2O)]} = \frac{k_1k_2}{k_3k_4}$$

From the measured rate constants k_3K_1 is found to be 5.7×10^{-3} so $k_3 = 2.32 \times 10^{-5}$. From polarimetric data on this same system, Craddock[2] found k_3K_1 to be 6.82×10^{-3}, or $k_3 = 2.78 \times 10^{-5}$. The agreement here is certainly satisfactory, especially when the difference

(9) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 174–175.

TABLE III

RATE CONSTANTS FOR THE HYDROLYSIS OF SOME ARSENIC(V) COMPLEXES IN WATER, L./MOLE-SEC.

Ligand	25.0° k	30.0° k	35.0° k	39.4° k
Catechol	5.71×10^{-3}	1.16×10^{-2}	2.15×10^{-2}	...
	5.71×10^{-3a}			
	6.82×10^{-3b}			
3-Methylcatechol	1.53×10^{-2}	2.98×10^{-2}	4.87×10^{-2}	...
4-Methylcatechol	8.57×10^{-3}	1.24×10^{-2}	2.23×10^{-2}	...
Pyrogallol	6.68×10^{-3}	1.19×10^{-2}	1.67×10^{-2}	...
4-Chlorocatechol	...	1.15×10^{-3}	1.90×10^{-3}	3.65×10^{-3}

[a] By pH methods, followed by Sargent Model S.R. recorder. [b] Polarimetric rate constant from work of J. H. Craddock. This value was obtained in a solution of much higher ionic strength. All other rate constants from conductance measurements.

TABLE IV

RATE CONSTANTS FOR HYDROLYSIS OF HAs(CATECHOL)$_3 \cdot 5H_2O$ IN WATER–ETHANOL SOLUTION, L./MOLE-SEC.

Vol. %– 95% ethanol	25.0° k	30.0° k	35.0° k
0	5.71×10^{-3}	1.16×10^{-2}	2.15×10^{-2}
10	9.71×10^{-3}	1.51×10^{-2}	2.22×10^{-2}
20	1.49×10^{-2}	2.55×10^{-2}	4.83×10^{-2}
30	2.65×10^{-2}	4.53×10^{-2}	7.62×10^{-2}
40	5.40×10^{-2}	7.70×10^{-2}	0.114
50	7.15×10^{-2}	9.60×10^{-2}	.199
60	0.102	0.154	.203
70[a]	.141	.200	.336
80[a]	.275	.416	.631
90[a]	.472	.639	1.34
100[a]	2.05	2.60	4.85

[a] The k values for the solutions up to 70–95% ethanol are in general ±2% of the average value. However, above the 70% solution, the variation becomes a limit of about ±10%. This variation is due both to the increased rate of the reaction and the very low concentrations of the complex that had to be used in order to have the reaction proceed at a measurable rate.

TABLE V

KINETIC PARAMETERS FOR HYDROLYSIS REACTION

Ligand	E_a, kcal.	A	ΔS, e.u.
Catechol	22.8	1.4×10^{12}	−3.12
3-Methylcatechol	13.6	4.4×10^{5}	−32.9
Pyrogallol	14.6	1.9×10^{6}	−30.0
4-Methylcatechol	20.7	6.4×10^{8}	−18.5
4-Chlorocatechol	15.3	1.2×10^{6}	−31.0

TABLE VI

EQUILIBRIUM CONSTANTS FOR LIGAND LOSS (K_0)

Ligand	25°	30°	35°	39.4°
Catechol	0.960	0.678	0.525	...
Catechol[a]	0.860	...	...	...
3-Methylcatechol	2.64	3.14	3.62	...
Pyrogallol	2.23	1.28	2.22	...
4-Methylcatechol	3.75	3.78	3.74	...
4-Chlorocatechol	...	1.15	3.18	3.03

[a] Determined from hydrogen ion consumption. All other values determined from conductometric rate data.

in ionic strength used for these two systems is considered.

For a reaction such as the type postulated here, the destruction of charge is an important feature. This should proceed more rapidly in solvents of low dielectric constant. This can be seen to be the case for ethanol–water mixtures from data collected in Table IV.
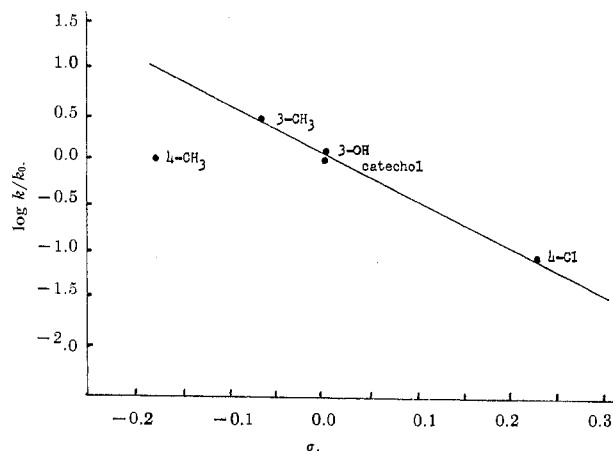

Fig. 3.—Hammett plot for the hydrolysis of complexes of arsenic(V) with substituted catechols.

TABLE VII

pK_a VALUES FOR WATER–ETHANOL SOLUTIONS OF THE CATECHOL–ARSENIC(V) COMPLEX

Vol. %–95% ethanol	25°	30°	35°
0	2.39	2.42	2.42
10	2.45	2.45	2.52
20	2.47	2.48	2.61
30	2.52	2.55	2.69
40	2.60	2.65	2.86
50	2.67	2.79	3.08
60	2.84	2.94	3.31
70	2.89	3.16	3.64
80	3.03	3.55	3.98

The consumption of protons also was checked and found to be in agreement with the proposed reaction scheme. For a concentration of the catechol complex of 1×10^{-2} M the loss of hydrogen ions at equilibrium corresponded to an uptake of 0.48 proton per molecule of complex (or 0.48 of the complex ions were destroyed by hydrogen ion consuming reactions.)

An attempt to correlate the rate constants of the complexes of substituted catechols with the Hammett equation met with reasonable success. The numbering of the positions on the aromatic ring used is
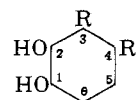
R = methyl, H, or OH
R′ = methyl, H, or Cl

A Hammett plot of log k/k_0 vs. σ for 30° is given in Fig. 3. The data, except for the 4-methylcatechol, fit a line with $\rho = -4.88$. The large negative value typifies a reaction which is aided by electron release to the aromatic ring. A Hammett plot which takes the 2-OH position as the starting point does not lead to a recognizable correlation. As a result of the correlation obtained, it seems reasonable to postulate a mechanism in which a hydronium ion attacks the oxygen of position 1 of the most loosely bound catechol. This leads to the intermediate in which hydrogen atoms are either on or close to the oxygen atoms of this catechol. This configuration is turn undergoes a rapid splitting off of a molecule of catechol and one of water. The mechanism can be described briefly as an Se2 one. This mechanism is consistent with structure I of the complex but not structure II, as the hydronium ion consumption is hardly consistent with a reaction in which two protons are needed to split out each mole of ligand.

Kinetics and Products of Hydrolysis of *cis*- and *trans*-Chlorohydroxobis-(ethylenediamine)-chromium(III) Cations[1a]

By DONALD C. OLSON[1b] and CLIFFORD S. GARNER

The kinetics and products of the aquation and base hydrolysis of *trans*- and *cis*-Cr(en)$_2$(OH)Cl$^+$ have been investigated in 0.1 F ethylenediamine buffer 0.1 F in LiClO$_4$ at 25 ± 1°. At pH 9.81–10.80, $k_{aq} = (4.6 \pm 0.3) \times 10^{-3}$ sec.$^{-1}$ and $k_b < 0.3$ M^{-1} sec.$^{-1}$ for the *trans* isomer; the reaction products are *trans*-Cr(en)$_2$(OH)$_2$$^+$ (87%) and *cis*-Cr(en)$_2$(OH)$_2$$^+$ (13%). For the *cis* isomer at pH 10.12–10.70, $k_{aq} = (3.3 \pm 0.3) \times 10^{-3}$ sec.$^{-1}$ and $k_b = 2.2 \pm 0.2$ M^{-1} sec.$^{-1}$, with the same reaction products (96% *cis*, 4% *trans*). For the *cis–trans* isomerization of Cr(en)$_2$(OH)Cl$^+$ cations ($k_c + k_t$) < 6 × 10^{-5} sec.$^{-1}$. Reaction solutions were initially 1–2 mF in reactant complex. Reaction paths consistent with the kinetic and stereochemical results are presented, and a comparison is made with the behavior of the Co(III) analogs. The visible absorption spectra of the previously unreported labile *trans*- and *cis*-Cr(en)$_2$(OH)Cl$^+$ cations are given.

The hydrolysis of *cis*- and *trans*-chlorohydroxobis-(ethylenediamine)-chromium(III) cations apparently has not been investigated previously, except for a qualitative observation[2] that loss of the second chloro ligand in the hydrolysis of *cis*- and *trans*-dichlorobis-(ethylenediamine)-chromium(III) in basic solution at 25° is rapid relative to the primary hydrolysis.

We report here a study of the kinetics and products of hydrolysis of the chlorohydroxo cations in aqueous ethylenediamine solution, together with considerations bearing on the rate of isomerization of these cations.

Experimental

cis- and *trans*-Dichlorobis-(ethylenediamine)-chromium(III) Chlorides.—The hydrated salts were prepared and characterized as described earlier.[3,4]

cis- and *trans*-Diaquobis-(ethylenediamine)-chromium(III) Bromides.—The hydrated compounds were synthesized by Woldbye's method[5] and characterized as reported previously.[6]

Lithium Perchlorate.—A stock solution of LiClO$_4$ was made by adding a stoichiometric amount of concentrated HClO$_4$ (J. T. Baker Analyzed Reagent) to reagent grade Li$_2$CO$_3$ and diluting to 2.0 F.

Ethylenediamine.—Eastman White Label ethylenediamine was distilled over NaOH. A 0.40 F aqueous solution was prepared and standardized by potentiometric titration with standard HClO$_4$.

***cis*- and *trans*-Chloroaquobis-(ethylenediamine)-chromium(III) Cations.**—Separate solutions of pure *cis*- and *trans*-Cr(en)$_2$(OH$_2$)-Cl^{+2} were obtained by aquating *cis*- and *trans*-[Cr(en)$_2$Cl$_2$]Cl, respectively, for 1 hr. in 0.1 F HNO$_3$ in the dark at 35°, and separating the chloroaquo complex away from other chromium species on H$^+$ Dowex AG50W-X8 cation-exchange columns as described earlier,[4,7] except that the columns were operated at 5°. Elution of the chloroaquo complexes was performed with 100 ml. each of 1.4 F (*trans*) or 2.0 F (*cis*) HNO$_3$. The HNO$_3$ was reduced to pH ~ 2 by treatment of each solution with Dowex AG 2-X8, 50–100 mesh, in the OH$^-$ form, at 10–25° by a technique reported earlier.[7,8] The identity and purity of the *cis*- and *trans*-chloroaquo solutions were then further established by agreement of their visible absorption spectra with those reported previously[4] for these complexes. The solutions were prepared immediately before their use in the chlorohydroxo hydrolysis measurements.

Hydrolysis Run Procedure.—The products and rates of hydrolysis of the labile *cis*- and *trans*-Cr(en)$_2$(OH)Cl$^+$ were determined by rapidly creating these complexes *in situ* from the corre-

(1) (a) Work partly supported under Contract AT(11-1)-34, Project No. 12, between the U. S. Atomic Energy Commission and the University. (b) NATO Post-doctoral Fellow at Chemistry Laboratory I, H. C. Ørsted Institute, Copenhagen, Denmark.

(2) R. G. Pearson, R. A. Munson, and F. Basolo, *J. Am. Chem. Soc.*, **80**, 504 (1958).

(3) D. J. MacDonald and C. S. Garner, *J. Inorg. Nucl. Chem.*, **18**, 219 (1961).

(4) D. J. MacDonald and C. S. Garner, *J. Am. Chem. Soc.*, **83**, 4152 (1961).

(5) F. Woldbye, *Acta Chem. Scand.*, **12**, 1079 (1958).

(6) D. C. Olson and C. S. Garner, *Inorg. Chem.*, **2**, 415 (1963).

(7) D. J. MacDonald and C. S. Garner, *ibid.*, **1**, 20 (1962).

(8) If visible absorption spectra are to be taken of column effluents, as was done here, great care must be exercised to wash out thoroughly with distilled water a yellow resin-decompositon product formed when Dowex AG 2-X8 resin is converted from the Cl$^-$ or NO$_3$$^-$ form to the OH$^-$ form.