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

Compound Formation between the Picolines and *o*-Chlorophenol

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The fact that a simple electron-releasing or electron-withdrawing effect, either *I* or *T*, of a substituent in the benzene ring, is transmitted mainly to the *ortho*- and *para*-positions, is both well established experimentally and easily explainable theoretically.[1] In toluene, for example, the electron release of the methyl group is transmitted more effectively to the *ortho*- and *para*-positions than to the *meta*-position; evidence for this conclusion is to be found in the fact that attack on the toluene molecule by electrophilic substituting reagents occurs preferentially at the *ortho*- and *para*-carbon atoms.

Similarly, the introduction of a methyl group at the α- or γ-position of the pyridine nucleus might be expected to increase the basicity of the nitrogen atom more markedly than would the substitution of a similar group in the β-position. Indeed, the fact that α- and γ-picoline, but not β-picoline, undergo numerous condensation reactions which depend upon the transfer, as a proton, of an acid methyl hydrogen,[2] indicates that electron withdrawal from the methyl group is considerably greater in the α- and γ-isomers than in β-picoline. It is somewhat surprising, therefore, that the dissociation constants for the picolines, although they do reveal a marked increase in basicity as compared with pyridine itself, nevertheless indicate that β-picoline is quite as basic as its γ-isomer. The K_b values, as determined by Constam and White[3] from conductivity measurements on water solutions of the pyridinium and picolinium picrates, are as follows

Pyridine	3.0×10^{-9}
α-Picoline	3.2×10^{-8}
β-Picoline	1.1×10^{-8}
γ-Picoline	1.1×10^{-8}

The present study was designed to make possible a comparison of the basicities of the picolines according to their tendencies toward compound formation with an acid of moderate strength. Choice of *o*-chlorophenol ($K_a = 7.7 \times 10^{-11}$) was dictated by its convenient melting point (8.0°) and by the fact that a freezing point study of the system *o*-chlorophenol–pyridine has been reported previously.[4]

Experimental

Purification of Materials.—The *o*-chlorophenol, obtained from the Eastman Kodak Co., was purified by distillation through a 50-cm. Vigreux column; b. p. 90°[5] at 50 mm.; n^{25}D 1.5565; f. p. (from cooling curve) 8.0°.[6]

The picolines, obtained from the Reilly Tar and Chemical Corp., were stored over sodium hydroxide pellets for two weeks prior to final purification. The α-picoline was then distilled through a 50-cm. Vigreux column; b. p. 129.0–129.3° at 736 mm.; f. p. (from cooling curve) −64.2°.[7]

Both the β- and γ-picolines were purified by fractional freezing; for β-picoline, f. p. (from cooling curve) −20.8°; for γ-picoline, f. p. (from cooling curve) 1.6°. No values for these constants could be found in the literature.

Apparatus and Procedure.—A freezing point cell similar to that described in a previous publication from this Laboratory[8] was employed in the determination of the temperature–composition diagrams for the three systems comprising *o*-chlorophenol and the three isomeric picolines. The temperature–time 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 supercooling was appreciably reduced if the sample was allowed to cool rapidly until crystallization occurred, then warmed until the last crystal had disappeared, and finally cooled again, this time 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. 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°.

All attempts to establish points in the *o*-chlorophenol–α-picoline curve in the region from 28 to 34% α-picoline, and in the *o*-chlorophenol–γ-picoline curve in the region from 20 to 32% γ-picoline, were unsuccessful because of the extremely high viscosities of the glassy mixtures formed in these concentration ranges. The conventional expedients, such as the introduction of a crystal of the expected solid phase, or the sudden cooling, with liquid air, of a short platinum wire fused into the bottom of the freezing point cell, failed to induce crystallization.

As a further means of comparison of the basicities of the three picolines, it seemed of interest to compare the f. p. depression curve for dilute solutions of *o*-chlorophenol in each of the three liquids with the calculated ideal curve for each of these solvents. The courses of the ideal curves were calculated (to $N = 0.9$) from the Schröder equation

$$\ln N = \frac{\Delta H}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)$$

where N is the mole fraction of solvent, ΔH its heat of fusion, R the gas constant, and T_0 and T the f. p. of pure solvent and of solution, respectively. The values of ΔH, which are not available in the literature, were determined indirectly from the molal f. p. constants by means of the equation

$$\Delta H = \frac{RT_0^2M}{1000K_f}$$

where M is the molecular weight of the solvent, and K_f the observed molal freezing point constant. The values of K_f were, in turn, determined experimentally from f. p. data on dilute solutions of the picolines in each other. These values of K_f and the corresponding values of ΔH are given in Table I.

The f. p. depression curves for *o*-chlorophenol were determined mainly by means of the Micromax recorder as described above, but in each case several points were checked by the use of a pentane thermometer which had

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[1] *Cf.* Remick, "Electronic Interpretations of Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 89–110.

[2] Ref. 1, p. 130.

[3] Constam and White, *Am. Chem. J.*, **29**, 1 (1903).

[4] Bramley, *J. Chem. Soc.*, **109**, 469 (1916).

[5] All boiling points are corrected.

[6] In complete agreement with the value given by Bramley, ref. 4.

[7] Jaeger, *Z. anorg. allgem. Chem.*, **101**, 157 (1917), reported the value −64°.

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

TABLE I

	K_f	ΔH
α-Picoline	6.70	1200
β-Picoline	6.21	1888
γ-Picoline	6.32	2210

been calibrated by the Bureau of Standards. The points so determined showed no appreciable divergence from the other data.

The three f. p. depression curves, with the corresponding ideal curves, are shown in Fig. 5.

Results

Below in tabular and graphical form are shown the experimental data. Compositions, as indicated, are given in mole %. Extrapolated portions of the curves are represented by broken lines. Freezing points of metastable forms are enclosed in brackets in the tables, and are represented in the curves by triangles. For purposes of comparison, the curve for *o*-chlorophenol–pyridine, as determined by Bramley, is shown in Fig. 1.

TABLE II

SYSTEM *o*-CHLOROPHENOL–α-PICOLINE

% α-picoline	Temp., °C.	% α-picoline	Temp., °C.
Solid phase HOC_6H_4Cl		54.5	−13.6
0.0	8.0	57.1	−16.0
6.0	4.7	59.0	−17.9
10.0	2.5	61.5	−21.2
14.1	− 2.8	63.1	−23.8
16.2	− 6.4	65.9	−28.0
20.0	−12.0	68.1	−31.7
22.2	−18.4	70.8	−37.1
24.4	−23.9	73.7	−41.2
26.7	−31.7	77.0	−48.1
		78.9	−51.8
Solid phase $CH_3C_5H_4N\cdot HOC_6H_4Cl$		82.5	−60.0
		85.3	−66.4
36.7	−30.0	89.1	−75.6
40.1	−23.9	91.4	−81.5
42.2	−19.2		
44.2	−15.9	Solid phase $CH_3C_5H_4N$	
46.0	−13.6	92.2	−78.8
47.8	−11.8	93.4	−76.0
	(−6.0)	94.9	−73.6
48.9	−11.1	96.3	−69.4
	(−5.5)	98.0	−66.4
50.0	−11.0	100	−64.2
	(−5.3)		
52.0	−11.4		

TABLE III

SYSTEM *o*-CHLOROPHENOL–β-PICOLINE

% β-picoline	Temp., °C.	% β-picoline	Temp., °C.
Solid phase HOC_6H_4Cl		49.0	−18.8
0.0	8.0	[49.9	−25.0]
3.8	6.8	[51.0	−29.5]
6.8	4.5	Solid phase $CH_3C_5H_4N\cdot HOC_6H_4Cl$	
9.9	1.5		
11.8	− 0.5	50.0	−18.0
14.5	− 4.0	51.0	−18.2
17.1	− 7.5	53.4	−18.8
20.0	−12.0	56.7	−21.2
[21.8	−13.2]	59.2	−24.6
Solid phase $CH_3C_5H_4N\cdot 2HOC_6H_4Cl$		61.3	−27.8
		63.5	−31.5
21.2	− 7.0	66.0	−36.0
22.6	− 3.5	68.0	−39.9
24.1	− 0.7	68.5	−41.4
26.0	2.5	[69.5	−45.0]
28.1	5.4	[70.0	−48.1]
30.9	7.6	Solid phase $CH_3C_5H_4N$	
32.8	7.9	69.7	−40.5
36.1	6.5	74.3	−35.4
38.9	4.0	80.0	−31.1
40.9	1.5	84.5	−28.1
42.7	− 2.0	90.0	−24.9
44.8	− 5.5	93.7	−23.0
46.5	−10.0	97.5	−21.5
47.7	−13.7	100	−20.8

TABLE IV

SYSTEM *o*-CHLOROPHENOL–γ-PICOLINE

% γ-picoline	Temp., °C.	% γ-picoline	Temp., °C.
Solid phase HOC_6H_4Cl		54.5	23.6
0.0	8.0	57.0	22.0
4.6	6.0	59.9	19.0
10.0	2.2	63.0	14.4
14.4	−1.2	65.8	10.1
15.9	−4.0	68.0	7.0
17.7	−6.3	70.8	2.1
		73.2	− 2.0
Solid phase $CH_3C_5H_4N\cdot HOC_6H_4Cl$		76.8	− 8.1
		78.7	−12.2
33.4	−3.5	80.0	−14.8
34.9	1.4		
36.7	6.0	Solid phase $CH_3C_5H_4N$	
38.5	10.5	82.5	−12.0
40.0	14.0	86.0	− 7.9
41.9	18.1	90.0	− 4.5
43.6	21.0	93.7	− 2.0
45.6	23.4	97.4	0
47.5	24.6	100	+ 1.6
50.0	25.5		
52.0	24.6		

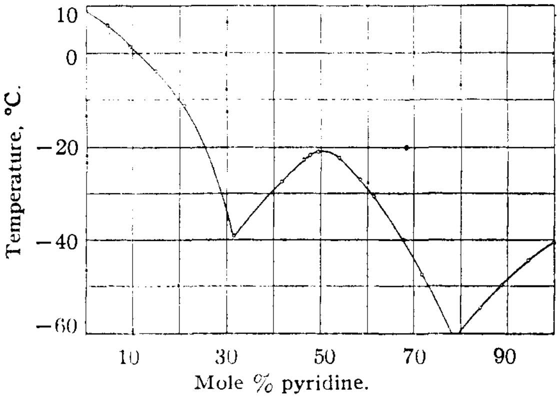

Fig. 1.—System *o*-chlorophenol–pyridine (Bramley).

A. As indicated in Fig. 2, *o*-chlorophenol and α-picoline form a stable compound, $CH_3C_5H_4N\cdot$

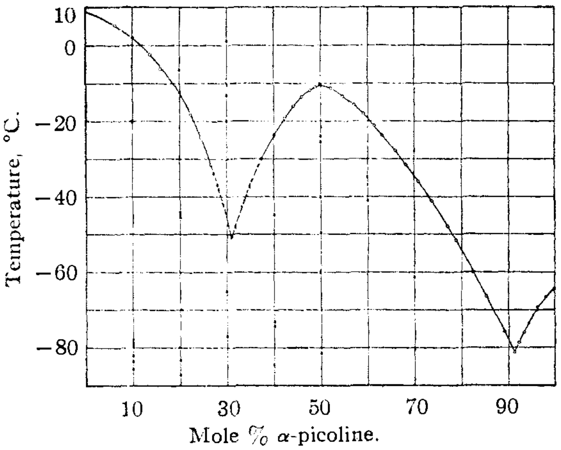

Fig. 2.—System *o*-chlorophenol–α-picoline.

HOC_6H_4Cl, which melts congruently at −11.0°. At compositions in the vicinity of 50 mole % a few freezing points about 6° higher than those shown in the curve were consistently obtained under certain conditions; these freezing points are given in parentheses in Table II. Although these observations suggested the possibility that the substance melting at −11.0° might be metastable with respect to a second crystalline form, no further evidence of metastability could be obtained, nor were similar divergences noted at other concentrations. The two eutectics are: (1) 31.5 (extrapolated) mole % α-picoline, f. p. −51.0° (extrapolated); and (2) 92.8 mole % α-picoline, f. p. −82.0°.

B. As shown in Fig. 3, *o*-chlorophenol and β-picoline form two stable compounds, (1) $CH_3C_5H_4N \cdot HOC_6H_4Cl$, which melts congruently at −17.8°. and (2) $CH_3C_5H_4N \cdot 2HOC_6H_4Cl$, which melts congruently at 8.1°. The three eutectics are: (1) 20.0 mole % β-picoline, f. p. −12.1°; (2) 48.8 mole % β-picoline, f. p. −18.6°; and (3) 68.4 mole % β-picoline, f. p. −42.4°.

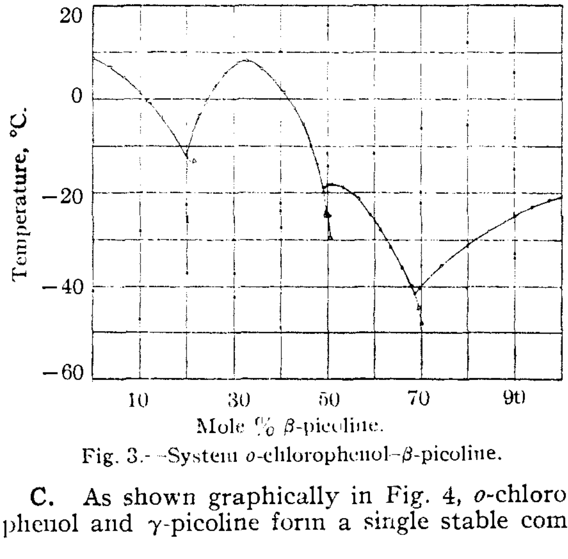

Fig. 3.—System *o*-chlorophenol–β-picoline.

C. As shown graphically in Fig. 4, *o*-chlorophenol and γ-picoline form a single stable compound, $CH_3C_5H_4N \cdot HOC_6H_4Cl$, which melts congruently at 24.9°. The two eutectics are: (1) 28.0 (extrapolated) mole % γ-picoline, f. p. −24.8° (extrapolated); and (2) 80.0 mole % γ-picoline, f. p. −14.5°.

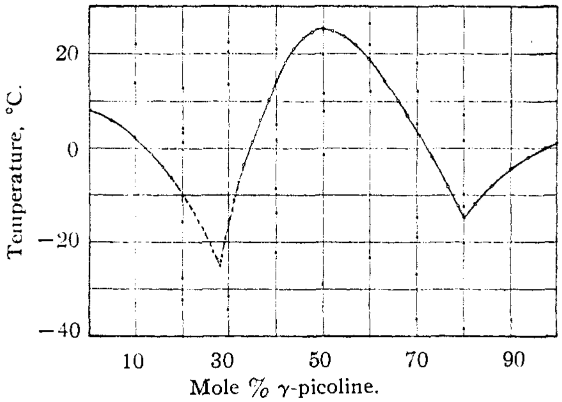

Fig. 4.—System *o*-chlorophenol–γ-picoline.

Discussion

It is of interest that the freezing point curves just described for the systems consisting of *o*-chlorophenol with α- and with γ-picoline bear a marked resemblance to the curve for the system *o*-chlorophenol–pyridine.[4] In each case, there is formed a single stable compound consisting of the two constituents in equimolecular proportions. The formation of these compounds is best explained on the assumption that the nitrogen atom of the amine is, in every case, linked through a hydrogen bond to the oxygen atom of the *o*-chlorophenol. The addition compound so formed may, of course, undergo partial dissociation into two ions, of the ammonium and the phenolate type, respectively.

The behavior of β-picoline in compound formation with *o*-chlorophenol stands in marked contrast to that of the other picolines and of pyridine. A stable 1:1 compound is indeed formed in this case, as in the others. However, not only is the m. p. of the 1:2 compound considerably higher, but the shape of the f. p. curve in the neighborhood of the two maxima indicates a considerably smaller dissociation of the 1:2 compound into its components, even at the higher temperature. Thus the 1:2 compound appears to be decidedly more stable than the simpler one.

The formation of the 1:2 compound, which has no analog in any of the other three systems, might be explained on the assumption that *o*-chlorophenol dimer is coördinated, through the hydrogen bond, with β-picoline. This assumption implies that the oxygen atoms of two *o*-chlorophenol molecules are linked through a hydrogen bond. However, the existence of an intermolecular linking sufficiently strong to account for the stability of such a compound seems somewhat improbable, as infrared absorption spectra indicate that the hydrogen bonding in *o*-chlorophenol is largely intramolecular in nature.[9]

Viewed from a slightly different standpoint, the existence of the 1:2 compound may be attributed to the fact that the 1:1 addition compound formed between *o*-chlorophenol and β-picoline is itself sufficiently basic to coördinate a second molecule of *o*-chlorophenol. Objection might be raised to this explanation, it is true, on the ground that it would imply that β-picoline is actually more basic than either its α- or its γ-isomer. It seems likely, however, that steric factors alone may suffice to rule out the possibility of a 1:2 compound between *o*-chlorophenol and α-picoline. The non-existence of such a compound with γ-picoline, must, for the present, remain unexplained.

Despite the uncertainties involved in the interpretation of f. p. depression data, especially in solvents of low dielectric constant, it seems not unjustifiable to draw some rough qualitative conclusions from the relative positions of the ideal and the actual f. p. depression curves for dilute solutions, as shown in Fig. 5.

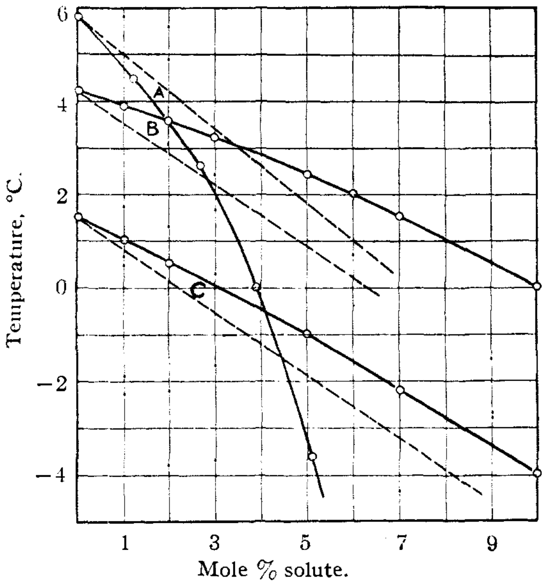

Fig. 5.—Freezing point depression curves for the picolines: broken lines, ideal solute; solid lines, observed data with *o*-chlorophenol as solute. A, α-picoline. Subtract 70° from temperature scale. B, β-picoline. Subtract 25° from temperature scale. C. γ-picoline, temperature scale correct.

The observed f. p. depression curves for *o*-chlorophenol in both the β- and γ-isomers lie above the ideal curve throughout. This displacement can scarcely be accounted for except on the assumption of partial association of the *o*-chlorophenol into dimers in these solutions. A possible mechanism for such association has indeed been suggested by Pauling.[10]

In the case of α-picoline, however, the observed curve lies considerably below the ideal. This deviation clearly indicates that here any tendency toward dimerization of the solute is more than outweighed by combination, of acid–base type, between solute and solvent. The greater basicity of α-picoline, as indicated by these deviations, is in accord with the evidence from the dissociation constants for the three picolines, cited earlier in this paper, which indicates that the β- and γ-isomers are of about the same strength, but considerably less basic than α-picoline.

This further confirmation of the lower basicity of γ-picoline as compared with what might be predicted by theory leads us to suggest that the lessened basicity of γ-picoline may be due to the type of internal neutralization which consists in the transfer of a proton from the methyl group to the nitrogen atom. If this internal protolysis does, indeed, occur to any appreciable extent, the resulting structure would be, like aniline, a vinylamine-type molecule, which would be considerably less basic than its tautomer. This type of tautomerism would be more probable for γ- than for α-picoline, as the molecule resulting from the proton transfer in the former case would possess the *p*-benzoquinoid structure, whereas the corresponding form of α-picoline would be of the less stable *o*-benzoquinoid type; electronic considerations preclude the possibility of similar tautomerism in β-picoline.

Summary

1. Temperature–composition data are presented for the systems consisting of *o*-chlorophenol and the three isomeric picolines.

2. It has been shown that *o*-chlorophenol forms a stable 1:1 addition compound with each of the three picolines, as well as a second compound, $CH_3C_5H_4N{\cdot}2HOC_6H_4Cl$, with the β-isomer.

3. Freezing point depression curves for dilute solutions of *o*-chlorophenol in each of the three picolines are compared with curves for an ideal solute. These curves indicate the markedly greater basicity of α-picoline as compared to the other two isomers.

4. Investigations of a similar nature on compounds closely related to the picolines are now in progress in this laboratory.

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[9] Pauling, THIS JOURNAL, **58**, 94 (1936).

[10] Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 2nd edition, 1942, p. 324.