alent amount of sulfuric acid. After filtration the solution was concentrated *in vacuo*, the remaining sirup dissolved in a little absolute alcohol and the solution mixed with absolute ether to incipient turbidity. The substance crystallized at 0° in colorless prisms which were easily soluble in water; yield, 1.1 g., m. p. 111–113°; $[\alpha]^{20}_D$ +12.6° in aqueous solution (*c*, 2.525).

Anal. Calcd. for $C_6H_{12}O_5$: C, 43.90; H, 7.37. Found: C, 43.94; H, 7.55.

Dianhydro-hexitol.—The solution of 1.8 g. of dianhydrohexitol diacetate in 12 cc. of alcohol was shaken for twenty-four hours with 7 g. of barium hydroxide in 80 cc. of water. After removal of the barium as described above and concentration of the solution *in vacuo*, there was obtained a sirup which was easily soluble in water and in alcohol; $[\alpha]^{20}_D$ +12.3° in aqueous solution (*c*, 3.079).

Anal. Calcd. for $C_6H_{10}O_4$: C, 49.31; H, 6.80. Found: C, 49.63; H, 7.02.

Reduction of the 6-*p*-Toluenesulfonyl 1,2-Acetone-glucofuranose by Sodium Amalgam.—Two grams of the substance was stirred at 15° for twenty-four hours in 30 cc. of 80% alcohol with 25 g. of 2% sodium amalgam. After neutralization and removal of the barium as described above, the solution was concentrated *in vacuo* and the residue extracted with ethyl acetate. The insoluble portion proved to be the sodium salt of *p*-toluenesulfinic acid. From its aqueous solution the crystalline acid with m. p. 88° was isolated. From the concentrated ethyl acetate solution the 1,2-acetone-glucofuranose with m. p. 158° crystallized; yield, 0.5 g. After evaporation of the mother liquid an oily residue (0.6 g.) remained.

The reduction was also carried out by simultaneous introduction of carbon dioxide gas. In this case a colorless substance was isolated which showed, after recrystallization from benzene, all the properties of the 5,6-anhydro-1,2-acetone-glucofuranose; yield, 70%, m. p. 132°. The crystals had $[\alpha]^{20}_D$ −26.4° in aqueous solution (*c*, 3.025).

Reduction of the 5,6-Di-*p*-toluenesulfonyl 1,2-Acetone-glucofuranose by Sodium Amalgam.—The reduction was carried out as described above. From the concentrated ethyl acetate extract a colorless substance was isolated which proved to be identical with 5-*p*-toluenesulfonyl 3,6-anhydro-1,2-acetone-glucofuranose; m. p. alone and also in admixture with an authentic sample 133°. The ethyl acetate mother liquor contained a small quantity of an oily product. When the reduction was carried out in the presence of carbon dioxide gas the starting material was recovered almost quantitatively.

Summary

The reductive cleavage of several *p*-toluenesulfonyl polyhydric alcohols by sodium amalgam has been investigated under various experimental conditions.

It has been found that the reaction, in consequence of reduction, often yields the corresponding polyhydric alcohols and *p*-toluenesulfinic acid, but simultaneously, as products of a competitive reaction, anhydro compounds may also form by splitting out of *p*-toluenesulfonic acid.

By treatment of 1-*p*-toluenesulfonyl 2,5-anhydro-L-iditol with sodium amalgam 2,5-anhydro-L-iditol in crystalline state has been prepared.

CLUJ-KOLOZSVÁR, RUMANIA RECEIVED JANUARY 31, 1947

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

Addition Compounds of Sulfur Dioxide with Three Isomeric Lutidines[1]

BY HENRY A. HOFFMAN AND CALVIN A. VANDERWERF

The interesting results obtained in a recent study[2] of the sulfur dioxide–pyridine and the three sulfur dioxide–picoline systems suggested the present investigation, which comprises temperature–composition equilibria studies of the three systems consisting of sulfur dioxide with each of the bases, 2,6-lutidine, 2,3-lutidine and 2,4-lutidine.

Experimental[3]

Purification of Materials.—Dry sulfur dioxide was obtained by passing commercial grade[4] gas through a train consisting of one tower containing saturated barium chloride solution, a tower containing calcium chloride granules, and finally two towers containing phosphoric anhydride. The rate of flow was controlled carefully and a slow stream of sulfur dioxide was allowed to pass through the train for an hour before the required amount was collected in a special freezing point cell[5] which was cooled in a Dry Ice-bath and attached to a drying tube containing phosphoric anhydride. The freezing point of sulfur dioxide collected in this manner was −74.0°.[6]

Purification of 2,6-lutidine[7] was accomplished through the crystalline urea–2,6-lutidine complex reported by Reithof.[8] The crystals of the complex were washed first with cold water, then with alcohol, and finally steam distilled. The portion of distillate boiling constantly at 95.6° under a pressure of 739 mm. was made alkaline with sodium hydroxide pellets and the lutidine layer separated and dried over three separate portions of sodium hydroxide pellets. Distillation of the dried product through a Todd column into a receiver protected from the atmosphere by means of a drying tube containing potassium hydroxide yielded 2,6-lutidine which boiled at 143.7°[9] at 741 mm. and gave a freezing point (from cooling curve) of −5.9°.[10]

The 2,3-lutidine was purified through a previously unreported urea–2,3-lutidine complex which melted at 119.8–121.7°. The crystalline complex was washed with cold water, then with alcohol, and dried. Fusion of the

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[1] Abstracted from a thesis presented by Henry A. Hoffman to the Graduate Faculty of the University of Kansas in partial fulfilment of the requirements for the degree of Master of Arts.

[2] K. R. Hoffman and VanderWerf, THIS JOURNAL, **68**, 997 (1946).

[3] All boiling points are corrected.

[4] Furnished by the Ohio Chemical and Mfg. Co., Cleveland, Ohio.

[5] Davidson, Sisler and Stoenner, THIS JOURNAL, **66**, 779 (1944).

[6] Dry sulfur dioxide prepared according to the method of Hoffman and VanderWerf (ref. 2) gave essentially the same results as the tank product described above despite the slight difference noted in the freezing point.

[7] All three lutidines used were obtained from the Reilly Tar and Chemical Company.

[8] U. S. Patent 2,295,606, September 15, 1942.

[9] Lidstone, *J. Chem. Soc.*, **241** (1940), reported the value 144.4° at 760 mm.

[10] In exact agreement with the value reported by Coulson and Jones, *J. Soc. Chem. Ind.* (*London*), **65**, 169 (1946).

dry material brought about decomposition with the formation of two layers. The top layer, consisting of 2,3-lutidine, was separated, dried for two weeks over sodium hydroxide pellets, refluxed over solid sodium hydroxide, and finally fractionated through a Todd column to yield the pure amine, b. p. 161.0° at 736 mm.,[11] f. p. (from cooling curve), −9.8°.

The 2,4-lutidine was first distilled through a three-foot Vigreux column, a middle fraction boiling between 142 and 150° at 743 mm. being collected in a receiver protected from the atmosphere by means of a drying tube containing sodium hydroxide pellets. The distillate was stored over sodium hydroxide pellets for two weeks, then refluxed over solid sodium hydroxide for twenty-four hours, and finally fractionated through a Todd column. The pure material boiled at 158.5° at 742 mm.; repeated attempts to obtain a freezing point resulted only in the formation, at low temperatures, of an extremely viscous glass.

Apparatus and Procedure.—A freezing point cell similar to that described in a previous publication from this Laboratory[5] was employed in the determination of the temperature–composition diagrams. A Leeds and Northrup Micromax recorder, calibrated at the melting point of ice, the boiling point of ammonia, the freezing point of pyridine, and the sublimation point of carbon dioxide, was used for the direct recording of the cooling curves. Appreciable reduction of the abnormal supercooling often encountered when an excess of any of the lutidines was present could be realized if the sample was first cooled rapidly until crystallization occurred, then warmed until the last crystal just disappeared, and finally cooled again, this time very slowly. The level to which the temperature rose immediately after the first break in the cooling curve for the second cooling, was taken as the equilibrium temperature. All freezing points were determined at least twice. Data obtained in this way are believed to be correct, even for the steeper portions of the freezing point curves, to 1.5°.

Results

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

A. As shown in Fig. 1, sulfur dioxide and 2,6-lutidine form a single stable compound, $SO_2 \cdot (CH_3)_2C_5H_3N$, which melts congruently at 4.0°. The eutectics are: (1) 3.7 mole per cent. 2,6-lutidine, f. p. −75.5°, and (2) 78.1 mole per cent. 2,6-lutidine, f. p. −18.0°.

B. As indicated in Fig. 2, sulfur dioxide and 2,3-lutidine form a single stable compound, $SO_2 \cdot (CH_3)_2C_5H_3N$, which melts congruently at 18.5°. The eutectics are: (1) 8.7 mole per cent. 2,3-lutidine, f. p. −78.8°, and (2) 76.5 mole per cent. 2,3-lutidine, f. p. −17.5°.

C. As indicated in Fig. 3, sulfur dioxide and 2,4-lutidine form two compounds, (1) probably either $2SO_2 \cdot (CH_3)_2C_5H_3N$ or $3SO_2 \cdot 2(CH_3)_2C_5H_3N$, which undergoes decomposition into sulfur dioxide and solution at a temperature somewhat below its melting point and (2) $SO_2 \cdot (CH_3)_2C_5H_3N$, which melts congruently at −8.3°. The eutectics are: (1) 4.9 mole per cent. 2,4-lutidine, f. p. −78.0°, and (2) 75.1 mole per cent. 2,4-lutidine, f. p. −23.1°. All attempts to establish points in the region beyond 80.0% 2,4-lutidine were unsuccessful because of the extremely high viscosities of the glassy mixtures formed in these concentration ranges.

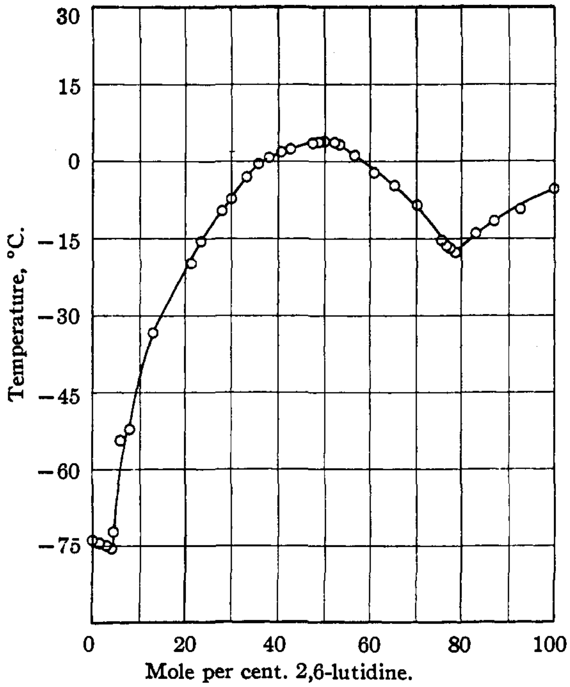

Fig. 1.—System sulfur dioxide–2,6-lutidine.

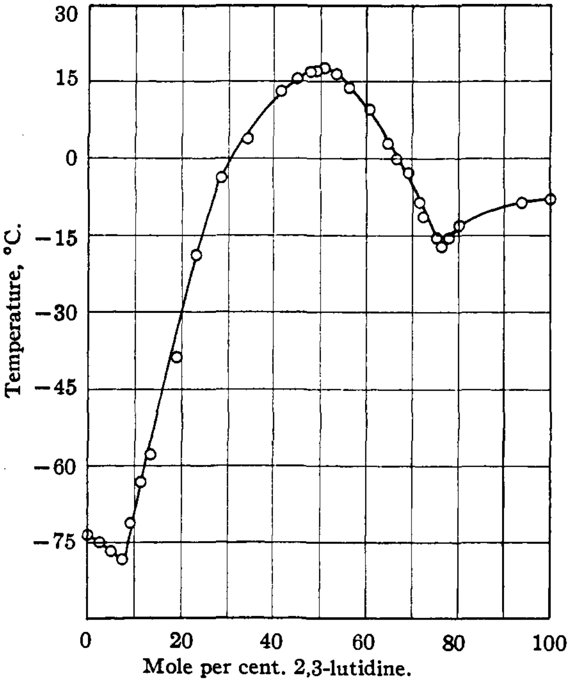

Fig. 2.—System sulfur dioxide–2,3-lutidine.

Discussion

A comparison of the behavior of the picolines and of the lutidines with respect to the formation of stable solid compounds with sulfur dioxide reveals that, in general, the presence of an additional methyl group, located at the α-position in the various picoline molecules, has little effect on the

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[11] Finkelstein and Elderfield, *J. Org. Chem.*, **4**, 365 (1939), reported a boiling point of 162–164° at 760 mm.

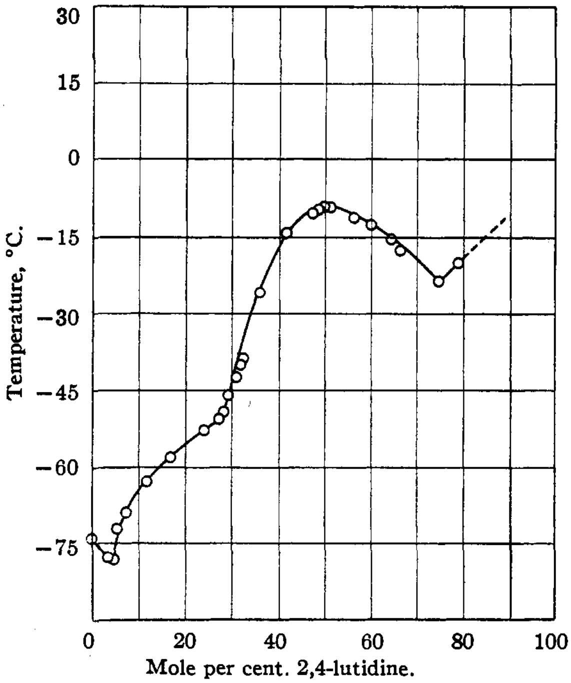

Fig. 3.—System sulfur dioxide–2,4-lutidine.

number or nature of solid compounds 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.

[2] Kansas University Fellow, 1945.

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

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