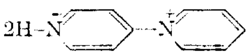
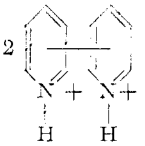
was ever noted. Benesi and Hildebrand,[10] in extensive studies on solutions of iodine in acetone, reported a similar disagreement.

A satisfactory explanation for the behavior of solutions of iodine in pyridine must account for the great increase in conductivity as well as for the disappearance of the original ionic species. In order to account for the fact that the limiting conductance is about twice as great as might be expected on the basis of a simple dissociation of the iodine molecule into a positive and negative ion, Audrieth and Birr[2] proposed a mechanism involving dissociation into a ternary salt of the formula $Py^{++},2I^-$. Since evidence has been presented that the ions responsible for the characteristic absorption peaks disappear with time, two alternative reactions may be proposed tentatively, one based on the preparation of pyridylpyridinium chloride,[11] best explained by the postulation of the $ClPy^+$ ion,[12] the other on the formation of dipyridyl when pyridine is heated with iodine.[13] The equations for the reactions are

(1) $IPy^+ + 3Py + I_3^- = 4I^- +$



(2) $IPy^+ + 3Py + I_3^- = 4I^- + 2$



Attempts to isolate these products from iodine-pyridine mixtures led only to the formation of tarry residues.

Summary

1. The absorption spectra of solutions of iodine and positive iodine salts in pyridine and their change with time have been studied.

2. Evidence for the existence of the IPy^+ and I_3^- ions in solutions of iodine in pyridine has been presented.

3. Tentative mechanisms have been proposed to explain the increasing conductivity and disappearance of absorption bands in these solutions.

LAWRENCE, KANSAS RECEIVED JUNE 28, 1950

---

(10) Benesi and Hildebrand, THIS JOURNAL, **71**, 2703 (1949).

(11) Koenigs and Greiner, *Ber.*, **64**, 1045 (1931).

(12) Elderfield "Heterocyclic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 413, 427.

(13) Willink and Wibaut, *Rec. trav. chim.*, **54**, 275 (1935).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

The Vapor Pressures and Freezing Points of Some Organic Fluorine Compounds[1,2]

BY JOHN C. POTTER[3] AND JOHN H. SAYLOR

The measurements reported in this paper were made in connection with a general program of research in this Laboratory concerning the solubility and other physical properties of organic fluorine compounds.

Experimental

Materials.—The three fluorotoluenes were Eastman Kodak Co. best grade. The three chlorobenzotrifluorides were furnished by the Hooker Electrochemical Company. The *p*-bis-(trifluoromethyl)-benzene was made in this Laboratory by Dr. A. R. Gilbert and Mr. J. B. Bond under the direction of Dr. C. K. Bradsher. The materials were dried over Drierite and then distilled at a high reflux ratio through a silvered vacuum-jacketed glass column packed with 1/8" glass helices. A two junction copper–constantan thermel was used to measure the still head temperature.

Vapor Pressures.—A modification of the method of Ramsay and Young which has been previously described[4] was used for pressures below 100–150 mm. For higher pressures a boiling point apparatus similar to that of Rossini and co-workers[5] was used. The pressure was controlled with a sulfuric acid manostat similar to that used by Huntress and Hershberg.[6] The pressure was measured with a mercury manometer and a cathetometer. The pressure over the reference limb of the manometer was reduced to less than 0.01 mm. with a mercury diffusion pump and then checked with a McLeod gage. The temperature was measured with a platinum resistance thermometer, a standard resistor, and a Leeds and Northrup Type K2 potentiometer. The platinum resistance thermometer and the standard resistor were placed in series with a 2-volt battery and a 2000-ohm resistor. The potential drops across the standard resistor and the platinum thermometer were measured with the potentiometer. From the ratio of these two potential drops and the resistance of the standard resistor the resistance of the platinum thermometer could be calculated. The boiling point apparatus, the manometer, the manostat, a rotary oil pump and a controlled air leak operated by the manostat were connected to a surge tank. The rate at which the air was removed from the system by the pump and the rate at which the controlled air leak admitted air to the system were controlled by means of needle valves. In operation, with the liquid boiling in the boiling point apparatus, the pressure in the system was reduced to the desired value and the two needle valves adjusted. After a few minutes the resistance of the platinum thermometer and the pressure were taken. As a check on the method the vapor pressure of water was measured. The mean deviation of the pressure values calculated from the data of Osborne and Meyers[7] and the experimental values was ±0.13 mm. for eleven measurements between 180 and 760 mm.

Freezing Points.—The cooling curves of the best fractions from the distillations were determined in a freezing point apparatus patterned after that of Schwab and Wichers.[8] From the cooling curves the freezing points and the freezing point depressions were obtained graphically by the method of Stull.[9]

Results

Approximately twenty to twenty-five individual

---

(1) The work reported was carried out under Contract N6ori-107, T. O. II with the Office of Naval Research.

(2) This paper was taken in part from the thesis submitted by John C. Potter to the Graduate School of Duke University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1950.

(3) Department of Chemistry, North Carolina State College, Raleigh, N. C.

(4) Stuckey and Saylor, THIS JOURNAL, **62**, 2922 (1940).

(5) Willingham, Taylor, Pignocco and Rossini, *J. Research Natl. Bur. Standards*, **35**, 219 (1945).

(6) Huntress and Hershberg, *Ind. Eng. Chem., Anal. Ed.*, **5**, 144 (1933).

(7) Osborne and Meyers, *J. Research Natl. Bur. Standards*, **13**, 1 (1934).

(8) Schwab and Wichers, *ibid.*, **34**, 333 (1945).

(9) Stull, *Ind. Eng. Chem., Anal. Ed.*, **18**, 234 (1946).

TABLE I

BOILING POINTS, FREEZING POINTS AND CONSTANTS OF THE VAPOR PRESSURE EQUATION

Substance	B. p., °C. Range	B. p., °C. Calcd.	B. p., °C. Prev. Obsd.	Ref.	F. p., °C. obsd.	F. p., °C. Dep. °C.	F. p., °C. Prev. obsd.	Ref.	*A*	*B*	*C*
Benzotrifluoride	102.01-102.02	102.04	102.3	10	−29.14	0.02	−29.05	10	7.0202	1335.5	220.58
p-Bis-(trifluoromethyl)-benzene	116.23-116.24	116.28			2.78	.02			7.0375	1351.6	208.89
o-Fluorotoluene	114.35-114.36	114.40	114.48-114.53	11	−62.0	.4	−60	12	6.9732	1356.8	217.15
m-Fluorotoluene	116.52-116.53	116.55	116.27-116.30	11	−87.7	.3	−87	12	7.0095	1382.7	218.34
p-Fluorotoluene	116.58-116.59	116.59	116.62-116.65	11	−56.8	.05	−53	12	7.0574	1410.8	221.19
o-Chlorobenzotrifluoride	152.32-152.33	152.31	152.8	10	− 6.37	.04	− 7.4 to 7.6	10	7.0144	1490.4	208.24
m-Chlorobenzotrifluoride	137.69-137.72	137.63	138.4	10	−56.7	.76	−55.4	10	7.0555	1458.9	211.82
p-Chlorobenzotrifluoride	138.69-138.71	138.63	139.3	10	−33.2	.14	−34.0	10	7.1640	1536.3	220.08

measurements were made on each compound from 10 to 760 mm. The experimental data were fitted by the method of least squares to the equation

$$\log p = -\frac{B}{t + C} + A$$

where p is the pressure in mm. and t is the temperature in degrees centigrade.

The mean deviation between the observed pressures and those calculated from the equation varied from ±0.24 mm. for *o*-fluorotoluene and *p*-chlorobenzotrifluoride to ±0.10 mm. for *o*-chlorobenzotrifluoride.

Table I gives the boiling point ranges corrected to one atmosphere, the boiling points calculated from the vapor pressure equation, the freezing points, the freezing point depressions, and the values of the three constants in the above equation.

The agreement of the data for the three fluorotoluenes with that of Stull[13] is not very good. The present data for benzotrifluoride agree fairly well with that of Stull[13] and Field[14] but do not agree very well with that of Booth, Elsey and Burchfield.[15]

Summary

The vapor pressures and the freezing points of benzotrifluoride, *p*-bis-(trifluoromethyl)-benzene, *o*- *m*- and *p*-fluorotoluene and *o*-, *m*- and *p*-chlorobenzotrifluoride have been measured.

The vapor pressure data have been fitted to a suitable equation.

---

(10) H. S. Booth, THIS JOURNAL, **57**, 2066 (1935).

(11) Deal, Thesis, Duke University, 1944.

(12) Klemm, Klemm and Schiemann, *Z. physik. Chem.*, **A165**, 379 (1933).

(13) Stull, *Ind. Eng. Chem.*, **39**, 517 (1947).

(14) Field, THIS JOURNAL, **68**, 2649 (1946).

(15) Booth, Elsey and Burchfield, *ibid.*, **57**, 2066 (1935).

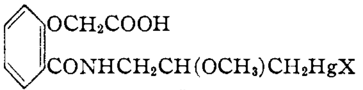
DURHAM, NORTH CAROLINA RECEIVED JUNE 26, 1950

[CONTRIBUTION FROM THE CHEMICAL RESEARCH DIVISION OF LAKESIDE LABORATORIES, INC.]

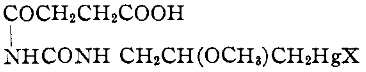
Mercurial Diuretics. II. Methoxymercuration of N-Allyl Amides

BY R. L. ROWLAND, WENDELL L. PERRY AND SAMUEL GERSTEIN

The organic mercurials which have been investigated as diuretics have generally been those obtained by methoxymercuration of the monoallylamide of a dibasic acid. Thus Salyrgan, I, and Mercuhydrin, II, contain a free carboxyl radical.



I



$$\begin{array}{l}\mathrm{COCH_2CH_2COOH}\\ |\\ \mathrm{NHCONH\ CH_2CH(OCH_3)CH_2HgX}\end{array}$$

II

The increased diuretic potency of $NH_2CONHCH_2CH(OCH_3)CH_2HgX$, (III), X = Cl, Br, SCH_2COOH, etc.,[1] which is a simplification of II by removal of the β-carboxypropionyl radical, has been noted. The possibility that a similar simplification of I might result in a compound with improved diuretic properties prompted the investigation of $C_6H_5CONHCH_2CH(OR)CH_2HgCl$ (IV) where R = CH_3. The methoxymercuration products of other simple aliphatic and aryl allyl amides were also of interest in the course of an exploratory study of variation of diuretic potency and toxicity with chemical structure. Although the preparation of mercurated allylacetamide has been claimed,[2] its physical and pharmacological properties have not been reported. No other reports are available on the preparation or properties of the mercurials obtained by the addition of mercuric acetate and alcohols to the allyl amides of unsubstituted aliphatic or aryl monocarboxylic acids. Perhaps the most nearly related compound is the isostere of IV, R = H, formed by the addition in water of mercuric acetate to the allyl amide of pyridine-3-carboxylic acid.[3]

A representative group of allyl amides was prepared. With the exception of allylacetamide and allylbenzamide, these compounds are new. Addition of mercuric acetate to the allyl amides was accomplished in methyl alcohol and, for convenience, the product was isolated as the chloromercuri derivative. The locations of the acetoxy-

---

(1) Rowland, Perry, Foreman and Friedman, THIS JOURNAL, **72**, 3595 (1950).

(2) Tabern, U. S. Patent 2,163,296 (1939).

(3) Hartmann and Panizzon, U. S. Patent 2,136,501 (1938).