

sociated phenol couples approximately 10^{-10} times as fast as the phenolate anion. The order of reactivity is then $RO^- >$ 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.

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The Systems Formic Acid-Ammonia and Propionic Acid-Ammonia

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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).

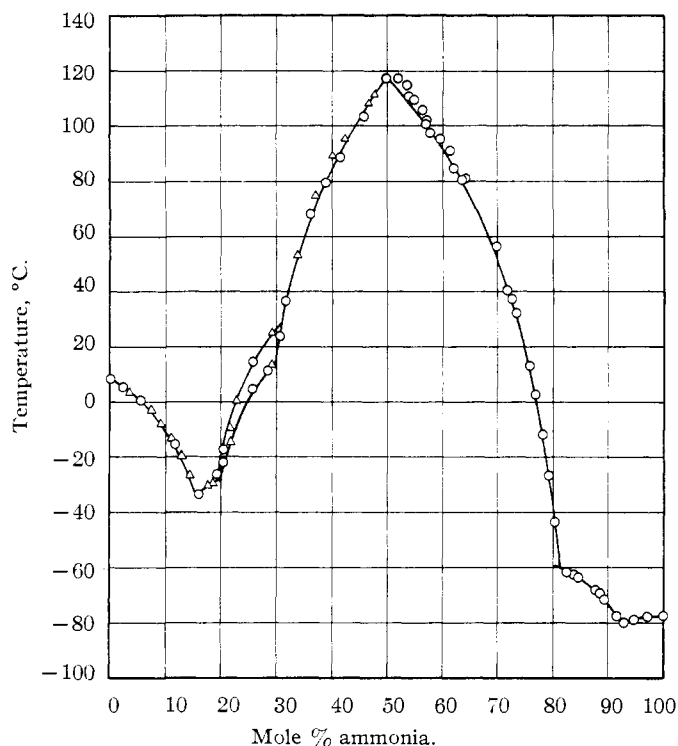


Fig. 1.—System formic acid—ammonia; the data of Kendall and Adler are indicated by triangles, those of the present work by circles.

mole % of ammonium propionate and 3.2 mole % of propionic acid. This material was not only highly deliquescent, but also appreciably volatile; in a closed weighing bottle, however, it could be stored in a desiccator for several weeks without change of composition.

Determination of Equilibrium.—Temperature-concentration curves were determined throughout this work by application of the synthetic or melting-point method, as described in previous papers from this Laboratory.^{3,6} Except for certain regions in which high ammonia pressure necessitated the use of sealed tubes, the containers used for melting point determinations were Pyrex cells, 10 cm. long and of 16 mm. internal diameter, which were provided at the upper end with a small stopcock, a glass rod to serve as a handle, and a side-arm of appropriate diameter to fit a sleeve-type serum bottle stopper. To aid in mixing the contents, a small Teflon-coated magnetic stirring bar was placed in the bottom of the cell. Such cells could be used for any combination of solid, liquid or gaseous starting materials, and were particularly well adapted to the introduction of a liquid component. In the acid-rich regions of the systems studied, the composition was conveniently varied by successive additions of measured volumes of pure acid to the cell with its weighed contents. Each increment of acid was introduced through the stopper by means of a calibrated hypodermic syringe (Yale 1-ml. tuberculin syringe no. 1YT) with a scale graduated in hundredths of a milliliter. In the ammonia-rich regions, however, ammonia was condensed into a cell containing a weighed quantity of solid salt, and its weight determined by difference. The composition of the mixture was then altered to a readily determinable extent by allowing gaseous ammonia to escape through the stopcock and collecting it in standard acid.

For equilibrium determinations at temperatures above 0°, the cell was immersed in a bath of water or paraffin oil contained in an insulated rectangular tank of glass or, for higher concentrations of ammonia (at which bursting of the cell occasionally occurred), of steel with glass windows. The temperature of the bath was raised by means of two immersion heaters, and measured by means of a calibrated mercury thermometer graduated in tenths of a degree. For temperatures below 0°, the bath vessel used was a large wide-mouthed Dewar flask. Down to -80°, acetone was used as the bath liquid, and the temperature was lowered by means of Dry Ice or raised by the addition of more acetone; below -80°, a mixture of ethanol and ether was substituted for the acetone, and liquid nitrogen served as coolant. Agitation of the bath liquid was effected by means of a magnetic stirring bar in the bottom of the Dewar, and temperature was

measured by means of a calibrated copper-constantan thermocouple in conjunction with a Leeds and Northrup K-2 potentiometer. For internal stirring, the cell was continuously twirled and occasionally shaken.

In every case, the contents of the cell were first completely liquefied and then rapidly cooled until a crop of uniformly small crystals was obtained. The temperature of the bath was then raised slowly—never at a rate greater than 1° per min. in the vicinity of the melting point—and the equilibrium temperature was taken as that at which the last visible trace of crystals disappeared. Each equilibrium temperature was determined at least twice.

When the pressure of ammonia at the melting point of a given mixture was too great to be contained by a sleeved stopper—as was the case in the formic acid system in the range 50 to 75 mole % of ammonia and in the propionic acid system from 43 to 59 mole % of ammonia—each determination was carried out in an individual heavy-walled Pyrex U-tube, about 30 cm. in over-all length and of 5 mm. internal diameter. The solid ammonium salt was weighed into the bend of the tube, and an appropriate amount of ammonia was condensed upon it. Both ends of the tube were then sealed by means of a blast-lamp, and the tube was weighed after having come to room temperature. In these cases internal stirring was accomplished simply by manual rocking of the tube. Equilibrium temperatures were determined as already described, at least twice for each sample. The mean values obtained by either method are believed to be correct to within $\pm 0.5^\circ$ except as noted below.

A difficulty which was encountered especially in the formic acid system should be mentioned at this point. At temperatures above 60°, irreversible decomposition of ammonium formate into formamide and water (which was confirmed by means of gas chromatography) occurred to an appreciable extent. The lowering of the melting point brought about by such decomposition increased with temperature, and was greater, at a given temperature, on the ammonia than on the formic acid side of the 50% point. When the temperature was maintained above 100° for a few minutes only, the apparent melting point might be lowered as much as 2°. Concordant corrected melting point values, under these circumstances, could be obtained only by means of back extrapolation of successive determinations. Although this procedure appeared to be fairly satisfactory, accuracy only to within $\pm 3^\circ$ is claimed for equilibrium temperatures above 80° in this system.

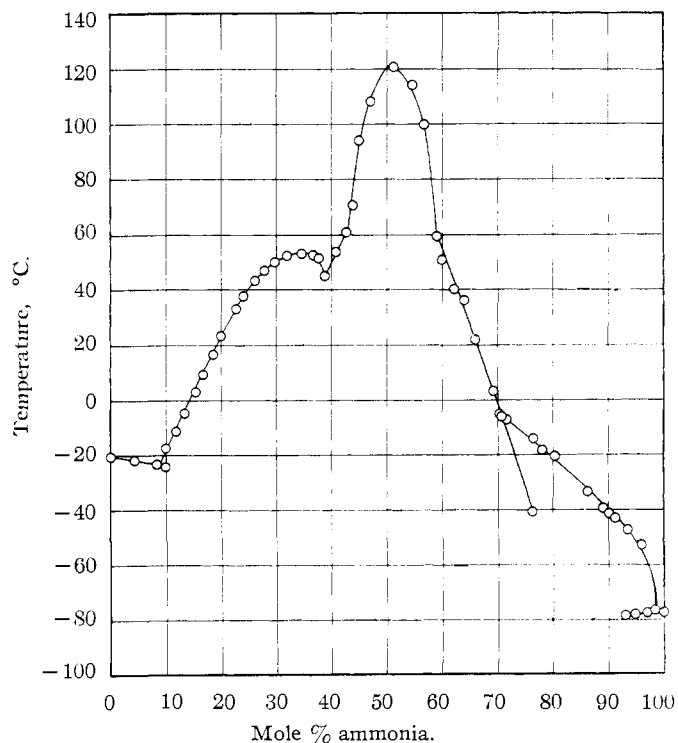


Fig. 2.—System propionic acid—ammonia.

Ammonium propionate is much less stable than ammonium formate with respect to reversible decomposition into ammonia and acid; irreversible decomposition of the former salt, however, although detectable at temperatures above 60°, occurs to a considerably smaller extent than with the latter. In the propionic acid system, equilibrium temperatures above 80° are believed to be correct to within $\pm 1^\circ$. On the other hand, because of the extreme slowness with which equilibrium was attained in solu-

(6) H. H. Sisler, A. W. Davidson, R. Stoenner and L. L. Lyon, *J. Am. Chem. Soc.*, **66**, 1888 (1944).

tions containing 60 to 90 mole % ammonia with propionic acid, equilibrium temperatures in this region are thought to be accurate only within $\pm 2^\circ$.

Results and Discussion

Concentration-temperature equilibrium data obtained in this work are available in tabular form from University Microfilms, Inc.⁷

The data for the formic acid-ammonia system (including those of Kendall and Adler,⁴ which were confirmed in the present work) are presented graphically in Fig. 1. Only one compound containing between 50 and 100 mole % of ammonia appears as solid phase; this compound is stable in contact with solutions containing from 81.0 to 92.7 mole % of ammonia, and melts incongruently, undergoing transition to ammonium formate, at -60° . Because of the short and very low temperature range of stability of the compound, it was not feasible to determine its composition by analysis. From the course of the curve near the transition point, however, it seems probable that the compound is $3\text{NH}_3 \cdot \text{HCHO}_2$; if this supposition is correct, its melting point, by a short extrapolation, would appear to be -58° . The eutectic temperature with ammonia is -80° .

The data for the propionic acid-ammonia system are shown graphically in Fig. 2. The 1:1 compound, ammonium propionate, is stable in contact with solutions containing from 39.1 to 70.5 mole % of ammonia. It evidently exists in two enantiotropic modifications, with a transition point at 61° . Although solutions in equilibrium with the low-temperature form were extremely viscous, it was possible roughly to confirm the composition of the separated crystals by means of a Kjeldahl analysis; the metastable melting point of this form, by extrapolation, appears to be about 85° . The equilibrium temperature at the 50% point constitutes a new figure, 121° , for the melting point of ammonium

(7) University Microfilms, Inc., Ann Arbor, Mich., L. C. Card No. Mic 60-893.

propionate, considerably higher than that previously reported by Zuffanti,⁸ 107° .

The solid phase stable in contact with solutions containing from 8.5 to 39.1 mole % of ammonia is the acid salt $\text{NH}_3 \cdot 2\text{HC}_3\text{H}_5\text{O}_2$ (or $\text{NH}_4\text{C}_3\text{H}_5\text{O}_2 \cdot \text{HC}_3\text{H}_5\text{O}_2$), the existence of which was previously reported by Reik.² This compound melts congruently at 53° , and exhibits eutectics with propionic acid and ammonium propionate at -24° and 45° , respectively.

On the ammonia-rich side of the diagram, a compound stable in contact with solutions containing from 70.5 to 98.5 mole % of ammonia undergoes transition to the low-temperature form of ammonium propionate at -5.5° ; its eutectic temperature with ammonia is -77.7° . Although this compound could not be analyzed directly, from the shape of the curve at the transition point it appears likely that the composition is $2\text{NH}_3 \cdot \text{HC}_3\text{H}_5\text{O}_2$ (or $\text{NH}_4\text{C}_3\text{H}_5\text{O}_2 \cdot \text{NH}_3$); if this is correct, the melting point of the compound, by extrapolation, appears to be about -2° .

The ammonia-acid ratios in the systems consisting of ammonia with formic, acetic and propionic acids are

$\text{NH}_3 : \text{HCHO}_2$	1:4	1:2 ^a	1:1	3:1	..
$\text{NH}_3 : \text{HC}_2\text{H}_3\text{O}_2$..	1:2	1:1	5:4	2:1	..	9:1
$\text{NH}_3 : \text{HC}_3\text{H}_5\text{O}_2$..	1:2	1:1 ^a	..	2:1

^a Two forms.

Each of the compounds occurring in the propionic acid system has its analog in the acetic acid system, and despite the intrusion of the unique 5:4 and 9:1 compounds with acetic acid, the general shapes of the concentration-temperature curves in the two cases are notably similar, especially in the regions of stability of the 1:2 and 2:1 compounds. The formic acid system, on the other hand, with its 1:4 and 3:1 compounds, differs markedly from the other two—a fact which might perhaps have been anticipated from the frequent divergence in the behavior of formic acid from that of its homologs.

(8) S. Zuffanti, *J. Am. Chem. Soc.*, **63**, 3123 (1941).

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

Systems of Methyl Substituted Formamides with Formic Acid and with Ammonia

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Temperature-concentration equilibrium curves for systems consisting of acetamide with formic acid, and of N-methyl- and N,N-dimethylformamide both with formic acid and with ammonia, have been determined throughout the entire concentration range. With formic acid, each of the three amides, like formamide itself, has been found to form a 1:1 addition compound which may appropriately be regarded as a substituted ammonium formate. With ammonia, each of the N-methyl substituted formamides forms a 1:1 compound also; these latter compounds, however, appear to be highly dissociated into their components in the liquid state even at -80° . Formation of an ammonium salt by proton donation from the amide, obviously impossible for the dimethylamide, is believed, because of the similarity of the temperature-concentration curves, to be unlikely for the monomethylamide; hence the addition compound in the latter case is not to be regarded as an ammonium aquo-methylammonio formate. It appears more probable that in both cases the ammonia shares its electron pair with the electron-deficient carbon atom of the carbonyl group of the amide.

Introduction

The amphoteric character of formamide and acetamide, as manifested by their ability to form addition compounds both with acetic acid and with ammonia, has been discussed in two previous papers from this Laboratory,^{2,3} in which it was suggested that the 1:1

(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) H. H. Sisler, A. W. Davidson, R. Stoenner and L. L. Lyon, *J. Am. Chem. Soc.*, **66**, 1888 (1944).

(3) H. H. Sisler, C. A. VanderWerf and S. Stephanou, *ibid.*, **68**, 2538 (1946).

compounds with acetic acid might appropriately be designated as formyl- and acetylammmonio acetate, and those with ammonia as ammonium aquo-ammonio formate and acetate, respectively. Much earlier, formamide had been found to form a fairly stable compound with formic acid,⁴ which may now conveniently be designated as formylammmonio formate. Since N-methylformamide (NMF) and N,N-dimethylformamide (DMF) are stronger bases than formamide, these substituted amides might be expected also to form stable formates. On the other hand, it might be doubted that either of the N-methyl substituted amides,

(4) S. English and W. E. S. Turner, *J. Chem. Soc.*, **107**, 774 (1915).