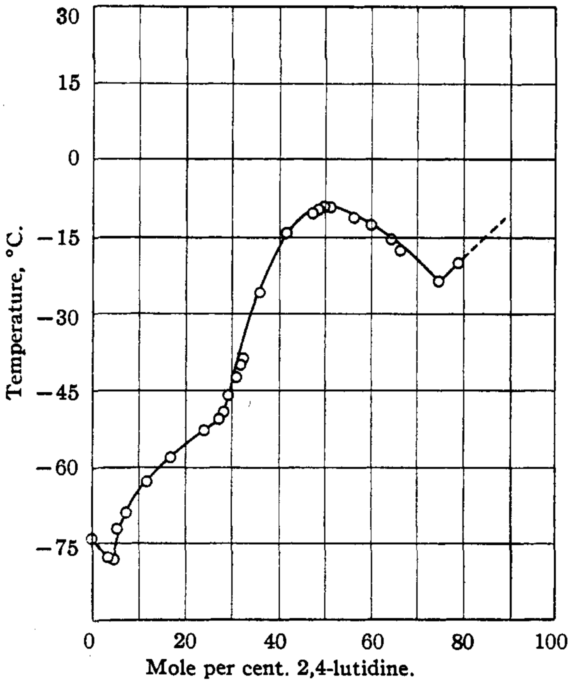

Fig. 3.—System sulfur dioxide–2,4-lutidine.

number or nature of solid cômpounds formed. Thus, the curve for the sulfur dioxide–2,3-lutidine system is strikingly similar to that for the sulfur dioxide–β-picoline system, a stable 1:1 solid compound being formed in each case. Likewise, the curve for the sulfur dioxide–2,4-lutidine system resembles closely that for the sulfur dioxide–γ-picoline system. Stable 1:1 solid compounds are formed in both cases; the unstable addition compound observed in the case of sulfur dioxide–2,4-lutidine appears to be either a 2:1 compound, corresponding exactly to that in the sulfur dioxide–γ-picoline system, or a 3:2 compound, which would correspond to the higher melting of the two compounds formed in the system sulfur dioxide–α-picoline.

In general, the slope of the sulfur dioxide–2,6-lutidine curve is markedly like that for sulfur dioxide–α-picoline. Stable 1:1 solid compounds are formed in both systems, but no stable solid analog of the 3:2 compound observed in the sulfur dioxide–α-picoline system was formed when 2,6-lutidine was used in place of α-picoline.

Summary

1. Temperature–composition data are presented for the three systems consisting of sulfur dioxide with 2,6-lutidine, 2,3-lutidine and 2,4-lutidine.

2. It has been shown that sulfur dioxide forms stable 1:1 solid addition compounds with each of the three lutidines studied. In addition, with 2,4-lutidine, either a 2:1 or a 3:2 compound, which undergoes transition near its melting point, is formed.

3. The behavior of sulfur dioxide in the formation of solid addition compounds with these three lutidines is compared with its behavior toward the picolines.

LAWRENCE, KANSAS RECEIVED AUGUST 25, 1947

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

Phase Equilibrium Studies on Pyridine–Amide Systems[1]

BY STEPHEN STEPHANOU,[2] CALVIN A. VANDERWERF AND HARRY H. SISLER[3]

In studies of the systems acetamide–ammonia and formamide–ammonia, previously reported from this Laboratory,[4] evidence for the existence of the addition compounds $CH_3CONH_2 \cdot NH_3$ and $HCONH_2 \cdot NH_3$ was presented. By analogy with the ammonium salts of acetic and formic acids and with the sodium salts of acetamide and formamide, these addition compounds were considered to be ammonium aquo-ammono salts, in which a single N-hydrogen atom of the amide is, in each case, involved in the bonding between the amide and ammonia molecules. Similarly, it was suggested that the formation of a second addition compound of probable formula $HCONH_2 \cdot 2NH_3$, formed in the formamide–ammonia system, may perhaps take place through the interaction of the second hydrogen atom on the amide group with an ammonia molecule. It was pointed out, however, that the possibility that a second molecule of ammonia might be joined by the sharing of its electron pair with the electron deficient carbon atom of formamide is not precluded.

In the present investigation, a series of systems consisting of pyridine with each of several different amides has been studied in an attempt to explore the possibility of the formation of addition compounds of amines with amides which have no hydrogen atom available for bonding. Choice of pyridine as the base was dictated by the following advantages: it has a convenient melting point, it exhibits little tendency to undercool, and, as a tertiary amine, it cannot undergo exchange reactions with amides. The N,N-disubstituted amides

[1] Abstracted from a thesis presented by Stephen Stephanou to the Graduate Faculty of the University of Kansas in partial fulfilment of the requirements for the Degree of Master of Science.

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[4] Sisler, Davidson, Stoenner and Lyon, THIS JOURNAL, 66, 1888 (1944); Sisler, VanderWerf and Stephanou, *ibid.*, 68, 2538 (1946).

used were studied in the order of increasing positive charge on the carbonyl carbon atom, as predicted on theoretical grounds.

Experimental[5]

Materials.—The pyridine was dried over sodium hydroxide pellets for at least two weeks and then distilled through a 5-foot packed column; b. p. 114.6° at 740 mm., f. p. (from cooling curve) −41.5°.

The formamide was purified as described previously.[4]

N-Phenylformamide was obtained by four hours of refluxing of aniline with formic acid. Recrystallized three times from diethyl ether, the product was isolated as colorless prisms, f. p. (from cooling curve) 45.3°.

N,N-Diethylacetamide, prepared by refluxing diethylamine with excess acetic anhydride for four hours, was purified by distillation through a 5-foot packed column; b. p. 90.1–91.0° at 30 mm.

N,N-Diphenylacetamide was prepared by acetylation of diphenylamine with acetic anhydride and was obtained as colorless needles, m. p. 100.1°, by repeated recrystallization from alcohol–water.

N,N-Diphenylformamide was isolated as colorless prisms, m. p. 71.5°, by the recrystallization from alcohol–water of the crude product obtained by refluxing diphenylamine with formic acid.

N-Methyldiacetamide, prepared from N-methylacetamide[6] by treatment with acetic anhydride, was purified by distillation through a 5-foot packed column; b. p. 114.0–114.5° at 61 mm., f. p. (from cooling curve) −25.0°.[7]

Anal. Calcd. for $C_6H_9O_2N$: N, 12.2. Found: N, 12.5, 12.4.

N-Methylphthalimide, obtained by the reaction of phthalic anhydride with methylamine, was purified by distillation; b. p. 285.0–286.1° at 736 mm., m. p. 133.1–133.5°.

Method.—The systems were studied by means of the freezing point method; all cooling curves were recorded directly by means of a Brown Electronik Strip Chart Potentiometer. The cell used was similar to the one described in a previous paper from this Laboratory.[8] All points were determined at least twice. Data obtained by this method are believed to be correct, even for the steeper portions of the freezing point curves, to 1.0°. In order to increase the accuracy, all equilibrium temperatures above 65° in the system pyridine-N-methylphthalimide were determined in sealed tubes as previously described.[9] Each f. p. determined by this method is believed to be correct within 0.7°.

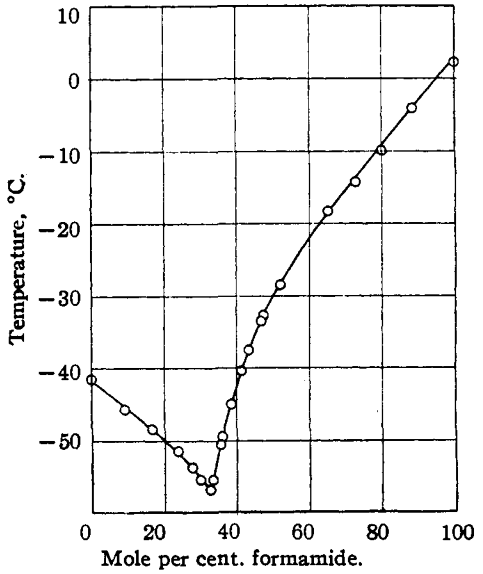

Fig. 1.—System pyridine–formamide.

Results

The experimental data are shown below in graphical form. Compositions, as indicated, are given in mole per cent.

As represented graphically in Figs. 1, 2, 3, 4, 5

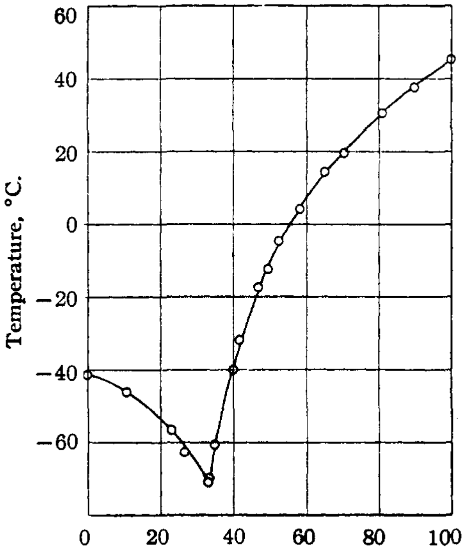

Fig. 2.—System pyridine–N-phenylformamide.

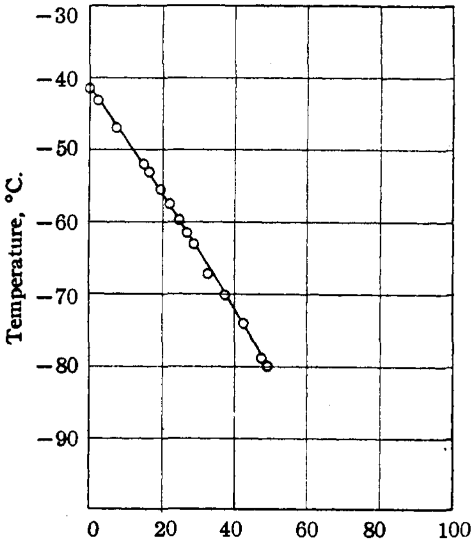

Fig. 3.—System pyridine–N,N-diethylacetamide.

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(5) All melting and boiling points are corrected.

(6) Best obtained by method of Galat and Elion, THIS JOURNAL, 65, 1566 (1943).

(7) D'Alelio and Reid, *ibid.*, 59, 109 (1937), reported a melting point of −46°. Our product boiled at 194.5° at 741 mm., in agreement with their value 194.2°.

(8) Davidson, Sisler and Stoenner, *ibid.*, 66, 779 (1944).

(9) Davidson and McAllister, *ibid.*, 52, 507 (1930).

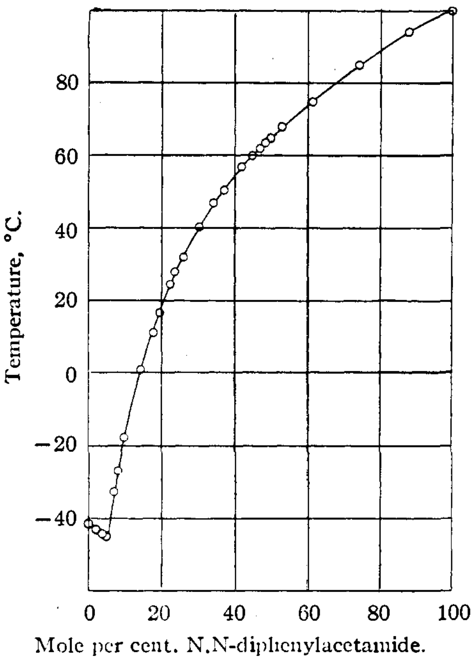

Fig. 4.—System pyridine-N,N-diphenylacetamide.

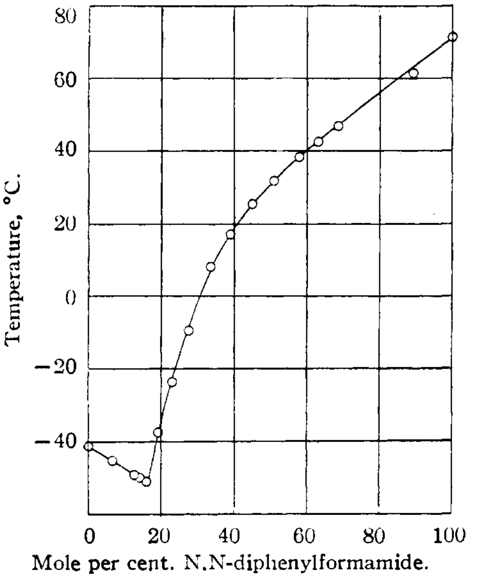

Fig. 5.—System pyridine-N,N-diphenylformamide.

and 6, respectively, the six systems consisting of pyridine with formamide, N-phenylformamide, N,N-diethylacetamide, N,N-diphenylacetamide, N,N-diphenylformamide and with N-methyldiacetamide showed no evidence of compound formation. The respective eutectics for the various systems are: 32.3 mole per cent. formamide, f. p. −56.7°; 33.0 mole per cent. N-phenylformamide, f. p. −71.0°; 4.9 mole per cent. N,N-diphenylacetamide, f. p. −44.9°; 16.2 mole per cent. N,N-diphenylformamide, f. p. −51.0°; 36.3 mole per cent. N-methyldiacetamide, f. p. −64.7°.

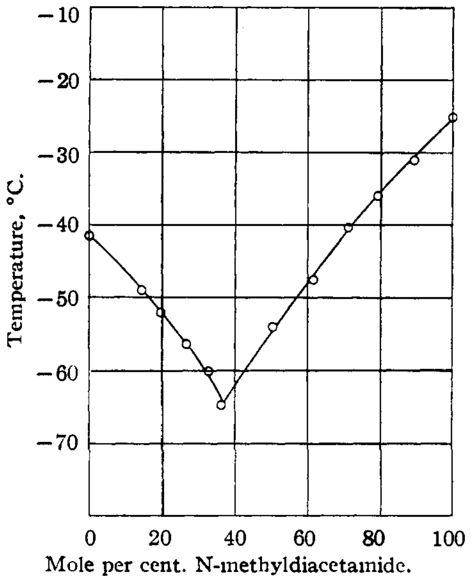

Fig. 6.—System pyridine-N-methyldiacetamide.

All attempts to establish points in the pyridine-N,N-diethylacetamide curve in the region from 49–100% amide were unsuccessful because of the extremely high viscosities of the glassy mixtures formed in this concentration range. The usual expedients, such as the sudden cooling, with liquid air, of a short platinum wire fused into the bottom

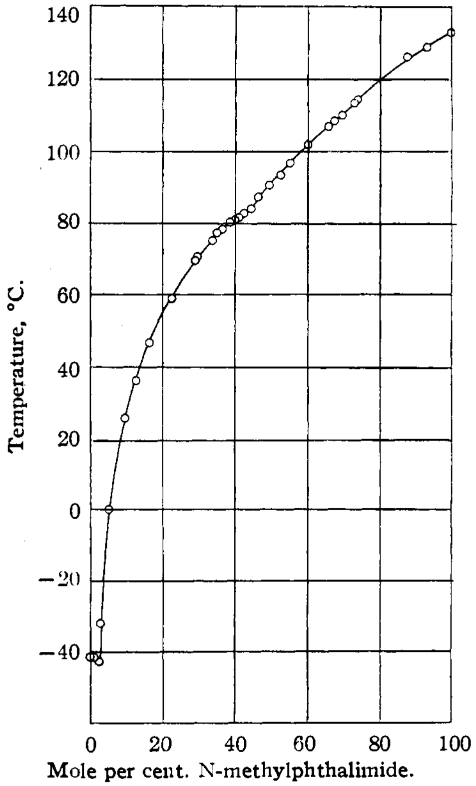

Fig. 7.—System pyridine-N-methylphthalimide.

of the freezing point cell, or prolonged storing of the mixture in a liquid air-bath, failed to induce crystallization.

As shown graphically in Fig. 7, pyridine and N-methylphthalimide form a single compound, $C_6H_4(CO)_2NCH_3 \cdot C_5H_5N$, which undergoes dissociation to N-methylphthalimide and solution at a temperature just below its melting point, which, as indicated by a short extrapolation, is approximately 82°. The eutectic is 2.2 mole per cent. N-methylphthalimide, f. p. −42.7°.

Discussion of Results

The fact that pyridine forms no solid addition compound with formamide in the temperature range indicated is not surprising, inasmuch as pyridine has a much lower tendency to donate its unshared electron pair than ammonia. Even with N-phenylformamide, which would be expected to be a stronger acid than formamide itself, no solid compound is observed. Of the remaining five amides, N,N-diethylacetamide, N,N diphenylacetamide, N,N-diphenylformamide, N-methyldiacetamide and N-methylphthalimide, the last-named would be expected, on the basis of the electron theory, to possess the most positive carbonyl carbon atom, *i. e.*, the carbonyl carbon atom of lowest electron density. It may possibly be significant, therefore, that, although no solid compound is formed between N,N-diethylacetamide, N,N-diphenylacetamide, N,N-diphenylformamide, or N-methyldiacetamide and pyridine, even down to eutectic temperatures as low as −51.0 and −64.7°, nevertheless N-methylphthalimide and pyridine form a solid 1:1 compound stable at temperatures up to 80°. At present, however, the structure of the compound $C_6H_4(CO)_2NCH_3 \cdot C_5H_5N$ is entirely problematical. Evidence for the type of bonding in such a solid binary compound can be obtained only by studies of the chemical reactions and crystal and molecular structures of the compound, and of the deviations from ideality in dilute solutions included in the system. Investigations of this type are in progress in this Laboratory.

Summary

1. Temperature–composition data are presented for the seven systems consisting of pyridine with each of the following amides: formamide, N-phenylformamide, N,N-diethylacetamide, N,N-diphenylacetamide N,N-diphenylformamide, N-methyldiacetamide and N-methylphthalimide.

2. It has been shown that N-methylphthalimide and pyridine form a 1:1 addition compound, the existence of which cannot be accounted for logically in terms of hydrogen-bonding.

LAWRENCE, KANSAS RECEIVED APRIL 4, 1947

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

The Absorption of Oxygen by Sodium in Liquid Ammonia: Evidence for the Existence of Sodium Superoxide

BY WILLIAM H. SCHECHTER, HARRY H. SISLER[1] AND JACOB KLEINBERG

It is well known that potassium, rubidium and cesium combine directly with oxygen[2] to form superoxides[3] of the formula MO_2, in which the oxygen exists as an ion of the structure $-:\ddot{O}\overset{\cdots}{-}\ddot{O}:$.[4] Similar compounds of alkaline earth metals have not yet been isolated in the pure form, although calcium superoxide (as an admixture to the extent of 8.7% in calcium peroxide) and barium superoxide (about 8% in barium peroxide) have been obtained by the action of 30% hydrogen peroxide on the corresponding hydroxides.[5] Magnetic studies on the impure calcium superoxide prepared in this manner demonstrate the presence of the O_2^- ion in this substance.[6]

Up to the present the existence of sodium superoxide has not been reported. Joannis[2a] described the preparation in liquid ammonia at −50° of an oxide of the formula Na_2O_3, whereas Kraus and Whyte[2d] found no evidence for any oxide higher than the peroxide in the same solvent at −33°. Preliminary experiments in this Laboratory at approximately −77° in liquid ammonia indicated the formation, by the direct combination of the elements, of a higher oxide than sodium peroxide. The results, however, were not consistent, indicating that the oxide formed was unstable; hence the oxygen uptake of sodium in liquid ammonia at −77° was studied quantitatively. In the present report an apparatus is described for the study of low temperature reactions in liquid ammonia involving gas absorption, and evidence for the existence of sodium superoxide is presented.

Experimental

The apparatus employed (Fig. 1) is suitable for use only at temperatures at which the vapor pressure of the solvent has a known, moderately low value. The volume of gas absorbed by a solution can be calculated from the observed change in volume in the gas buret C; if the reaction is not too rapid, it is possible to determine its rate.

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[1] Present address: Department of Chemistry, The Ohio State University, Columbus, Ohio.

[2] (a) Joannis, *Compt. rend.*, **116**, 1370 (1893); (b) Holt and Sims, *J. Chem. Soc.*, **65**, 432 (1894); (c) Rengade, *Ann. chim. phys.*, [8] **11**, 348 (1907); (d) Kraus and Whyte, THIS JOURNAL, **48**, 1781 (1926).

[3] The investigators cited above believed that they had obtained tetroxides of the formula M_2O_4; however, later work (ref. 4) showed the correct formula to be MO_2.

[4] Neuman, *J. Chem. Phys.*, **2**, 31 (1934).

[5] Traube and Schulze, *Ber.*, **54**, 1626 (1921).

[6] Ehrlich, *Z. anorg. Chem.*, **252**, 370 (1944).