

integrals J and K can be reasonably extrapolated within an isoelectronic sequence,¹³ it follows that the same is true for L . But the L 's for the isoelectronic sequence B^- , C , N^+ and O^{2+} can be obtained as the energy difference of the equivalent two states.

There is one flaw in the above derivation: if $n > 1$, the second state, $Be(d_{11}^{n+1}d_{12})$, is a state violating the Pauli principle, and cannot be dealt with. For cases of this

(13) F. Rohrlach, *Phys. Rev.*, **101**, 69 (1956).

type, another procedure is possible. In order to establish the desired quadratic equations, any three points are sufficient. When, as is the case for $Be(d_{11}^2d_{12}^2)$, the energy value cannot be obtained, one may well establish the curve by use of three points, $n = 0$, $n = 1$, and an intermediate value, which is obtained by the method described in the preceding paragraph. Although this procedure is liable to greater uncertainties, it appears satisfactory.

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The Effect of Coördination on the Reactivity of Aromatic Ligands. V. Diazo Coupling

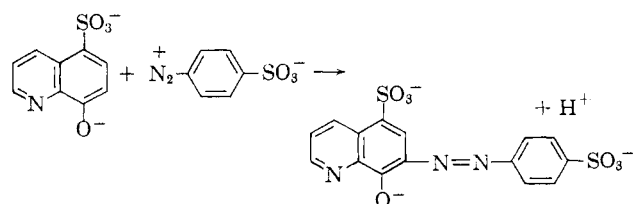
BY KEITH E. MAGUIRE AND MARK M. JONES

RECEIVED JUNE 1, 1962

A kinetic study of the coupling reaction of both free and coördinated 8-hydroxyquinoline-5-sulfonic acid with diazotized sulfanilic acid shows the rate to be strongly affected by coördination. The coördination of the phenolate anion to zinc(II) reduces the rate of coupling by a factor of 10^4 , but does not change the position at which the electrophilic reagent attacks the ligand. The zinc(II) chelate is much more reactive than the phenol itself, however, by a factor of approximately 10^6 . The deactivation of the ligand occurs through an enormous decrease in the frequency factor; much of the change must be attributed to the change in the charge on the reactants. The activation energy for substitution on the complex is less than that for the phenolate anion.

Coördination does not drastically alter the relative reactivity of positions in alternant aromatic systems toward electrophilic reagents. This has been clearly established in several specific cases in the previous papers in this series.¹⁻³ It should alter the rates of such reactions, however, either by changes of a steric nature which aid or hinder the reaction or by changes in the electronic density at the reaction site or by both. For aromatic systems there are no quantitative data available which indicate how large such rate differences might be. The present work had the acquisition of such quantitative data as its principal goal. The chief justification for such an empirical approach lies in the uncertainty of the magnitude of the theoretically anticipated changes in electronic densities which should accompany the coördination act. Calculations using a number of different procedures⁴⁻⁶ all give different estimates of this change. Since the variation in chemical reactivity is extremely dependent on the variation of electronic charge density,⁷ experimental data are needed as guideposts if further theoretical work is to be fruitful.

In order to determine the nature of such changes in rates, a kinetic study has been carried out on the diazo coupling of 8-hydroxyquinoline-5-sulfonic acid and its zinc(II) chelate with diazotized sulfanilic acid. The reaction proceeds *via* an electrophilic attack on the 7-position of the phenolate ion derived from the ligand. The electrophilic reagent is the diazonium ion. This reaction is



The products of the reaction of the free ligand and its zinc complex were shown to be identical by means of absorption spectra and analyses. For the free ligand, this type of coupling reaction has been studied by Phillips and Price⁸ and by Matsumura.⁹ When the 5-position is blocked, as in the present case, the coupling occurs at the 7-position. The mechanism of the diazo coupling reaction has been thoroughly reviewed¹⁰ and is sufficiently well delineated that the interpretation of the kinetic data is unambiguous.

Experimental

8-Hydroxyquinoline-5-sulfonic Acid.—The preparative method described by Liu and Bailar¹¹ was employed. The compound does not have a sharp melting point, but decomposes at 300°. The *S*-benzylisothiourrea derivative of the compound melts at 199°, lit.¹² 197°. *Anal.* (after drying at 120°): Calcd. for $C_9H_7O_4NS$: C, 47.99; H, 3.13; N, 6.22; S, 14.23. Found: C, 47.87; H, 3.26; N, 6.01; S, 14.00.

p-Diazobenzenesulfonate was prepared using the method recommended by Fierz-David and Blangey.¹³

The dried product may be stored in a caged vacuum desiccator prior to use for no longer than one week, and in quantities not exceeding one gram. This solid, when dissolved in sodium acetate-acetic acid buffer solution of pH 5, gave a clear water-white solution. If the temperature of the solution was maintained below 15° the solution remained free from discoloration and nitrogen evolution for approximately 8 hours. This material exists as an inner salt or zwitterion.

7-(4-Sulfobenzeneazo)-5-sulfo-8-hydroxyquinoline is the red, water-soluble azo dye formed when diazo-sulfanilic acid is coupled with oxine-5-sulfonic acid. It will be called the "red azo dye" in the rest of this paper.

Sulfanilic acid (17.3 g., 0.1 mole) is dissolved in 2 *M* ammonia solution (60 ml.) and diluted to approximately 250 ml. with water. This solution is then cooled to 0-5° with an ice-bath, and acidified with concentrated hydrochloric acid (10 ml.). The suspension of sulfanilic acid produced is then diazotized by the addition of sodium nitrite (7 g., 0.1 mole) dissolved in water (100 ml.). The addition of sodium nitrite is continued until an immediate dark blue color is produced when a piece of starch-iodide paper is spotted with the reaction mixture.

(8) J. P. Phillips and S. Price, *J. Am. Chem. Soc.*, **73**, 1875 (1951).

(9) K. Matsumura, *ibid.*, **49**, 810 (1927).

(10) H. Zollinger, "Diazo and Azo Chemistry, Aliphatic and Aromatic Compounds," Interscience Publishers, Inc., New York, N. Y., 1961, Ch. X.

(11) J. C. Liu and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **73**, 5432 (1951).

(12) Staff of Hopkin and Williams Research Laboratory, "Organic Reagents for Organic Analysis," Chemical Publishing Co., Inc., Brooklyn, N. Y., 1946, p. 162.

(13) H. E. Fierz-David and L. Blangey, "Fundamental Processes of Dye Chemistry," trans. by P. W. Vittum, Interscience Publishers, Inc., New York, N. Y., 1949, pp. 248 and 261.

(1) J. C. Taft and M. M. Jones, *J. Am. Chem. Soc.*, **82**, 4196 (1960).

(2) R. L. Jetton and M. M. Jones, *Inorg. Chem.*, **1**, 309 (1962).

(3) K. D. Maguire and M. M. Jones, *J. Am. Chem. Soc.*, **84**, 2316 (1962).

(4) H. L. Schlafer and E. Konig, *Z. physik. Chem. N.F.*, **30**, 145 (1961).

(5) A. Goudot, *Compt. rend.*, **252**, 125 (1961).

(6) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., third ed., 1960, Chs. 3, 5.

(7) Examples may be seen in R. Daudel, R. Lefebvre and C. Moser, "Quantum Chemistry," Interscience Publishers, Inc., New York, N. Y., 1959, Chs. XI, XII.

Oxine-5-sulfonic acid (22.5 g., 0.1 mole) is dissolved in water (250 ml.) containing potassium hydroxide (15 g.). This solution is cooled to 0–5°, and constant stirring is maintained while the diazosulfanilic acid (prepared as above) is added. An immediate orange-red solution is produced, which increases in depth of color as the diazo compound is added. The solution is then stirred for 2 hours at 0–5°, acidified with concentrated hydrochloric acid (approximately 20 ml.) and a heavy red solid precipitates. This suspension is then heated to the boiling point (the solid dissolves) and evaporated to a volume of approximately 400 ml. Cooling the solution overnight in the refrigerator produces an orange-red solid product. This solid is separated by filtration, washed with acetone, and dried at 100°. The yield of crude product is 34.4 g. (sodium salt). The crude product is purified by three recrystallizations from 5 *M* hydrochloric acid, and consists of dark red needles. The compound does not melt, but decomposition commences about 300°. *Anal.* Calcd. for C₁₅H₁₁O₇N₃S₂: C, 44.01; H, 2.71; N, 10.27; S, 15.67. Found: C, 43.72; H, 3.05; N, 10.33; S, 15.25.

The spectrophotometric estimation of this compound proved to be easily effected. A Bausch and Lomb Spectronic 20 colorimeter fitted for controlled temperature operation and employing 1-cm. partitioned Vycor cells was used for this purpose. Standard solutions of the pure compound were prepared by the solution of known weights in 2.5 *M* sulfuric acid. The maximum absorption occurred at 450 m μ at a pH of 7.5 and shifted to 525 m μ at pH values of 2 or less. In 2.5 *M* sulfuric acid the maximum absorbance occurs at 525 m μ and the average value of the molar extinction coefficient at this wave length is 20,400.

Kinetic Studies.—At pH values less than 3 the zinc(II) chelate of 8-hydroxyquinoline-5-sulfonic acid is dissociated to zinc(II) ions and the free acid. The diazo compound, *p*-diazobenzenesulfonate, undergoes decomposition in aqueous media at pH values of 6 or greater to give a variety of products. The coupling reaction at pH values greater than 6 is extremely rapid (90% complete in less than 5 minutes). However, considerable experimentation showed that good kinetic data could be obtained under the following conditions: (1) a pH of 5.00 maintained by a sodium acetate-acetic acid buffer, (2) a temperature in the range 5–15° and (3) the presence of a large excess (50:1) of *p*-diazobenzenesulfonate to obtain pseudo-first-order kinetics. In all the kinetic runs, the concentration of *p*-diazobenzenesulfonate was 5 $\times 10^{-3}$ *M* while that of the coupling component was 1.0 $\times 10^{-4}$ *M*.

In order to test the reproducibility of the procedure, one complete run for one set of reaction conditions was carried out in triplicate. Three separate runs were performed, employing identical conditions, and the results showed that the absorbance of the solution does not vary by more than 0.5% transmittance from run to run. The reproducibility of the rate constants was better than $\pm 5\%$.

Kinetic measurements were made at 5°, 10° and 15°. All runs were made at pH 5.00.

Kinetic Measurements on the Zinc Chelate.—If the chelate under examination is composed of two ligand molecules per zinc atom then there will be two different rates of substitution. The rates of substitution of the first ligand would not be exactly the same as the rate of substitution of the second ligand. Furthermore, if the zinc chelate is dissolved in water some dissociation will take place, and the rate will be affected by the dissociation products. In order to overcome these difficulties, the reactions are carried out in the presence of a large excess of zinc ions. This method ensures that all the ligand is chelated to the metal, and also ensures that a 1:1 zinc:ligand complex is present. In order to determine what excess of zinc ion is necessary the following experiments were carried out. Solutions 2.00 $\times 10^{-4}$ *M* in oxine-5-sulfonic acid in pH 5.00 buffer were prepared containing zinc sulfate varying in concentration from 1.00 $\times 10^{-4}$ *M* to 2.00 $\times 10^{-2}$ *M*, *i.e.*, the zinc:ligand ratio varied from 1:2 to 100:1.

Using solutions of the zinc chelate, the rates of coupling with *p*-diazobenzenesulfonate were measured in the same manner as that used for the free ligand. The molar ratio of Zn(II) to ligand was varied from 0 to 100.

Since the chelate is decomposed in acid solution, the use of 5 *M* sulfuric acid for quenching the reaction serves a dual purpose. Firstly it prevents further reaction, and secondly it breaks down the zinc chelate to yield the red azo dye. Thus, the concentration of red azo dye may be determined spectrophotometrically at 525 m μ , and the concentration of the dye is directly proportional to the concentration of the substituted chelate.

Measurements of the rate of substitution of the zinc chelate were carried out at pH 5.00 at temperatures of 5°, 10° and 15°.

p*K*₂ of 8-Hydroxyquinoline-5-sulfonic Acid.—The method of Nasänen and Ekman¹⁴ was used to determine the p*K*₂ of the ligand. This method is based on the fact that pH = p*K*₂ when the concentration of base is one and a half times that of the ligand. The pH of a solution containing 8-hydroxyquinoline-5-

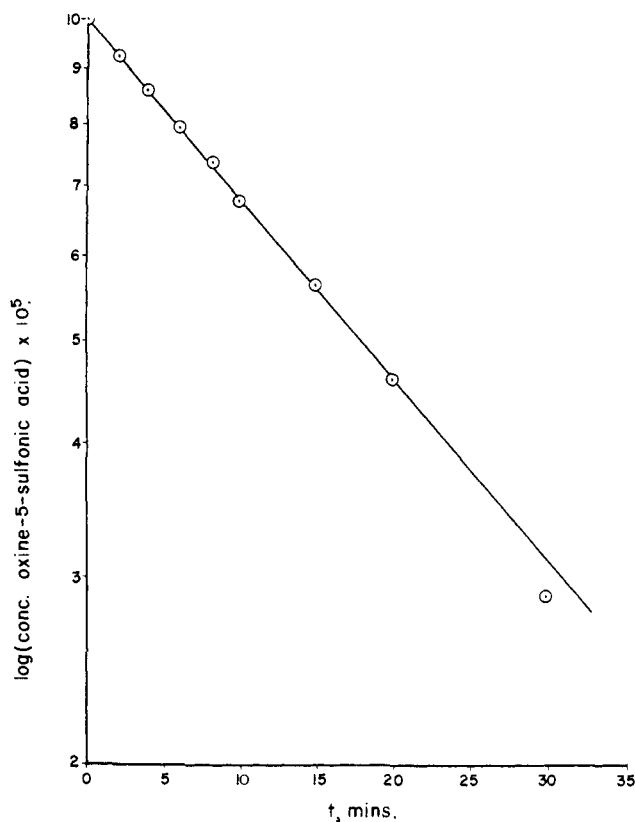


Fig. 1.—Pseudo-first-order plot for the coupling of 8-hydroxyquinoline-5-sulfonic acid and *p*-diazobenzenesulfonate at pH 5 and 15°.

sulfonic acid (3.0×10^{-3} *M*) and sodium hydroxide (4.5×10^{-3} *M*) was measured using a Radiometer pH M-4 pH meter at 5°, 10° and 15°. It was found that the p*K* decreased by 0.01 per 1° rise in temperature. Nasänen and Ekman reported the temperature dependence as a decrease in p*K* of 0.095 per 1° rise. This value is apparently in error by a factor of approximately 10.

Results

The pseudo-first-order rate constants obtained with 8-hydroxyquinoline-5-sulfonic acid and its zinc chelate are presented in Table I. The pseudo-first-order rate

TABLE I
PSEUDO-FIRST-ORDER RATE CONSTANTS FOR COUPLING WITH
p-DIAZOBENZENESULFONATE

8-Hydroxyquinoline-5-sulfonic acid			Zinc chelate (100:1 Zn/ligand ratio)		
pH	T, °K.	$k_1 \times 10^2$ min. ⁻¹	pH	T, °K.	$k_1 \times 10^4$ min. ⁻¹
5	288	3.9	5	288	7.8
5	283	2.3	5	283	5.1
5	278	1.4	5	278	3.4

constants were obtained graphically. In Fig. 1 may be seen the data for a typical run involving the free ligand; in Fig. 2 may be seen the analogous data obtained with a 100:1 ratio of zinc to ligand. The data obtained with varying amounts of zinc(II) present indicated no abnormal kinetic behavior and conformed in every case to the pseudo-first-order rate law. The

TABLE II
PSEUDO-FIRST-ORDER RATE CONSTANTS IN THE PRESENCE OF
ZINC IONS

pH	T, °K.	Zinc:ligand ratio	$k_1 \times 10^4$ min. ⁻¹
5	288	1:2	33
5	288	1:1	26
5	288	5:1	13
5	288	10:1	10
5	288	50:1	7.9
5	288	100:1	7.9

(14) R. Nasänen and A. Ekman, *Acta Chem. Scand.*, **6**, 1384 (1952).

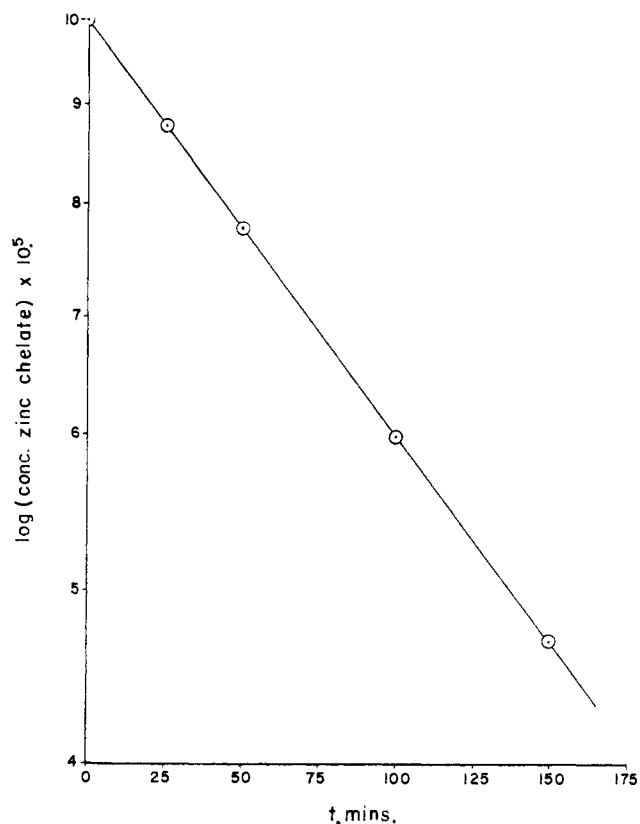


Fig. 2.—Pseudo-first-order plot for the coupling of the zinc(II) chelate of 8-hydroxyquinoline-5-sulfonic acid and *p*-diazobenzene-sulfonate at *pH* 5 and 15°. The zinc(II) to ligand ratio is 100.

data collected on these solutions are presented in Table II.

Discussion

The diazo coupling reaction has been recognized as second order for many years¹⁰ It has been shown quite definitely that the phenolate anion is the species that couples and not the undissociated phenol.¹⁵⁻¹⁸ Hence, in order to compare the reactivity of the species actually participating in the reaction the comparison should be made between the rate of reaction of the phenolate anion and the zinc chelate.

Since the reaction is second order, the pseudo-first-order rate constants are first converted into second order rate constants by use of the relation

$$k_2' = k_1'/[\text{RN}_2]$$

where $[\text{RN}_2^+]$ is the stoichiometric concentration of the diazotized sulfanilic acid. Since the phenolate anion is derived from the phenol by an ionization process, which is governed by the *pH* and the equilibrium constant, it is possible to convert the rate constant k_2' to a rate constant k_2 which is representative of the phenolate anion rather than the undissociated phenol. For a reaction preceded by an equilibrium that controls the concentration of a reactive species this may be accomplished by use of the relation¹⁹

$$k_2' = k_2 K/[\text{H}^+]$$

where K is the equilibrium constant for the dissociation of the phenol and $[\text{H}^+]$ is the hydrogen ion concentration. The rate constants k_2 computed in the above manner are shown in Table III.

(15) R. Wistar and P. D. Bartlett, *J. Am. Chem. Soc.*, **63**, 413 (1941).

(16) R. Putter, *Angew. Chem.*, **63**, 188 (1951).

(17) C. R. Hauser and D. S. Breslow, *J. Am. Chem. Soc.*, **63**, 418 (1941).

(18) H. Zollinger, *Experientia*, **12**, 165 (1956).

(19) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1961, second edition, pp. 193-196.

TABLE III

SECOND-ORDER RATE CONSTANTS FOR THE COUPLING OF THE PHENOLATE ANION

<i>pH</i>	<i>T</i> , °K.	k_2' , l. mole ⁻¹ sec. ⁻¹	<i>pK</i>	k_2 , l. mole ⁻¹ sec. ⁻¹
5	288	1.3×10^{-1}	8.50	4.2×10^2
5	283	7.7×10^{-2}	8.55	2.2×10^2
5	278	4.6×10^{-2}	8.60	1.7×10^2

Using the new rate constants the energy of activation is found to be 19 kcal. mole⁻¹, the entropy of activation is 24 e.u., and the frequency factor is found to have the very high value of 9.7×10^{17} . There are, oddly enough, very few other diazo coupling reactions on which comparable information is available. Use of the data of Conant and Peterson²⁰ leads to an estimated frequency factor of about 10^{17} if the dissociation constant of 1-naphthol-4-sulfonic acid is taken as 10^{-9} . The data on the zinc(II) chelate studied here leads to an energy of activation of 13 kcal. mole⁻¹, an entropy of activation of -18 e.u. and a frequency factor of only 7.7×10^8 . It might be argued that the free phenolate is again the only reactive species in the presence of zinc(II). This is ruled out by the way in which successive additions of zinc(II) effect the pseudo-first-order rate constants (Table II). The rate of the reaction in such a case would be proportional to the concentration of phenolate $[\text{RO}^-]$. This can be shown to be given by

$$[\text{RO}^-] = \frac{[\text{ROH}]_t}{\left\{ K_b [\text{Zn}^{+2}] + \frac{[\text{H}^+]}{K_a} + 1 \right\}}$$

for situations where the zinc to ligand ratio is high. Here $[\text{ROH}]_t$ is the total concentration of the phenol in all its forms, K_b is the formation constant for the 1:1 zinc-phenolate complex, and K_a is the ionization constant of the phenol. Under the conditions of *pH* employed, this expression would predict an approximately linear decrease in the rate with the concentration of added zinc if only the phenolate form reacts. This is clearly not occurring. The number of other protonic equilibria (five) in these solutions precludes a meaningful test of the hydrogen ion dependence of this expression.

A general expression for the rate of the coupling reaction can be written, based on the assumption that both the phenolate ion and its metal complexes can undergo diazo coupling. This is, simply

$$\text{rate} = [\text{RN}_2^+] \{ k_2' [\text{RO}^-] + k_2'' [\text{Zn}(\text{OR})_2] + k_2''' [\text{Zn}(\text{OR})] \}$$

While the use of the buffer precludes an exact test of this equation (because it results in large amounts of acetate complexes), the general trend of rates *vs.* ligand ratio predicted by such a rate law is in reasonable agreement with that found. Thus at low concentrations of zinc, only the first term is important. At higher concentrations of zinc the first and second terms contribute with a decrease in the rate, as $k_2'' < k_2'$. As the concentration of zinc is increased further and further, the relative importance of the third term increases, while that of the first two decreases. Finally when all of the ligand is complexed, a constant rate will be reached which is governed by the last term only.

If we compare the second-order rate constants for the phenolate anion and the zinc(II) chelate, both at 15°, we find $k_2' = 4.1 \times 10^2$ l. mole⁻¹ sec.⁻¹ for the phenolate anion and $k_2''' = 2.6 \times 10^{-2}$ l. mole⁻¹ sec.⁻¹ for the zinc(II) chelate. Thus the free phenolate reacts approximately 10^4 times faster than the coordinated species. It should be recalled that the reaction of the phenol itself is much much slower than either of these. According to Zollinger¹⁰ the undis-

(20) J. B. Conant and W. D. Peterson, *J. Am. Chem. Soc.*, **52**, 1220 (1930).

sociated phenol couples approximately 10^{-10} times as fast as the phenolate anion. The order of reactivity is then $RO^- > \text{zinc chelate} > ROH$. This very dramatically illustrates the difference between protonation and coordination in the deactivation of aromatic systems. The proton is a much more efficient deactivator of both phenolate or aniline than a metal ion. Just *why* this is so is not at all clear but its implications are very important. The most important of these is that the withdrawal of electrons from the ligand by the zinc(II) occurs to a lesser extent than that caused by the addition of a proton. Furthermore, the *frequency factor* is the chief means by which this effect is transmitted rather than the activation energy which is usually assumed to be the route by which electrical charge effect reaction rates.²¹ The changes in the charges of the reacting species when the phenolate is coordinated to zinc(II) would lead one to expect coordination to *decrease* the entropy change on activation by approximately 20 e.u.²² but this model is incapable of explaining the *greater* deactivation which results from protonation. The changes are similar to those found for ionic reactions in aqueous solutions when the charges on the reactant species are varied.¹⁹ It is apparent that the separation of polar effects from the effect of coordination is not necessarily meaningful as the coordination act, in general, will also change polar

(21) P. B. D. de la Mare and J. H. Ridd, "Aromatic Substitution," Butterworths Scientific Publications, London, 1959, esp. Ch. 18.

(22) Calculated using the simple electrostatic model presented in ref. 19. A more refined model might give a larger change. Steric effects are also expected to decrease the entropy of activation in this case.

factors in a reaction. Furthermore, this change will be very directly dependent upon the charge of the cation to which the ligand is coordinated.

The results obtained here, as well as those previously reported in this series, can be incorporated into the usual valence bond theory of organic reactions in two ways. The first, and perhaps the most satisfactory, method is to consider that no-bond resonance forms for the *metal-ligand bond* are the most important contributing structures while those with typical electron pair coordinate bonds are correspondingly less important. The importance of the bonding forms may be expected to increase as the electronegativity of the donor atom increases. This accounts for both the deactivation which results from coordination and the lack of a change in orientation.

An alternative explanation can be developed which is based upon the canonical forms in the transition state. Here those canonical forms which are used to explain the *ortho-para* orientation in aniline or phenol are assigned a different relative importance than is customary. Those forms which have a positive charge on the nitrogen or oxygen are assigned a much smaller importance than those which do not. This second explanation is somewhat less flexible than the first but they are both capable of rationalizing the lack of change in orientation in most instances of coordination.

This work was supported by a grant from the Army Research Office (Durham) for which we wish to express our thanks. We also wish to thank Dr. Erling Grovenstein for his comments.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS, LAWRENCE, KAN.]

The Systems Formic Acid-Ammonia and Propionic Acid-Ammonia

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RECEIVED JULY 16, 1962

Temperature-concentration equilibrium curves for the systems formic acid-ammonia and propionic acid-ammonia have been determined throughout the entire concentration range. In each case, in addition to the normal and acid salts previously known, the existence of a new compound richer in ammonia than the normal ammonium salt has been established. The compound $NH_3 \cdot HC_2H_3O_2$ (ammonium propionate), which has an appreciable vapor pressure of ammonia at temperatures above 60° , has been found to exist in two distinct enantiotropic forms, with a transition point at 61° ; the high temperature form melts in a sealed tube at 121° . The acid salt, $NH_3 \cdot 2HC_2H_3O_2$ or $NH_4C_2H_3O_2 \cdot HC_2H_3O_2$, melts without appreciable decomposition at 53° .

Introduction

In view of the existence of not only an acid ammonium acetate² but also three amines of ammonium acetate, one of the latter compounds ($4NH_4C_2H_3O_2 \cdot NH_3$) being of surprising stability (m.p. 119.5°),³ an investigation of solid-liquid equilibria in binary systems consisting of ammonia and the acids adjacent to acetic in the homologous series promised to be of interest. The system formic acid-ammonia has indeed been studied previously,⁴ but only at concentrations up to 50 mole % of ammonia, *i.e.*, as far as the especially stable 1:1 compound commonly designated as ammonium formate, NH_4CHO_2 . No thorough study of the system propionic acid-ammonia has previously been reported. In the present work, both of these systems have been investigated throughout the entire range of concentrations.

(1) From part of a thesis submitted by Brooks Becker in partial fulfillment of the requirements for the degree of Doctor of Philosophy, University of Kansas, 1959. Supported in part by a grant from the General Research Fund of the University of Kansas.

(2) R. Reik, *Monatsh.*, **23**, 1033 (1902).

(3) A. W. Davidson, H. H. Sisler and R. Stoenner, *J. Am. Chem. Soc.*, **66**, 779 (1944).

(4) J. Kendall and H. Adler, *ibid.*, **43**, 1470 (1921).

Experimental Methods

Preparation of Materials.—Anhydrous formic acid was prepared by the dehydration, in two steps, of Baker and Adamson 90% purified formic acid by the method of Pavlopoulos and Strehlow,⁵ which consists in treatment of the frozen acid, externally cooled, with fuming sulfuric acid, followed by vacuum distillation at room temperature. The product so obtained had a m.p. of $8.4 \pm 0.1^\circ$, in good agreement with the generally accepted value. Pure ammonium formate was prepared by recrystallization of the reagent grade salt from 100% ethanol, followed by vacuum desiccation over anhydrous calcium sulfate. Kjeldahl analysis of the product gave a mean value of 49.92 mole % of ammonia. Care was taken to exclude moisture in the handling of this very deliquescent substance.

Commercial synthetic anhydrous ammonia, which was found to have a m.p. of $-77.5 \pm 0.4^\circ$, was used without purification.

Propionic acid was prepared from Matheson, Coleman and Bell 99% acid by allowing it to stand over molecular sieve for 2 days and then distilling it through a 4-foot column packed with glass beads. The middle fraction of the distillate had a m.p. of -20.7° , in good agreement with the highest value found in the literature. The solid used as a source of ammonium propionate was prepared by adding pure propionic acid dropwise to an excess of liquid ammonia; the excess ammonia was allowed to evaporate, and the solid residue was washed with anhydrous ethyl ether and then dried under vacuum. Kjeldahl analysis showed the product to contain 48.4 mole % of ammonia; hence it consisted of 96.8

(5) T. Pavlopoulos and H. Strehlow, *Z. physik. Chem.*, **202**, 474 (1954).