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

Addition Compounds of Sulfur Dioxide with Pyridine and the Picolines[1]

BY KENNETH R. HOFFMAN AND CALVIN A. VANDERWERF

Despite the great interest which has been evinced in the structure of addition compounds of sulfur dioxide with amines,[2] only a few complete temperature–composition equilibrium diagrams for sulfur dioxide–amine systems have been reported.[3] The fact that an addition compound of sulfur dioxide with pyridine has been described,[4] suggested that this system, together with those of sulfur dioxide with the three isomeric picolines, should be worthy of further investigation. The present study consists of temperature–composition equilibria studies of these four systems.

Experimental[5]

Preparation and Purification of Materials.—Dry sulfur dioxide was prepared by the dropwise addition of C. P. sulfuric acid to C. P. sodium sulfite. The liberated sulfur dioxide was passed through concentrated sulfuric acid to remove sulfur trioxide, then through towers containing phosphoric anhydride, and collected in a special cell which was cooled by means of a Dry Ice-bath and attached to a closed drying tube containing phosphoric anhydride. Here it was stored for three weeks, during which time the freezing point gradually rose from −75.0° to a maximum of −72.4°.[6]

The sulfur dioxide was distilled from the storage cell directly into the freezing point cell.

The pyridine was first dried for at least three weeks over sodium hydroxide pellets, then distilled twice through a 50-cm. Vigreux column into a receiver protected from the atmosphere by a tube containing potassium hydroxide and soda lime, and finally stored in a dark bottle; b. p. 114.1° at 730 mm.; f. p. −41.5°.[7]

Each of the picolines[8] was first stored over sodium hydroxide pellets for at least two weeks. The α-picoline was then distilled twice through a special, 5-foot packed column; b. p. 128.1° at 740 mm.; f. p. (from cooling curve) −64.2°.[9]

The β-picoline was distilled through a 50-cm. Vigreux column, separated by fractional freezing, refluxed for forty-eight hours with sulfur and a small amount of sodium hydroxide,[10] again distilled, refluxed over sodium hydroxide pellets for twenty-four hours, and finally distilled through the 5-foot column mentioned above; b. p. 141.7° at 735 mm.; f. p. (from cooling curve) −18.3°.

The γ-picoline was first distilled through a 50-cm. Vigreux column, separated by fractional freezing, and then converted to the hydrochloride, which was recrystallized from hydrochloric acid.[11] A water solution of the pure crystals was neutralized with excess potassium hydroxide and the γ-picoline extracted with ether. After the combined extracts had been dried over potassium carbonate, and the ether removed, the residue was refluxed with barium oxide for forty-eight hours, and distilled through a 5-foot column; b. p. 142.8° at 740 mm.; f. p. (from cooling curve) 3.5°.

Apparatus and Procedure.—A freezing point cell similar to that described in a previous publication from this laboratory[12] was employed in the determination of the temperature–composition diagrams. The cooling curves were recorded directly by means of a Leeds and Northrup Micromax recorder, which had been calibrated at the m. p. of ice, the b. p. of ammonia, the f. p. of pyridine, and the sublimation point of carbon dioxide. It was found that the abnormally great supercooling, which was encountered when an excess of any of the picolines was present, was reduced appreciably if the sample was first cooled rapidly until crystallization occurred, then warmed until the last crystal just disappeared, then cooled slowly. The level to which the temperature rose, immediately after the first break in the cooling curve for the second cooling, was taken to be the equilibrium temperature. Each freezing point was determined at least twice. Data so obtained 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

TABLE I

SYSTEM SULFUR DIOXIDE–PYRIDINE

Mole % pyridine	Temp., °C.	Mole % pyridine	Temp., °C.
Solid phase SO_2		49.2	− 7.0
0.0	−72.4	49.8	− 7.4
4.2	−74.5	50.8	− 7.4
8.5	−77.2	53.0	− 7.4
13.2	−82.0	53.9	− 8.6
16.0	−87.3	56.2	−11.1
		57.5	−11.2
Solid phase $SO_2 \cdot C_5H_5N$		65.0	−21.6
17.0	−84.5	71.0	−32.3
23.2	−68.0	75.7	−42.5
25.4	−61.8	79.2	−50.8
26.6	−59.0	80.5	−54.0
30.6	−46.6	Solid phase C_5H_5N	
35.1	−31.8	83.3	−52.0
41.3	−17.8	89.6	−47.4
45.2	−11.6	100.0	−41.5

---

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

[2] See for example: (a) Jander and Wickert, *Z. physik. Chem.*, **A178**, 57 (1936); (b) Jander and Mesech, *ibid.*, **A183**, 255 (1939); (c) Jander and Wickert, *Ber.*, **70B**, 251 (1937); (d) Jander, *Naturwissenschaften*, **48**, 779 (1938); (e) **49**, 793 (1938); (f) Jander, Knöll and Immig, *Z. anorg. allgem. Chem.*, **232**, 229 (1937); (g) Jander and Immig, *ibid.*, **233**, 295 (1937); (h) Wickert, *ibid.*, **239**, 89 (1938); (i) Bright and Jasper, THIS JOURNAL, **63**, 3486 (1941); **65**, 1262 (1943); **66**, 105 (1944); (j) Burg, *ibid.*, **65**, 1629 (1943); (k) Bateman, Hughes, and Ingold, *J. Chem. Soc.*, 243 (1944).

[3] For recent examples, see: (a) Albertson and Fernelius, THIS JOURNAL, **65**, 1687 (1943); (b) Bright and Fernelius, *ibid.*, **65**, 637 (1943).

[4] (a) André, *Compt. rend.*, **130**, 1714 (1900); (b) Hill and Fitzgerald, THIS JOURNAL, **57**, 250 (1935), suggested that a compound of sulfur dioxide with pyridine exists at low temperatures.

[5] All boiling points are corrected.

[6] Points ranging from −75.5 to −72.3° have been reported. Representative values are given in the following references: (a) Walden and Centnerszwer, *Z. physik. Chem.*, **42**, 432 (1903); (b) Baumé, *Compt. rend.*, **148**, 1322 (1909); (c) Giauque and Stephenson, THIS JOURNAL, **60**, 1389 (1938); (d) Bond and Crone, *ibid.*, **56**, 2028 (1934); (e) Booth and Martin, *ibid.*, **64**, 2198 (1942).

[7] Hazlet and Morrow, *ibid.*, **64**, 2625 (1942), reported −41.7°.

[8] Obtained through the courtesy of the Koppers Co., Pittsburgh, Pa.

[9] Jaeger, *Z. anorg. allgem. Chem.*, **101**, 157 (1917), reported −64.0°.

[10] Method of Cislak and Wheeler, British Patent 556,533, Oct. 8, 1943.

[11] Leis and Curran, THIS JOURNAL, **67**, 79 (1945).

[12] Davidson, Sisler and Stoenner, *ibid.*, **66**, 779 (1944).

tabular and graphical form. Compositions, as indicated, are given in mole %. In the system sulfur dioxide–γ-picoline, the points on the solidus curve are represented by two concentric circles.

A. As shown in Fig. 1, sulfur dioxide and pyridine form a single stable compound, $SO_2 \cdot C_5H_5N$, which melts congruently at −7.4°. The eutectics are: (1) 16.0 mole % pyridine, f. p. −87.3° and (2) 80.5 mole % pyridine, f. p. −54.0°.

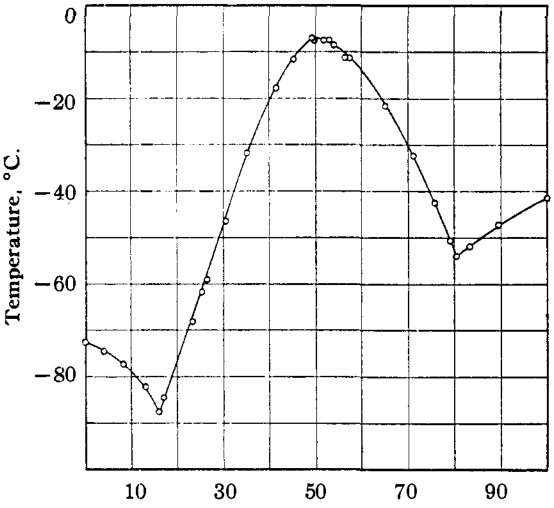

Fig. 1.—Sulfur dioxide–pyridine.

Table II

System Sulfur Dioxide–α-Picoline

Mole % α-picoline	Temp., °C.
Solid phase SO_2	
0.0	−72.4
2.2	−74.0
4.8	−75.0
5.5	−75.3
7.6	−76.8
Solid phase $3SO_2 \cdot 2(CH_3C_5H_4N)$	
8.0	−76.2
9.7	−66.6
12.8	−57.2
13.7	−51.3
16.8	−43.2
16.9	−42.8
20.7	−36.5
21.0	−36.2
22.9	−33.5
25.4	−29.5
29.2	−25.6
29.8	−25.1
33.9	−20.8
35.9	−19.3
36.6	−18.7
39.5	−17.7
40.0	−17.8
40.7	−17.9
41.5	−17.6
42.0	−18.0
43.7	−18.7
45.5	−19.5
46.3	−20.1
Solid phase $SO_2 \cdot CH_3C_5H_4N$	
46.8	−20.0
48.3	−19.6
49.4	−19.5
50.0	−19.4
51.3	−19.8
53.4	−21.5
55.8	−24.6
59.5	−30.6
62.8	−36.9
64.1	−39.7
66.7	−44.0
68.2	−47.7
70.2	−52.6
71.8	−55.5
73.5	−59.8
75.0	−63.4
76.6	−69.2
77.8	−73.5
79.3	−78.9
Solid phase $CH_3C_5H_4N$	
79.7	−78.4
80.3	−77.6
81.7	−74.6
83.8	−73.0
90.4	−67.9
100.0	−64.2

B. As indicated in Fig. 2, sulfur dioxide and α-picoline form two stable compounds, (1) $3SO_2 \cdot 2CH_3C_5H_4N$, which melts congruently at −17.8°, and (2) $SO_2 \cdot CH_3C_5H_4N$, which melts congruently at −19.4°. The three eutectics are: (1) 7.6 mole % α-picoline, f. p. −76.8°; (2) 46.3 mole % α-picoline, f. p. −20.1°; and (3) 79.3 mole % α-picoline, f. p. −78.9°. Because of the unexpected course of the curve at 40 mole %

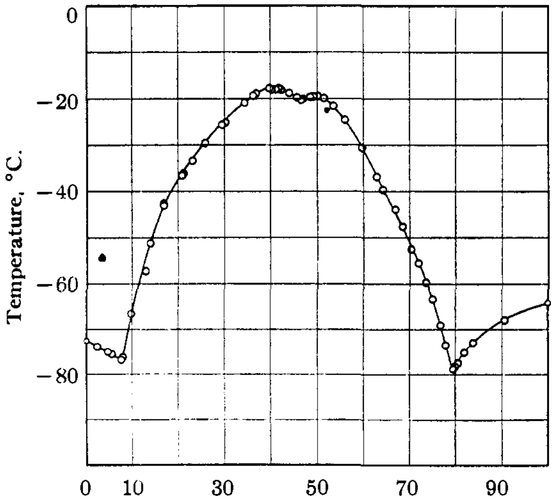

Fig. 2.—Sulfur dioxide–α-picoline.

Table III

System Sulfur Dioxide-β-Picoline

Mole % β-picoline	Temp., °C.
Solid phase SO_2	
0.0	−72.4
4.1	−76.6
7.7	−78.9
13.4	−84.7
15.4	−86.9
Solid phase $SO_2 \cdot CH_3C_5H_4N$	
18.7	−76.0
25.9	−59.1
26.5	−57.1
32.3	−46.7
35.9	−39.8
37.8	−36.0
38.2	−35.1
43.9	−25.8
45.0	−23.2
46.9	−19.2
48.2	−16.9
49.7	−15.0
51.5	−15.0
53.8	−16.3
56.1	−19.5
59.8	−25.3
63.4	−31.7
65.8	−36.8
68.3	−41.9
71.5	−50.3
74.4	−56.2
75.8	−60.0
77.7	−63.7
79.0	−66.8
Solid phase $CH_3C_5H_4N$	
80.0	−62.8
81.4	−58.4
85.9	−44.6
90.3	−33.9
94.5	−26.4
100.0	−18.3

α-picoline, the region from 35 to 55 mole % α-picoline was studied with special care; the data reported below are representative of a much larger number of independent determinations made on different samples. The evidence for the eutectic at 46.3 mole % α-picoline and of a surprisingly stable compound at 40.0 mole % α-picoline is unmistakable.

C. As shown graphically in Fig. 3, sulfur dioxide and β-picoline form a single stable compound, $SO_2 \cdot CH_3C_5H_4N$, which melts congruently at −15.0°. The two eutectics are: (1) 15.4 mole % β-picoline, f. p. −86.9°, and (2) 79.0 mole % β-picoline, f. p. −66.8°.

D. As represented in Fig. 4, sulfur dioxide and γ-picoline form two compounds, (1) $2SO_2 \cdot CH_3C_5H_4N$, which, so nearly as is possible to determine, undergoes transition at its m. p., −26.5°, and (2) $SO_2 \cdot CH_3C_5H_4N$, which is stable at its m. p., 5.0°. The solid solutions observed in this system were clearly established in the area from 26.9 to 100 mole % γ-picoline. Definite evidence of solid solutions was observed in the remainder of the curve, but the exact nature of the solidus curve was difficult to determine, owing to low temperatures, high viscosities, and a tendency toward supercooling.

TABLE IV

SYSTEM SULFUR DIOXIDE–γ-PICOLINE

Mole % γ-picoline	Temp., °C. Liquidus	Temp., °C. Solidus
Solid phase SO_2		
0.0	−72.4	
1.1	−73.4	
2.2	−74.0	
3.4	−74.8	
4.3	−75.5	
Solid phase solid solution I[a]		
4.9	−74.0	
6.0	−68.0	
6.6	−65.4	
6.5	−65.0	
7.2	−62.5	
8.8	−60.3	
9.7	−59.2	
10.0	−59.2	
11.4	−56.2	
11.8	−56.4	
14.5	−51.2	
14.8	−51.5	
16.1	−48.0	
18.0	−45.0	
18.8	−43.8	
20.6	−40.9	
21.5	−38.7	
23.4	−35.9	
24.0	−33.7	
24.8	−33.8	
26.9	−30.8	−38.8
27.8	−29.1	−36.9
28.6	−27.8	−36.2
29.5	−28.2	
29.7	−27.8	−34.2
29.9	−27.0	
30.9	−27.6	
31.2	−27.2	−30.9
31.5	−26.6	
32.2	−27.0	
32.7	−26.4	
Solid phase solid solution II[b]		
33.5	−24.8	−26.5
35.2	−21.2	−26.6
36.5	−17.3	−23.1
37.3	−14.7	−21.0
38.4	−12.8	
39.5	− 9.3	−15.8
41.2	− 5.4	−11.0
41.7	− 4.2	− 9.3
44.7	+ 1.5	− 0.9
45.9	+ 3.8	+ 2.3
46.7	+ 4.8	
49.0	+ 5.2	
49.5	+ 5.0	
50.0[c]	+ 5.0	
Solid phase solid solution III[d]		
51.0	+ 4.8	
54.4	+ 3.4	0.0
55.9	+ 2.3	− 1.6
58.3	0.0	− 6.4
		Eutectic (III + IV[e])
61.4	− 5.1	−25.1
64.0	−10.0	−25.0
67.1	−15.0	−24.5
68.9	−19.8	−24.9
69.6	−24.0	
70.0	−24.9	
Solid phase solid solution IV		
72.6	−20.8	−24.7
76.0	−16.5	−25.0
79.8	−12.5	−18.8
83.5	− 8.3	−14.0
91.0	− 3.3	− 6.2
94.9	0.0	− 2.1
100.0	+ 3.5	

[a] Consisting of $2SO_2 \cdot CH_3C_5H_4N + SO_2$. [b] Consisting of $SO_2 \cdot CH_3C_5H_4N + SO_2$. [c] Pure $SO_2 \cdot CH_3C_5H_4N$ is obtained only at this composition. [d] Consisting of $SO_2 \cdot CH_3C_5H_4N + CH_3C_5H_4N$. [e] Consisting of $CH_3C_5H_4N + SO_2 \cdot CH_3C_5H_4N$.

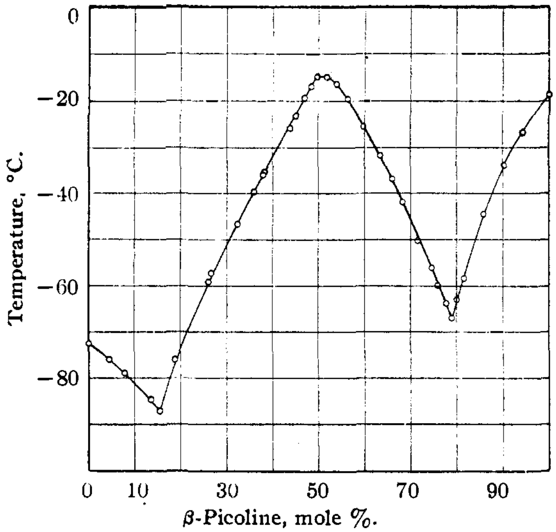

Fig. 3.—Sulfur dioxide-β-picoline.

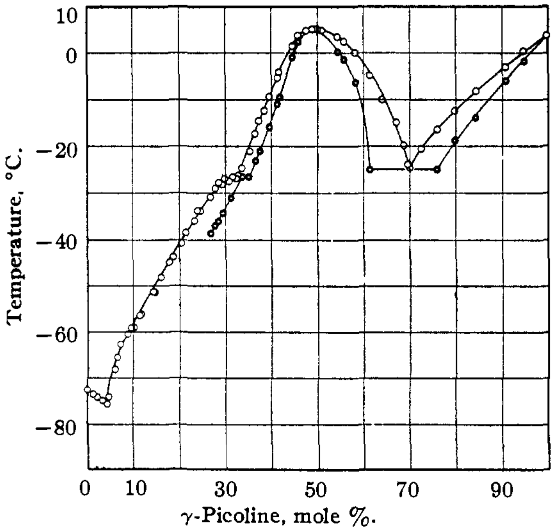

Fig. 4.—Sulfur dioxide–γ-picoline: ○, liquidus; ◉, solidus.

Discussion

The existence of a 1:1 addition compound between sulfur dioxide and pyridine, predicted by

Hill and Fitzgerald[4b] on the basis of the marked absorption of sulfur dioxide by pyridine with the formation of an orange-red solution, is clearly indicated by the data of Table I. The solutions usually obtained in our study of the system sulfur dioxide–pyridine, however, were a light yellow color throughout the entire range of concentrations. Red or orange-red solutions were observed only when moisture was admitted to the system or when samples containing an excess of pyridine were heated above 100° for several hours in a sealed tube.

Addition of appreciable amounts of water to the sulfur dioxide–pyridine system at any concentration led to the immediate formation of a colorless, crystalline solid which was stable at room temperature provided an excess of solution was present. The solid was probably a mixture of the acid and normal sulfites analogous to those observed in the case of sulfur dioxide and aniline.[13] This observation suggests that the solid which André[4a] obtained upon passing sulfur dioxide into pyridine at room temperature may, perhaps, be attributed to the presence of moisture, just as Bateman, Hughes and Ingold[2k] account for the high melting solid which Jander and Wickert[2a] reported in the sulfur dioxide–triethylamine system.

Similar color and precipitation phenomena were observed, as well, in all of the sulfur dioxide–picoline systems. Unlike most of the previously reported addition compounds of sulfur dioxide with simple amines, those with pyridine and with the three picolines are colorless.

From an electronic standpoint, it would be predicted that the substitution of a methyl group at the β-position in pyridine would alter its basicity to a lesser degree than a similar substitution at either the α- or the γ-position. The striking similarity of the sulfur dioxide–pyridine and sulfur dioxide–β-picoline curves, each of which differs markedly from both the sulfur dioxide–α-picoline and sulfur dioxide–γ-picoline curves, verifies this prediction.

The fact that sulfur dioxide forms not only a 1:1, but also a 2:1 compound with γ-picoline is not altogether anomalous,[14] and may be explained quite simply on the basis of the solvation of the simple 1:1 coördination compound with one mole of sulfur dioxide.

The 3:2 compound formed in the sulfur dioxide–α-picoline system, which is without any exact analogy in the literature, is difficult to account for unless we assume a structure of the general type proposed by Jander and Wickert,[2a] in which the sulfite ion is solvated by a single molecule of sulfur dioxide.

Summary

1. Temperature–composition data are presented for the four systems consisting of sulfur dioxide with pyridine and with each of the three isomeric picolines.

2. It has been shown that sulfur dioxide forms 1:1 addition compounds with pyridine and with each of the three isomeric picolines. In addition a stable 3:2 compound is formed with α-picoline and a 2:1 compound, which undergoes transition at its melting point, with γ-picoline.

3. Unsuccessful attempts to formulate reasonable structures for all of the compounds of sulfur dioxide with pyridine and with the picolines on the basis of any single, generally accepted theory of the addition reactions of sulfur dioxide, have indicated the necessity of further investigation of the structure of such addition compounds. Studies of this type are being conducted in this laboratory at the present time.

Lawrence, Kansas Received February 11, 1946

---

(13) Hill, This Journal, 53, 2598 (1931).

(14) Burg, ref. 2j, cited evidence indicating that the 1:1 addition compound of sulfur dioxide with trimethylamine is solvated in liquid sulfur dioxide.