metal chloride would permit the use of the tensiometric titration technique to follow the stoichiometry. Tris-dimethylamino alane was allowed to react with boron trichloride since one of the expected products, dimethylamino boron dichloride, has been well characterized.[6] When tris-dimethylamino alane was titrated tensiometrically with gaseous boron trichloride, a sharp increase in pressure was noted after the addition of two moles of boron trichloride per mole of the amino alane. (See Fig. 1a.) Approximately fifteen minutes was required to reach apparent equilibrium. Both dimethylamino boron dichloride and dimethylamino dichloro alane were isolated.

$$2BCl_3 + [(CH_3)_2N]_3Al \longrightarrow 2(CH_3)_2NBCl_2 + (CH_3)_2NAlCl_2$$
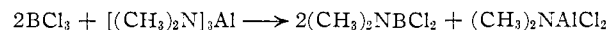
However, if an excess of boron trichloride was allowed to react with tris-dimethylamino alane in a sealed bulb for 24 hr., three moles of boron trichloride was consumed per mole of the amino alane. The observed effect is most probably due to a difference in the rate of exchange between the non-bridging dimethylamino groups and the dimethylamino group involved in the bridge. Such a difference in reactivity is not unexpected, since two of the six nitrogens in dimeric tris-dimethylamino alane must be tetra co-ordinated. It is felt that under the conditions of the tensiometric titration only the non-bridging amino groups were exchanged. In dimeric bis-dimethylaminochloro alane, two of the four nitrogens are believed to be involved in bridge formation. Therefore, only

one mole of boron trichloride ought to be consumed per mole of bis-dimethylaminochloro alane monomer. This was confirmed by a tensiometric titration (see Fig. 1b). Dimethylamino boron dichloride was again isolated from the reaction mixture.

$$BCl_3 + [(CH_3)_2N]_2AlCl \longrightarrow (CH_3)_2NBCl_2 + (CH_3)_2NAlCl_2$$
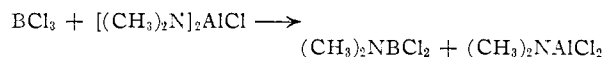
Tris-di-isopropylamino alane is monomeric in benzene and thus has three non-bridging amino groups. Although a di-isopropylamino group is not strictly comparable to a dimethylamino group, especially in view of the steric requirements of boron, the reactivity of the di-isopropylamino groups should be equivalent if reaction does occur. When tris-di-isopropylamino alane was titrated tensiometrically with boron trichloride, a sharp linear pressure increase was noted after the mole ratio of boron to aluminum exceeded three (see Fig. 1c).

The lability of the non-bridging dialkylamino groups on aluminum in exchange reactions may result in new synthetic routes to dialkylamino derivatives of other elements, as well as, to new dialkylamino derivatives of aluminum itself.

The Hydrolysis of Octahedral Complexes of Arsenic(V): The Kinetics of Hydrolysis of the Catechol Complex

BY JOHN H. CRADDOCK AND MARK M. JONES[1]

A study of the kinetics of hydrolysis of the arsenic(V)–catechol complex has been carried out to provide information on the behavior of a typical inert outer-orbital complex of a non-transition element. Examination of the levo complex indicates that it does not racemize or hydrolyze 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. In this region, the rate of hydrolysis is given by the second-order expression $-d\,[l(-)\text{-complex}]/dt = k_2[H^+]\,[l(-)\text{-complex}]$. The temperature dependence of the rate in various buffered solutions over the range 25–35° leads to the following values for the free energy, enthalpy and entropy of activation: $\Delta F^{\ddagger} = 20$ kcal., $\Delta H^{\ddagger} = 24$ kcal., and $\Delta S^{\ddagger} = 15$ e.u. The rate of hydrolysis is unaffected by added arsenite or arsenate. The addition of catechol is found to increase the rate of hydrolysis slightly. The over-all results indicate that the gross mechanism of the hydrolytic process may not be radically different from that found for some complexes of transition element ions.

Although a great deal of work has been done on the racemization and hydrolysis of transition element complexes, very little information is available on the racemization of complexes of non-transition elements. The present work was undertaken to provide information of this sort on the inert outer-orbital complex of arsenic(V) and catechol. It was hoped that such evidence would allow a decision to be made concerning possible differences in mechanisms of racemization which may be found for transition and non-transition element complexes. Inasmuch as the inner d orbitals of arsenic(V) are completely filled by non-bonding elec-

trons, the octahedral complexes of arsenic(V) must involve sp^3d^2 hybridization. In the resultant complexes, arsenic has *not* achieved the electronic configuration of the next highest inert gas (krypton) but has more electrons than are required by the effective atomic number rule.

The complex selected for this study is the one formed by the reaction of aqueous solutions of catechol and arsenic acid. The free acid was first prepared by Weinland and Heinzler[2] by the addition of catechol to a boiling aqueous solution of arsenic acid. Upon cooling, colorless crystals separated which had the composition $HAs(C_6$-

(1) To whom correspondence concerning this paper should be addressed.

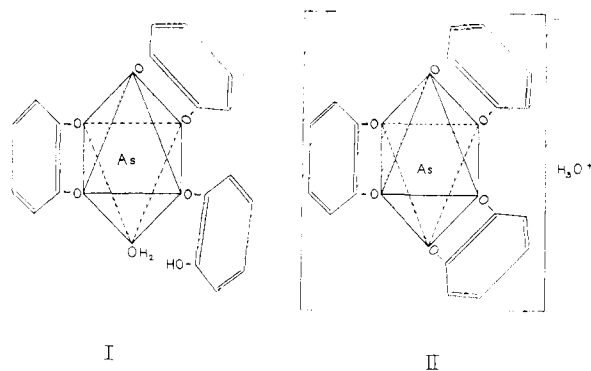(2) R. F. Weinland and J. Heinzler, *Ber.*, **52**, 1316 (1919).

I   II

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

$H_4O_2)_3 \cdot 5H_2O$. To this compound they assigned the "structure" $H_3[O-As-(OC_6H_4O)_3]\cdot 4H_2O$. Simple salts of this acid also were prepared and in all cases the compound behaved as a monobasic acid. Subsequently, Reihlen, Sapper and Kall[3] studied this compound and proposed a somewhat uncommon structure for it, given in a modernized version in Fig. 1, I (the original structure had a free proton outside the coördination sphere). The experimental evidence on which this structure was based consisted of (a) the fact that the compound behaved as a monobasic acid and (b) the claim that dehydration can only remove *four* molecules of water from the pentahydrate. These investigators also showed that in similar complexes of antimony(V), the coördinated water molecule could be replaced by a molecule of pyridine. At this same time Rosenheim and Plato[4] proposed structure II, Fig. 1, in which all three of the catechol molecules were chelated. However, they were never able to remove more than four molecules of water from the pentahydrate without causing its decomposition. This is understandable if one molecule of water is required for the hydration of the proton or if structure I represents the complex correctly. It should also be noted that the free acid possesses a considerably lower order of thermal stability than the salts prepared from it. The free acid undergoes marked decomposition at temperatures of 50–60° while the barium salt is stable up to 100°.

Rosenheim and Plato (ref. 4) successfully resolved the anion into optically active forms. If the acid possessed the structure suggested by them, this would be expected. However, the structure proposed by Reihlen, et al., would also give rise to optically active forms if the unchelated catechol ligand and the coördinated water molecule occupied cis positions. For this reason, a thorough examination of the physical and chemical properties of the free acid and its barium salt was undertaken.

In this paper are presented the results of a detailed study of the phenomena which occur when the levo form of this complex anion loses its optical activity in aqueous solutions of pH 1.2 to 2.2. As will be seen, this loss of optical activity is the direct result of the hydrolytic decomposition of the anion. While the final equilibrated solution will contain

small equal amounts of both the d- and l-forms of the anion the larger portion of the arsenic will not be present in complexed form. Acting on the suggestion of the referee, this over-all process is not designated racemization, though some similar cases in the literature have been so designated.

Experimental

Preparation of the Complex Acid and its Barium Salt.— The free acid was prepared by allowing a solution of stoichiometric amounts of arsenic acid and catechol to crystallize slowly in a vacuum desiccator. Thus 40 g. of C.P. arsenic acid was dissolved in 100 ml. of distilled water and 100 g. of catechol (resublimed) was dissolved in the resulting solution. This was then put into a vacuum desiccator over anhydrous calcium chloride. After standing approximately ten days, large, clear, colorless, cubic crystals were obtained. The resolution of the anion *via* the cinchonine salt and the subsequent conversion to the barium salt were effected by the method of Mann and Watson.[5] Considerable difficulty was encountered in the analysis of the barium salt because of the large and variable amount of water present in the freshly prepared salt. The barium in the barium salt was determined as barium sulfate and the arsenic as arsenic pentasulfide. These analyses were run on samples dehydrated to the dihydrate stage in an Abderhalden drying pistol at 60°. The specific rotation of various samples was −419 to −422° compared with the literature[5] value of −417°. *Anal.* Calcd. for $Ba[As(C_6H_4O_2)_2 \cdot (C_6H_5O_2) \cdot (H_2O)]_2$: Ba, 14.1; As, 15.4; C, 44.5; H, 2.9. Found: Ba, 14.8; As, 14.8; C, 43.7; H, 3.5.

Structural Evidence.—The additional evidence collected for this purpose consists of (a) determination of the pK_a of the parent acid, (b) determination of the equivalent conductance of the parent acid as a function of concentration, (c) infrared absorption spectra and (d) dehydration studies on the barium salt.

(a) **Determination of the pK_a of the Parent Acid.**—The pK_a of the parent acid was determined by titration of an aqueous solution with standard sodium hydroxide solution using a Beckman Model GS pH meter. From the half-neutralization point of several titrations a value of 2.75 was found for the pK_a. This is somewhat greater than would be expected for a species containing an already formed H_3O^+ ion but is not inconsistent with the ionization of a hydrogen from a molecule of water which is coördinated to the arsenic.

(b) **Determination of the Equivalent Conductance of the Parent Acid.**—The conductance of aqueous solutions of the parent acid was measured at 25°, using a bridge of moderate precision and cells of the type designed by Jones and Bollinger.[6] The equivalent conductance underwent a steady drift with time, so values taken at various times were extrapolated back to $t = 0$. These values are presented in Fig. 2 where the results for a typical strong acid and a typical weak acid are presented for comparison. It can be seen that the equivalent conductance varies in a manner expected for an acid of intermediate ionization constant.

(c) **Infrared Absorption Spectra.**—The infrared absorption spectra were obtained on a Perkin–Elmer Model 21 infrared spectrophotometer using sodium chloride optics. The samples were prepared using the potassium bromide disk method. Both the free acid and the barium salt exhibit infrared absorption bands in the region 800–1000 cm.$^{-1}$ of the type attributed by Fujita and his co-workers[7] to coördinated water. A sample of the free acid also was prepared using deuterium oxide as the solvent. This sample had an infrared spectrum in which the bands in this region had a very different appearance. In general a shift toward longer wave lengths occurred such as would be expected to result from the change of an O–H band to an O–D band.

(d) **Dehydration of the Barium Salt.**—Because of the earlier claims concerning the impossibility of removing all of the water of hydration from either the free acid or its salts, the structure of the anion which contains coördinated water assumes importance. A very careful study of the

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

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

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

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

(7) J. Fujita, K. Nakamoto and M. Kobayashi, ibid., 78, 3963 (1956).

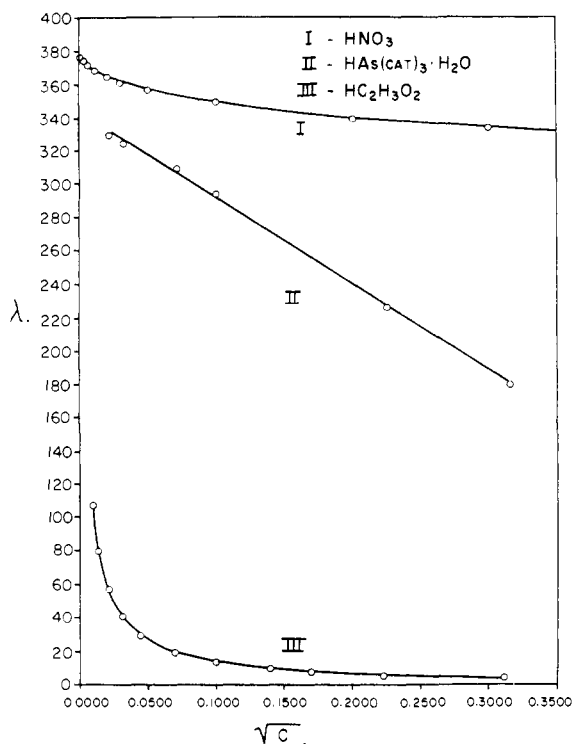Fig. 2.—The equivalent conductances of HNO_3, the arsenic(V)–catechol complex, and acetic acid as a function of concentration.

Fig. 3.—Dependence of the pseudo first-order rate constant on pH at 25, 30 and 35°.

vacuum dehydration of the barium salt, $Ba[As(C_6H_4O_2)_3]_2 \cdot 10H_2O$ has been carried out using prolonged dehydration of this salt. For this, an Abderhalden drying pistol was used which was kept at the boiling point of methanol (64.1°) under a vacuum which was maintained below 0.3 mm. by continuous pumping. While a greater weight loss may be obtained by using higher temperatures, the sample always showed pronounced discoloration under such conditions. A sample dried for 72 hr. under these conditions lost 12.38% of its weight. The theoretical weight loss for eight molecules of water is 12.9%; that for 10 molecules of water is 16.2%.

Kinetic Data.—The kinetic studies described below involve the use of the levo(−)-anion. The resolution of the racemic mixture was accomplished by the procedure of Rosenheim and Plato[4] which uses the second-order asymmetric transformation that occurs in the presence of cinchonine to furnish an essentially quantitative yield of the diastereoisomer of the $l(-)$-anion. The quinine and cinchonidine diastereoisomers may be used in a similar manner to obtain the $d(+)$-anion. After the cinchonine diastereoisomer was obtained, it was converted to the barium salt using the procedure of Mann and Watson.[5] The barium salt is water soluble, has a high rotation and a remarkable optical stability in the absence of acids.

The loss of optical activity of buffered aqueous solutions 2.25×10^{-3} to $5.0 \times 10^{-3}M$ in the barium $l(-)$-salt was followed polarimetrically using a Rudolph polarimeter (reading to $\pm 0.05°$), a sodium lamp and a 4 dm. jacketed cell. Water was circulated continuously through the cell jacket from a constant temperature bath. The temperature was controlled to within $\pm 0.01°$ during the runs. Where necessary, filtration was used to get clear solutions.

The rate of loss of optical activity was followed at various pH values, temperatures and in the presence of various added substances. An aqueous solution of the barium $l(-)$-salt is stable indefinitely in buffered alkaline solutions (pH 8), and no measurable loss of optical activity is observed in buffered neutral solutions. As the pH is lowered, the rate of loss of optical activity attains readily measurable values in the region of pH values from 3 to 1.2 at 25°. As the pH decreases in this region the rate of loss of optical activity increases quite rapidly.

The buffers used were HCl-KCl mixtures prepared ac-

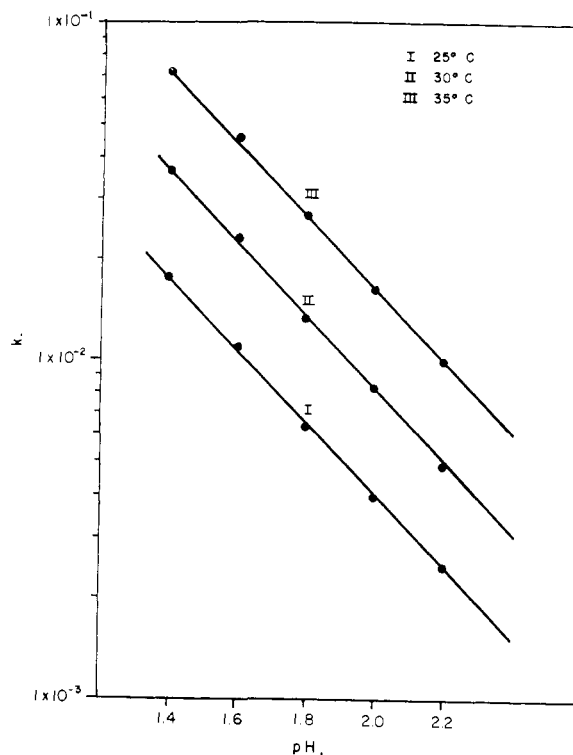cording to the directions of Clark and Lubs.[8] The pH was generally checked using a Beckman Model GS pH meter which had been standardized with a potassium acid phthalate buffer of pH 4.01. Because of the large amount of electrolytes used in making up the buffer solutions, some control was lost over the variation possible in the ionic strength. The ionic strengths (μ) of the resultant buffer solutions used were

pH	1.2	1.4	1.6	1.8	2.0	2.2
$\mu \times 10^2$	6.34	6.73	7.33	8.30	9.82	12.12

In the study of the effect of the ionic strength upon the rate, the added electrolyte used was sodium perchlorate. This required that the buffers used in such work be made up from NaCl–HCl mixtures to avoid the precipitation of potassium perchlorate. The pH values of these solutions were checked in the manner described above.

The pseudo first-order rate constants k_1', for each kinetic run were determined from a plot of log α vs. t, where α is the observed rotation at a time t minutes from the preparation of the solution.

The effectiveness of the buffer was checked in some runs by allowing the reaction to proceed essentially to completion. In one case, the pH of the reaction medium which was initially 1.7 had changed to 1.8 at the end of the reaction. Any difficulties which might have arisen from this source were obviated by using the initial straight line portion of the log α vs. t curves in the determination of the rate constants.

The temperature dependence of the rate was examined in several pairs of buffered solutions at 25, 30 and 35°. Figure 3 shows a plot of the pseudo first-order rate constants for various pH values in the region 1.4 to 2.2 at 25, 30 and 35°. The enthalpy of activation is 25 ± 1 kcal. and the entropy of activation was found to be 15 e.u. From these figures the free energy of activation is 20.5 kcal. at 300°K.

The rate of loss of optical activity is unaffected by the presence of added arsenite or arsenate in the pH region 1.2 to 2.0, over which such studies were made. However, the addition of catechol is found to increase the rate of loss of optical activity slightly if the molar ratio of added catechol

(8) Cited in I. M. Kolthoff and H. A. Laitinen, "pH and Electrotitrations," John Wiley and Sons, Inc., New York, N. Y., 1941.
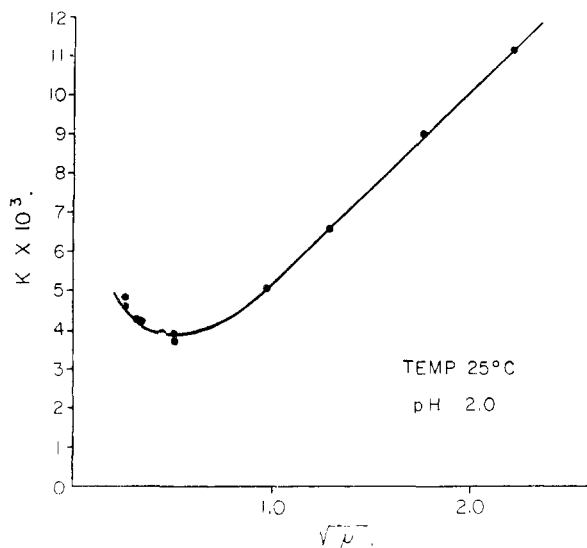
Fig. 4.—Variation of the pseudo first-order rate constant with ionic strength at pH 2.0 and 25°.

to the $l(-)$ anion is 3–6. In addition it was noted that the pH of the buffered solutions had increased slightly by the end of each run. Inasmuch as this indicates that a dissociation process is occurring during the loss of optical activity, a more detailed study of this phenomenon was carried out using a pH-stat.[9,10] The hydrolysis was allowed to proceed under experimental conditions similar to those used previously, but the rate of consumption of hydrogen ion was followed as a function of time using a Radiometer automatic titrator. A standard acid solution was added automatically from a syringe type microburet to maintain the initial pH value throughout the run; the rate of consumption of hydrogen ion was recorded on a strip chart from which it could be obtained directly. The pH-stat data show that hydrogen ion is consumed during this reaction, and at a steady rate which is apparently greater than the rate of loss of optical activity under comparable conditions. This is consistent with a dissociation mechanism for the reaction in which an initial process involving destruction of the asymmetry of the complex is succeeded by a rapid breaking of chelate rings in the complex.

An examination of the effect of the ionic strength upon the rate of loss of optical activity was carried out polarimetrically at a pH of 2 and 25°. Added sodium perchlorate was used to increase the ionic strength. For the point of lowest ionic strength it was necessary to decrease the concentration of barium salt to such an extent that a more precise polarimeter was required. This point was established using a Schmidt and Haensch polarimeter, reading to ±0.01° and a 2 dm. jacketed cell. The results of this work are presented in Fig. 4.

Results and Discussion

The disagreement on the structure of the complex has been resolved to the extent that all information presently available is consistent with structure I, Fig. 1 for the solid salt. It is still possible, though not very probable, that the second structure occurs in aqueous solution.

The over-all rate of the reaction is first order in the concentration of the complex, as readily can be seen from a plot of log α vs. t; it is also first order in the concentration of hydrogen ion, as can be seem from the slopes in Fig. 3. This gives the over-all rate as

(9) A. K. Shamsuddin Ahmed and R. G. Wilkins, *J. Chem. Soc.*, 3700 (1959).

(10) D. Glick, ed. "Modern Methods of Biochemical Analysis," Vol. IV, Interscience Publishers, Inc., New York, N. Y., 1954, p. 171 ff.

$$-\frac{d[l(-)\text{-complex}]}{dt} = k_2[\text{H}^+][l(-)\text{-complex}]$$

The results obtained thus indicate that the gross mechanism of the hydrolytic process shows several features not radically different from those found for the racemizations of some inert transition metal complexes. There are several possible mechanisms for this process, all of which predict the kinetic dependence observed. The experimental data at present allow some of these to be ruled out.

Historically, two main types of mechanism have been favored in the discussion of the racemization of inert complexes: the dissociation mechanism and the intramolecular rearrangement. Werner[11] first suggested an intramolecular mechanism and this has since been proposed in several revised forms by Ray and Dutt,[12] Basolo and Pearson[13] and Bailar.[14] The dissociation mechanism can be traced back to the work of Thomas[15] on oxalato complexes and has since also been subjected to various modifications to cover different reactions.[13] While the specific racemizations for which Thomas proposed this kind of mechanism subsequently have been shown to proceed by a different mechanism, a dissociation mechanism has been shown to be exhibited in at least two other racemizations.[16,17] Basolo, Hayes and Neumann[17] have shown that the rates of dissociation and racemization are equal for the Ni(II) complexes with o-phenanthroline and with dipyridyl. Because the corresponding Fe(II) complexes racemize by a process which is primarily intramolecular,[13] it is of interest to note that inner (d^2 sp^3) and outer (sp^3 d^2) orbital complexes, quite similar in other respects, may racemize by completely different mechanisms. Inasmuch as the As(V) complex is of the outer orbital variety, a similarity in mechanism to Ni(II) was expected and, in fact, found. The very thorough investigation of the Ni(II) complexes by the workers mentioned above as well as by Wilkins and his co-workers[9] has shed further light on the dissociation mechanism found with these complexes and also has provided alternative experimental tests of the dissociation mechanism.

The experimental evidence on the loss of optical activity of the arsenic(V)–catechol complex is consistent only with an over-all dissociation mechanism. The simplest mechanism consistent with the rate expression is an intramolecular racemization of the free acid. Since this is a weak acid, the concentration of the free acid itself would be given by the expression

$$[\text{HA}] = \frac{1}{K_a}[\text{H}^+][\text{A}^-]$$

and if $[\text{A}^-] \gg [\text{HA}]$ an intramolecular mechanism would lead to the alternative rate expressions

$$-\frac{d[l(-)\text{-complex}]}{dt} = \frac{k_1}{K_a}[\text{H}^+][\text{A}^-]$$

(11) A. Werner, *Ber.*, **45**, 3061 (1912).

(12) P. Ray and N. K. Dutt, *J. Indian Chem. Soc.*, **20**, 81 (1943).

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

(14) J. C. Bailar, Jr., *J. Inorg. Nuclear Chem.*, **8**, 165 (1958).

(15) W. Thomas, *J. Chem. Soc.*, **119**, 1140 (1921).

(16) N. R. Davies and F. P. Dwyer, *Trans. Faraday Soc.*, **48**, 244 (1952); **49**, 180 (1953).

(17) F. Basolo, J. C. Hayes and H. M. Neumann, *J. Am. Chem. Soc.*, **75**, 5102 (1953).

Although this is the desired form of the rate expression, this particular mechanism may be ruled out by the change in pH which occurs during the loss of optical activity. If the loss of optical activity is accompanied by dissociation as it is here, then it seems more probable that an alternative mechanism will be more satisfactory since here the dissociation and racemization are probably *concurrent* processes.

Three additional mechanisms can be invoked which are consistent with the information which is presently on hand for this system. The first would be merely a reaction in which the racemization process of the free acid mentioned above is a dissociative one which results in the release of ligand to the solution. The second is one in which a rate-determining attack by a hydronium ion produces a seven-coördinate sp^3d^3 intermediate which subsequently undergoes rapid dissociation. Arsenic-(V) has empty d orbitals of the same energy as those involved in the octahedral hybridization. This would lead to an intermediate with the ZrF_7^{-3} structure.[13] A *trans* attack by H_3O^+ on the parent complex will then lead to racemization by loss of $C_6H_4(OH)O^-$ and a proton. The proton simultaneously or subsequently is taken up by $C_6H_4(OH)O^-$ to form $C_6H_4(OH)_2$. Following this the complex breaks up completely at a rate more rapid than this initial step. This mechanism will also yield the rate expression found. If the complex only loses one molecule of catechol in the racemization, the product with two chelated catechols may or may not be of sufficient stability to be isolated. The third possible mechanism is one in which the rate-determining step involves the transfer of a proton from hydronium ion to one of the coördinated catechol chelate oxygens. The resulting complex in which two catechols are coördinated through a single oxygen atom then can racemize readily by rearrangement to a symmetrical configuration more readily attacked by protons than the initial complex. The catechols then all leave the arsenic at some rate faster than this rate of rearrangement.

The rather large entropy of activation observed here demands some comment. This large positive value indicates that the constituents of the activated complex enjoy a greater degree of freedom in the activated state than they do before forming it. Such might be the result of a very considerable loosening of the bonds in the activated complex. The value observed is close to the entropies of activation observed[13] for the racemization of $Fe(o\text{-phen})_3^{+2}$. In the case of the Fe(II) complexes however, this large entropy of activation is explained in terms of crystal field theory, *viz.*, the higher energy, spin-free state of the complex which has larger ion–ligand distances and weaker bonding.

It is of some interest to compare the results of this study with the only other comparable study of an octahedral complex of a non-transition element: that of Dhar, Doron and Kirschner[18] on $l(-)[Si(acac)_3]Cl$. In this case the rate of racemization is equal to the rate of aquation and both are *independent* of the pH below a pH of 9.25. Above this pH, a rapid alkaline hydrolysis occurs. Thus there is every reason to believe that the detailed mechanisms of these two processes are different. It should also be noted that the racemization of the silicon complex involves an irreversible dissociation in which the acetylacetonate groups are all split off. Furthermore, the silicon complex cannot be formed in aqueous solution from its constituents. In the case of the arsenic(V) complex this reaction is a reversible one, although slowly so, and appreciable amounts of the complex can be obtained if the concentrations of the constituents are increased as in the preparative method used.

(18) S. K. Dhar, V. Doron and S. Kirschner, *J. Am. Chem. Soc.*, **81**, 6372 (1959).

Iodine Atom Combination in Hexamethylbenzene–Carbon Tetrachloride Solutions. The Iodine Atom–Hexamethylbenzene Complex

BY R. L. STRONG AND J. PÉRANO

Kinetic studies have been made spectrophotometrically following the flash photolysis of I_2 in hexamethylbenzene–carbon tetrachloride solutions at room temperature. The second order rate constant for the formation of I_2 (7.9×10^9 l. mole^{-1} sec.$^{-1}$) is obtained from data taken at 489 mμ, where observed absorbance changes are due to changes in I_2 concentration alone. By combining these data with data taken at 605 or 646 mμ (where most of the change in absorbance is due to the iodine atom-hexamethylbenzene charge-transfer complex) at different hexamethylbenzene concentrations, an equilibrium constant for the complex of *ca.* 2.7 l. mole^{-1} is estimated. Observed kinetics at 605 and 646 mμ are explained.

Introduction

The formation of a transient charge-transfer complex involving an iodine atom and an aromatic molecule following the flash photolysis of iodine in several pure aromatic solvents has been demonstrated.[1,2] In all systems studied the I_2 and com-

(1) S. J. Rand and R. L. Strong, *J. Am. Chem. Soc.*, **82**, 5 (1960).
(2) R. L. Strong, S. J. Rand and J. A. Britt, *ibid.*, **82**, 5053 (1960).