

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 acetyl ammonium 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 formyl ammonium 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).

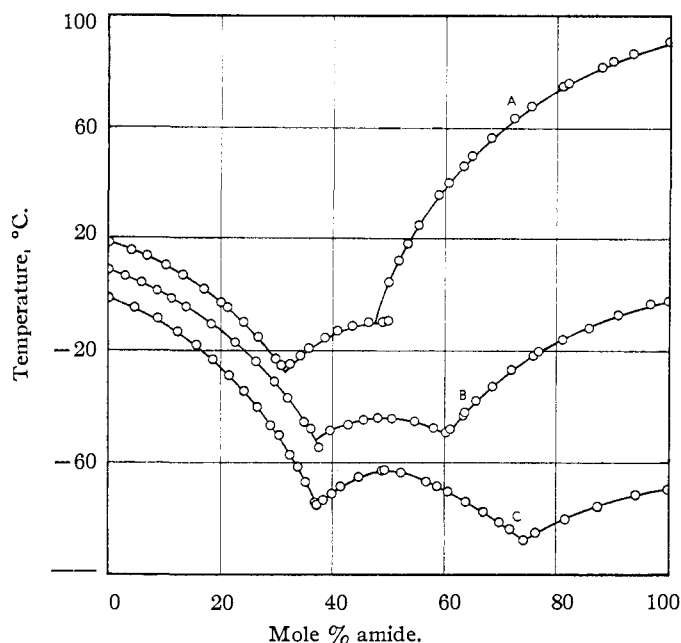


Fig. 1.—Formic acid-amide systems: curve A, acetamide—subtract 10° from temperature scale; curve B, N-methylformamide—temperature scale correct; curve C, N,N-dimethylformamide—add 10° to temperature scale.

and especially the latter, would exhibit as strong a tendency as formamide to combine with ammonia. In the present paper, studies are reported of the system acetamide-formic acid, and of the systems consisting of NMF and DMF both with formic acid and with ammonia; in each case, a 1:1 addition compound was found to occur as a solid phase.

Experimental Methods

Materials.—Acetamide was purified by crystallization from methanol on the addition of ether, as described by Wagner.⁵ The product melted sharply at 80.2° , in good agreement with literature values. The metastable modification of acetamide (m.p. 69°) was not encountered in this work.

Eastman Kodak Co. N-methylformamide (99%) was allowed to stand over molecular sieve for 2 days and then distilled at 20-mm. pressure through a 30-cm. column packed with glass helices. Although Kjeldahl analysis of the middle fraction showed it to contain the theoretical percentage of nitrogen, this purified material nevertheless melted over the range -6° to -3° (literature values -5.4° and -3.8°). Since, in the phase diagram, equilibrium temperatures were taken to be those at which the last crystal disappeared, -3° was used as the melting point of NMF. Incidentally, supercooling to the extent of 60° commonly occurred in attempts to determine the melting point of this material.

Eastman Kodak Co. white label N,N-dimethylformamide was distilled at atmospheric pressure through a 4-ft. column packed with glass beads. The middle fraction, in which gas chromatography revealed no impurities, had a m.p. of -60.2° , 0.8° higher than the best value previously reported.⁸

Anhydrous formic acid, prepared by the method of Pavlopoulos and Strehlow,⁹ had a m.p. of 8.6° . Commercial synthetic anhydrous ammonia, m.p. -77.5° , was used without purification.

Determination of Equilibrium.—Equilibrium determinations were made in Pyrex cells identical with those described in a previous paper.¹⁰ The methods used for varying the concentration and temperature, the thermometers, and the details of procedure were the same as there described. Some of the difficulties encountered in the previous work, however, were magnified in these amide systems. Especially in acetamide-formic acid mixtures containing 45 to 70 mole % acetamide and in ammonia-NMF mixtures containing 30 to 40 mole % NMF, crystallization could be induced only after extreme supercooling—sometimes even to liquid nitrogen temperature, at which the mixture had

become a hard clear glass. In such cases crystallization occurred very slowly, usually along cracks which were formed during the expansion of the glass. Another source of difficulty was the extreme viscosity of some of the mixtures at the equilibrium temperature; this was especially troublesome in approximately equimolecular acetamide-formic acid mixtures, in NMF-ammonia mixtures containing 30 to 50 mole % NMF, and in DMF-ammonia mixtures in which ammonia appeared as the solid phase. Because of these experimental difficulties, there was considerable variation in the accuracy of the melting point determinations. In general, in the ammonia systems the data are believed to be correct to within $\pm 1.5^\circ$, in the acid systems to within $\pm 0.5^\circ$.

Results

Concentration-temperature equilibrium data obtained in this work are available in tabular form from University Microfilms, Inc.¹¹

The data for the three amide-formic acid systems are presented graphically in Fig. 1. In each case a single addition compound, equimolecular in amide and acid, appears as solid phase. Two of these melt congruently; the acetamide-acid compound, however, undergoes transition to acetamide and solution at a temperature only very slightly below its melting point. The stability ranges and melting points of the com-

TABLE I
AMIDE-FORMIC ACID COMPOUNDS

Name, formate	Stability range (% of HCOOH)	Eutectic temp., $^\circ\text{C}$. With amide	With HCOOH	M.p., $^\circ\text{C}$.
Formylammonium ⁴	23.7-72.5	-18	-19	1
Acetylammonium (methylformyl- ammonium)	52.2-68.4	-20.2 ^a	-37	-20 ^b
Formylmethyl- ammonium	39.1-62.2	-50	-52	-44
Formyldimethyl- ammonium	25.7-62.5	-78	-66	-53

^a Transition temperature. ^b By a short extrapolation.

pounds are given in Table I, in which corresponding data for the formamide-formic acid system⁴ are included for comparison.

The data for the amide-ammonia system are presented graphically in Fig. 2. Here again a single

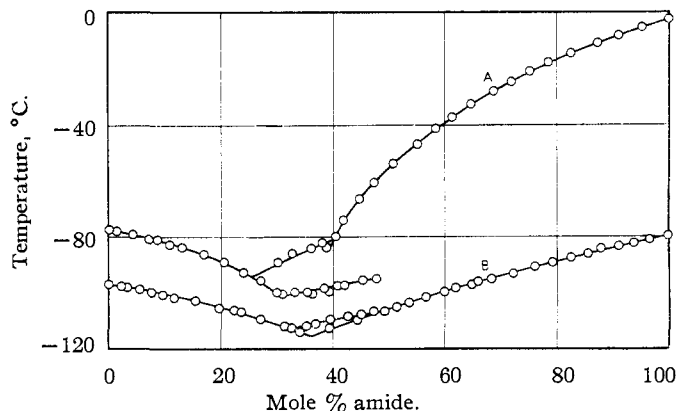


Fig. 2.—Ammonia-amide systems: curve A, N-methylformamide—temperature scale correct; curve B, N,N-dimethylformamide—add 20° to temperature scale.

addition compound appears as solid phase in each case. Unlike the substituted ammonium formates, however, both of these compounds melt incongruently at very low temperatures, and the equilibrium curves are so flat as to indicate a high degree of dissociation into amide and ammonia in the liquid state. Although from the course of the curves the composition of the compounds cannot be determined with complete certainty,

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

(5) E. C. Wagner, *J. Chem. Educ.*, **7**, 1135 (1930).

(6) G. F. D'Alelio and E. E. Reid, *J. Am. Chem. Soc.*, **59**, 109 (1937).

(7) G. R. Leader and J. F. Gormley, *ibid.*, **73**, 5731 (1951).

(8) J. R. Ruhoff and E. E. Reid, *ibid.*, **59**, 401 (1937).

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

(10) B. Becker and A. W. Davidson, *J. Am. Chem. Soc.*, **85**, 157 (1963).

TABLE II
AMIDE-AMMONIA COMPOUNDS

Probable formula	Stability range (% of NH ₃)	Transition temp. to amide, °C.	Eutectic temp. with NH ₃ , °C.	M. p., °C. (by-extr.)
NH ₃ ·HCONH ₂ ^a	53.5-71	-75.5	.. ^a	-75
NH ₃ ·CH ₃ CONH ₂ ²	68-92	-32	-82	-25
NH ₃ ·HCONHCH ₃ (metastable)	-102	-96
NH ₃ ·HCONHCH ₃ (stable)	61-74	-82	-96	-75
NH ₃ ·HCON(CH ₃) ₂	52-67	-87.5	-94	-87

^a A second addition compound, 2NH₃·HCONH₂, undergoes transition to the 1:1 compound and solution at -92°; its eutectic temperature with ammonia is -96°.

it appears highly probable that each of them consists of amide and ammonia in equimolecular ratio. The NMF-ammonia compound occurs in two modifications, one of which appeared here only as a metastable phase. Stability and melting point data are shown in Table II, in which the 1:1 compounds of acetamide and formamide with ammonia, reported in previous papers,^{2,3} are included for comparison.

Discussion

Since the amide-formic acid compounds of Table I are relatively stable at their melting points and since they are all formally analogous to ammonium formate, the names by which they are designated in the table appear to be appropriate. It is significant that the sharpness of the maxima in the equilibrium curves,

and the steepness of these curves in the region where formic acid is solid phase, both increase in the order formamide < NMF < DMF. This variation indicates increasing extent of compound formation in solution in the same order, corresponding to the known increase in basicity of the amides with successive introduction of N-methyl groups. It may be noted that according to the above criteria, acetamide, although it differs little from formamide in basicity, closely resembles its isomer NMF with respect to extent of compound formation with formic acid.

In the amide-ammonia systems, the order of increasingly extensive compound formation in solution, as indicated by the same criteria, is reversed, increasing in the order DMF < NMF < acetamide < formamide. In this case, however, the nature of the addition compounds is by no means obvious. The suggestion in an earlier paper from this Laboratory³ that the 1:1 formamide-ammonia compound, by analogy with the sodium salts of formamide, might be regarded as an ammonium aquo-ammonio formate of the formula HCONHNH₄, loses much of its plausibility in view of the fact that a similar compound with ammonia is formed not only by NMF but even by DMF, in which there is no hydrogen available for proton donation to ammonia. Because of the general similarity of the equilibrium curves in all the amide-ammonia systems considered, it appears preferable to suppose, in line with an alternative suggestion made in the paper just mentioned, that compound formation in these systems may result from the sharing of the electron pair of the ammonia molecule with the electron-deficient carbon atom of the carbonyl group of the amide.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON STATE UNIVERSITY, PULLMAN, WASH.]

Calculated Bond Characters in Phosphoryl Compounds

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The bond characters of a series of symmetrically substituted phosphoryl molecules, Y₃PO, have been calculated using the internally consistent LCAO-MO method previously developed for the π-electrons of such systems, but also taking into account the varying polarities of the YP and OP σ-bonds and the changing hybridization of the π-bonding orbital of the central phosphorus atom. The resulting PO bond characters are directly related to the electronegativities of the substituent Y-groups. The calculated PO π-bond orders correlate well with the experimental bond vibrational frequencies and the charge distributions are consistent with the observed dipole moments and other properties of the molecules.

In many phosphoryl molecules, Y₃PO, the PO bond stretching frequencies and bond lengths, the YPY angles, and the relative YP bond distances, all seem to vary considerably as the Y-group is varied, indicating significant changes in the PO bond characters. It has been shown¹ that there is a correspondence between the phosphoryl frequency and the electronegativity of the substituent groups, as seen in Table I, but the quantitative nature of these bonds apparently has not been discussed. Since bond character of the type involved in the phosphoryl group can be calculated by the internally consistent molecular orbital method previously developed for such systems,² it is possible to deduce the effects of changing the substituents Y on the PO bond in the different Y₃PO molecules.

We have applied this MO method to a series of symmetrically substituted phosphoryl compounds taking into account the varying polarity of the σ-bonds, the changing hybridization of the π-bonding orbital

of the central P-atom, and the different degree of π-bonding involved in each compound. The method predicts appreciable participation of the P-atom d-orbitals in the π-bonding such that the total order of the PO bonds varies from a nearly pure coordinate single bond in (CH₃)₃PO to almost a triple bond in F₃PO. The charge distributions vary in the series in such a way that the calculated dipole moment completely reverses direction. The calculated π-bond orders of the PO bond give a good correlation with the PO bond stretching frequencies or force constants when a reasonable set of β(dπ) values is chosen, indicating that our calculated bond strengths, based on bond orders, at least vary in a consistent manner.

Now if we consider only symmetrically substituted molecules of symmetry C_{3v}, the "group" orbitals of the three Y-atoms which enter into the σ-bonding with phosphorus can be represented by (σ_{a1}) and (σ_e), the corresponding P-atom hybrid orbitals which combine with these are the (3s3p_z)-hybrid represented by (3r_{a1}) and the (3p_x3d_z)-hybrid represented by (3r'_e). The other components of these P-atom hybrids, (3t_{a1})

(1) J. V. Bell, J. Heister, H. Tannenbaum and J. Goldenson, *J. Am. Chem. Soc.*, **76**, 5185 (1954); L. W. Daasch and D. C. Smith, *Anal. Chem.*, **23**, 853 (1951).

(2) E. L. Wagner, *J. Chem. Phys.*, **37**, 751 (1962).