

in ethylidene chloride at 25° have been determined.

The relative values of the dissociation constants of the nine salts in ethylene chloride are shown to be qualitatively accounted for by the effect of the substituent on the intensity of the positive charge on the nitrogen of the  $N(CH_3)_3$  group. An estimation of this effect is deduced from the known inductive and tautomeric effects of the particular substituent.

The greater dissociation constants of the ortho methoxy and chloro substituted salts, relative to those of their meta and para isomers, is attributed

to the "ortho" or "proximity" effect which involves an electrostatic interaction between these ortho substituents and the  $N(CH_3)_3$  group rather than a steric (or screening) effect.

It is concluded that the much smaller dissociation constant obtained for *o*-chlorophenyltrimethylammonium perchlorate in ethylidene chloride, relative to that in ethylene chloride, must be accounted for by the difference in the dipole moments and/or polarizabilities of these solvents since they have substantially the same dielectric constants at 25°.

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

## Compound Formation between Pyridine and Polyhalogenated Methanes

BY ARTHUR W. DAVIDSON, CALVIN A. VANDERWERF AND LESLIE G. BOATRIGHT

In a recent paper from this Laboratory,<sup>1</sup> evidence was presented for the formation of addition compounds which might be accounted for in terms of hydrogen bonding between the oxygen atom of *o*-chlorophenol and the nitrogen atom of pyridine, or of one of the three isomeric picolines. In the present work, the study of the formation of crystalline addition products, as revealed by phase equilibrium data, between pyridine and compounds of an acidic nature, was extended to systems consisting of this base and each of the trihalogenated methanes chloroform, bromoform and iodoform. Because some of the compounds obtained in these systems could not be accounted for in terms of hydrogen bonding alone, phase equilibria in two additional systems, pyridine-carbon tetrachloride and pyridine-carbon tetrabromide, were investigated also.<sup>2</sup>

The temperature-composition data obtained in the present work provide conclusive evidence of the existence in the solid state of numerous addition compounds between pyridine and polyhalogenated compounds. These data do not, of course, preclude the possibility of the presence of still other compounds in the liquid phase.

### Experimental<sup>3</sup>

**Purification of Materials.**—The pyridine was dried for two weeks over sodium hydroxide pellets, then distilled through a five-foot packed column into a receiver protected from the atmosphere by a tube containing potassium hydroxide and soda lime; b. p. 114.6° at 736 mm., f. p. (from cooling curve) -41.3°.

The chloroform, bromoform and carbon tetrachloride

(1) Lemmerman, Davidson and VanderWerf, *THIS JOURNAL*, **68**, 1361 (1946).

(2) After this work had been completed, it was learned that the system pyridine-carbon tetrachloride had been studied by Sr. M. Kennard and P. A. McCusker, who have been kind enough to make their unpublished data available to us. Because our equilibrium temperatures are slightly higher throughout the system, and because our interpretation of the curve differs slightly from theirs, we are including our data for this system in the present paper.

(3) All boiling points are corrected.

were dried over Drierite, then distilled through a column. The physical constants observed for the pure compounds are: for chloroform, b. p. 60.0° at 740 mm., f. p. (from cooling curve) -62.6°; for bromoform, b. p. 148.1° at 740 mm., f. p. (from cooling curve) 8.0°; for carbon tetrachloride, b. p. 76.1° at 741 mm., f. p. (from cooling curve) -22.0°.

Eastman Kodak Co. iodoform and carbon tetrabromide were recrystallized twice from alcohol; the former melted at 121.3° and the latter at 90.1°.

**Apparatus and Procedure.**—The freezing point cell used in the determination of the temperature-composition diagrams was similar to that described in a previous publication from this Laboratory<sup>4</sup> except that, in order to permit easy removal of the stirrer, the cell was constructed in two pieces which were joined to each other by means of a ground glass joint. The cooling curves were recorded directly by means of a Leeds and Northrup Micromax recorder, which had been calibrated at the melting point of ice, the boiling point of ammonia and the sublimation point of carbon dioxide.

Excessive supercooling, frequently encountered during the course of the investigation, could usually be eliminated if, when the temperature of the liquid in the cell was just a few degrees below the expected freezing point, the regular cooling jacket was removed and a small platinum wire sealed into the bottom of the cell was cooled momentarily with liquid air. After the first crystals had appeared, the cooling jacket was replaced and the level to which the temperature rose was taken as the equilibrium temperature. Each freezing point was determined at least twice. Data so obtained are believed to be correct, except for the steeper portions of the pyridine-iodoform curve, to  $\pm 1.5^\circ$ .

### Results

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

As shown in Fig. 1, pyridine and chloroform form a single stable compound,  $C_5H_5N \cdot CHCl_3$ , which melts congruently at -65.9°. The eutectics are: (a) 30.3 mole per cent. chloroform, f.p. -68.8°, and (b) 74.6 mole per cent. chloroform, f.p. -80.4°.

As indicated in Fig. 2, pyridine and bromoform form two compounds, (1) probably

(4) Davidson, Sisler and Stoener, *THIS JOURNAL*, **66**, 779 (1944).

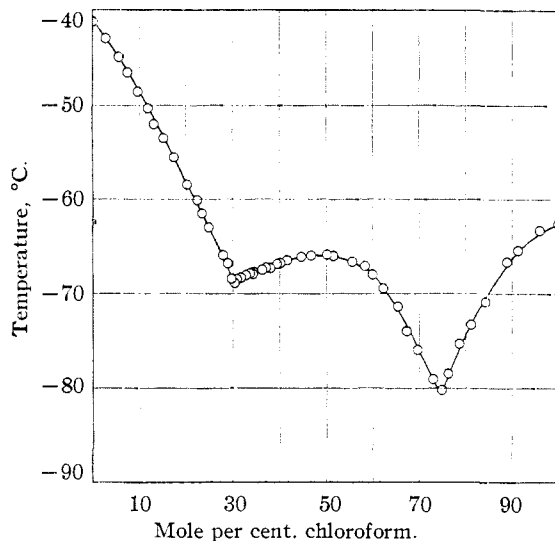


Fig. 1.—System pyridine-chloroform.

$3C_5H_5N \cdot CHBr_3$ , which undergoes transition at  $-52.2^\circ$  to (2)  $2C_5H_5N \cdot CHBr_3$ , which melts congruently at  $-45.3^\circ$ . The freezing point of (1), as obtained by extrapolation, appears to be about  $-51.7^\circ$ . The two eutectics are: (1) 14.5 mole per cent. bromoform, f.p.  $-54.0^\circ$ , and (2) 46.9 mole per cent. bromoform, f.p.  $-50.5^\circ$ .

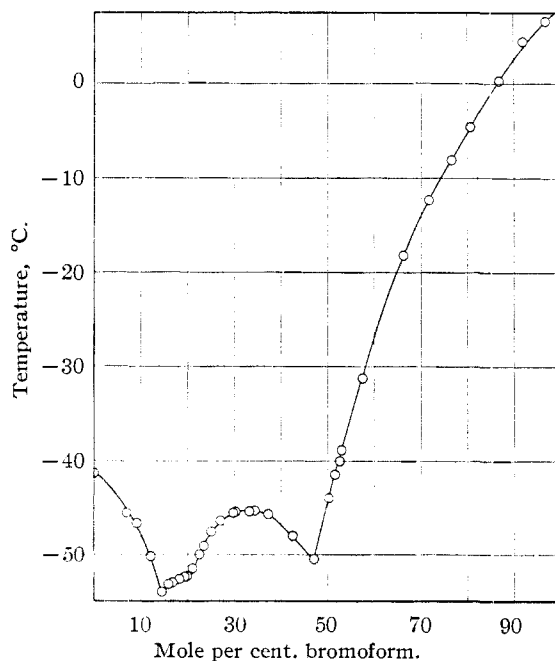


Fig. 2.—System pyridine-bromoform.

As represented in Fig. 3, pyridine and iodoform form a single compound, presumably  $3C_5H_5N \cdot CHI_3$ , which undergoes transition to iodoform and solution at  $-46.0^\circ$ . Its approximate melting point, as obtained by extrapolation, is  $-44.0^\circ$ . The eutectic is: 10.0 mole per cent. iodoform, f.p.  $-50.1^\circ$ .

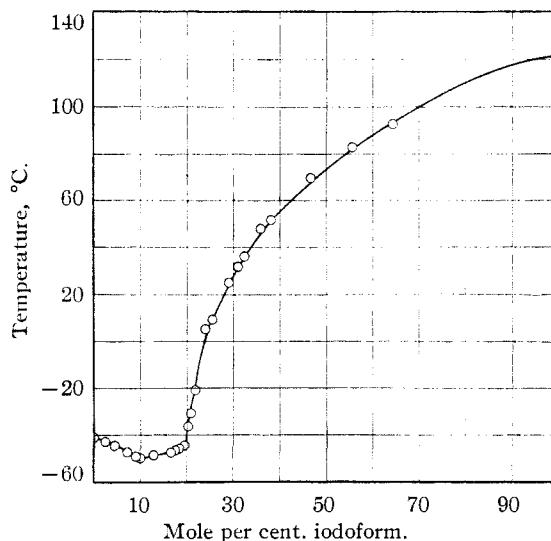


Fig. 3.—System pyridine-iodoform.

As shown graphically in Fig. 4, pyridine and carbon tetrachloride form a single compound  $C_5H_5N \cdot 2CCl_4$ , which melts congruently at  $-42.6^\circ$ . The eutectics are: (1) 26.7 mole per cent. carbon tetrachloride, f.p.  $-63.8^\circ$  and (2) 78.4 mole per cent. carbon tetrachloride, f.p.  $-47.9^\circ$ .

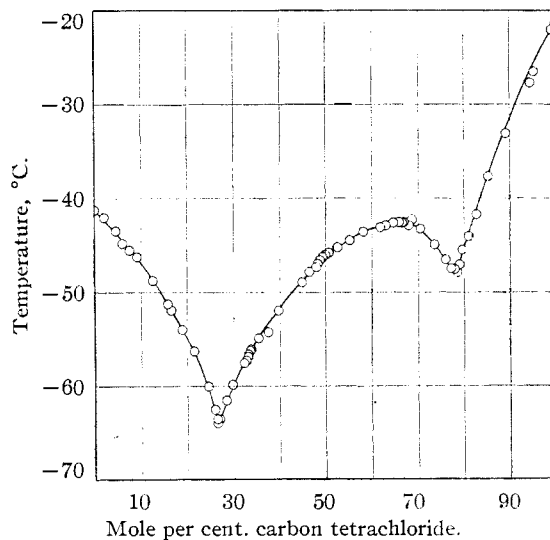


Fig. 4.—System pyridine-carbon tetrachloride.

The unusually steep slope of the portion of the curve in which carbon tetrachloride is the solid phase, is to be accounted for by the fact that the heat of fusion of carbon tetrachloride has the strikingly low value of only 644 calories per mole.<sup>5</sup>

(5) Latimer, *THIS JOURNAL*, **44**, 90 (1922). We are indebted to our colleague, Dr. W. J. Argersinger, for calling our attention to the fact that the entropy of fusion of carbon tetrachloride, 2.57 cal./degree, is so low that the freezing point curve for an ideal solution with carbon tetrachloride as solid phase would be concave upward over a considerable range, and that the experimental curve for the system chloroform-carbon tetrachloride does indeed show such curvature.

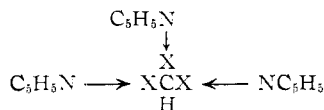
The curve in which carbon tetrabromide is the solid phase, Fig. 5,

As represented in Fig. 5, pyridine and carbon tetrabromide form three compounds: (1) probably  $3C_5H_5N \cdot CBr_4$ , the freezing point of which appears, upon extrapolation, to be approximately  $-17.0^\circ$ , and which undergoes transition at  $17.3^\circ$  to (2)  $2C_5H_5N \cdot CBr_4$ , which melts congruently at  $-7.8^\circ$ ; (3) probably  $C_5H_5N \cdot CBr_4$ , which apparently melts congruently at  $-12.5^\circ$ . The eutectics are: (1) 2.8 mole per cent. carbon tetrabromide, f.p.  $-43.0^\circ$  and (2) 44.6 mole per cent. carbon tetrabromide, f.p.  $-14.0^\circ$ . The distinct change in the slope of the curve at  $47^\circ$  results from the fact that  $47^\circ$  is the temperature of transition for the  $\alpha$ - to the  $\beta$ - form of carbon tetrabromide.

### Discussion

Of the eight compounds which are clearly indicated by the results just presented, there is only one,  $C_5H_5N \cdot CHCl_3$ , whose existence might plausibly be attributed to hydrogen bonding. In view of the fact that coordination from a donor atom to hydrogen occurs much more readily than does the expansion of the valence shell of chlorine,<sup>6</sup> it appears not unlikely that the structure of this compound may be correctly represented by the formula  $C_5H_5N \rightarrow HCCl_3$ . The absence of analogous 1:1 compounds of pyridine with bromoform and iodoform may, according to this viewpoint, be attributed to the smaller effect of the less electronegative halogens bromine and iodine upon the acidity of the hydrogen atom.

The formation of all of the remaining addition compounds except  $C_5H_5N \cdot 2CCl_4$  may possibly result from the expansion of the valence shell of one or more of the halogen atoms, as has been suggested by Wyatt<sup>7</sup> for solid addition compounds of chloroform or carbon tetrachloride with oxygen compounds. This hypothesis appears especially pertinent with respect to the compounds  $3C_5H_5N \cdot CHBr_3$  and  $3C_5H_5N \cdot CHI_3$ , the structure of which may be supposed to be as represented by the formula



It is worthy of mention that an analogous solid compound of iodoform and quinoline has long been known.<sup>8</sup> The fact that chloroform and carbon tetrachloride do not, like bromoform and tetrabromide, form solid addition compounds with two and three molecules of pyridine, may be accounted for in terms of the lower tendency of chlorine than of bromine to expand its valence shell.<sup>9</sup>

(6) Glasstone, *Trans. Faraday Soc.*, **33**, 200 (1937).

(7) Wyatt, *ibid.*, **24**, 429 (1928); **25**, 43, 48 (1929).

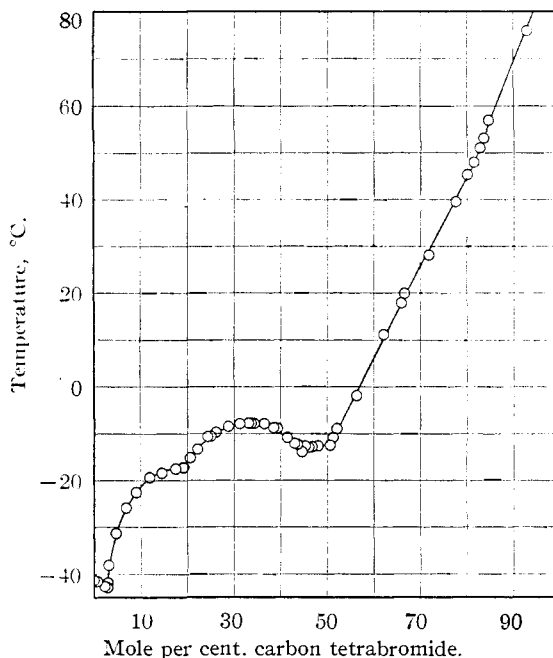


Fig. 5.—System pyridine-carbon tetrabromide.

### Summary

1. Temperature-composition data are presented for the systems consisting of pyridine and each of several polyhalogenated methanes. The existence of eight new addition compounds is reported.

2. It has been pointed out that only one of these addition compounds,  $C_5H_5N \cdot CHCl_3$ , may conceivably be accounted for in terms of hydrogen bonding, whereas all the others, except the anomalous  $C_5H_5N \cdot 2CCl_4$ , may be attributed to expansion of the valence shell of one or more halogen atoms.

3. Investigations of a similar nature with bases other than pyridine are now in progress in this Laboratory.

LAWRENCE, KANSAS

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(8) Rhuissopoulos, *Ber.*, **16**, 202 (1883).

(9) Sidgwick, "The Electronic Theory of Valence," Oxford University Press, London, 1932, p. 291.