esters, which now seem the more significant and useful, are summarized in the table. All of the hydrogenations were carried out at 50° for seven hours, except for the first two entries which were stopped after four and five hours, respectively. The hydrogen was under 150 to 200 atmospheres pressure. The reaction medium was 20 to 35 ml. of dry alcohol contained in a steel reaction vessel of 96-ml. capacity. The names and amounts of ester, type and amount of catalyst and the yield of the major product are given in the table.

In general the esters were prepared and isolated by procedures previously described.[14] The products of hydrogenation were isolated by fractional distillation except as noted under Table I. The amino alcohols were characterized, and in some instances estimated by neutral equivalents, as well as in most instances by solid derivatives.

The catalyst W-2 prepared by the Mozingo procedure gave in some instances a good yield of an amino alcohol. However, with the α- and β-piperidino propionates, and the α-piperidinoisobutyrate and phenylalaninate, the hydrogenation proceeded to the extent of from 0 to 6% while over the preferred catalyst W-4 yields of 30 to 52% were obtained with these esters. Data are not available for a precise comparison of the activity of the catalysts used, but it seems certain that the catalysts W-3 and W-4, prepared by a short digestion at 50°, are in every case equal to and in several cases very superior to the catalysts prepared under more drastic conditions.

The average yield given in the table, of amino alcohols obtained from eight different alpha aminoesters, is about 75% of the theoretical. Thus the process as described has good preparational value. Less favorable yields of amino alcohol were obtained from the two beta-aminoesters tested. The process is apparently also applicable to α-oxysubstituted esters since α-tetrahydrofuroate was converted in 55% yield to tetrahydrofurfuryl alcohol. The successful application of the process to a considerable number of alpha amino and hydroxy esters at 25 to 100° will be described in a subsequent paper.

Summary

A procedure has been described whereby esters of alpha amino acids may be hydrogenated in rather good yields to the corresponding amino alcohols. A properly prepared Raney nickel catalyst is effective at 50° with a rather high ratio of nickel to amino ester. The low temperature required is advantageous in that the alkylation of the amino group and the racemization of the amino alcohol may be avoided.

MADISON, WIS.

RECEIVED JUNE 23, 1947

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(14) F. W. Forman, *J. Biochem.*, **13**, 378 (1919); Uchida and Sanye, *J. Soc. Chem. Ind. Japan*, **36**, 221 (1933), *C. A.*, **27**, 3489 (1934).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Dissociation Constants of Some Substituted Phenyltrimethylammonium Perchlorates in Ethylene Chloride; Effect of Ion Asymmetry

BY J. B. RAMSEY AND E. L. COLICHMAN[1]

It is well known that all salts which are typically strong electrolytes in aqueous solution and in which the binding force between the positive and negative constituents is solely electrostatic, or coulombic, are only partially dissociated into free ions in dilute solution in solvents of sufficiently low dielectric constant. That the molecular structures of the constituent ions of a salt are important factors in determining its dissociation constant has been amply shown by Kraus[2] and co-workers from the results of electrolytic conductance measurements. The effective volume, or size, of the ions and the charge distribution within the ions are among the structural features which have been found to influence the extent of association of the ions of a salt into short-range ion-pairs.

In order to determine the effect of varying any particular structural feature of an ion on the dissociation constant, a series of salts is desired in which this structural feature alone is appreciably changed from one salt to another. The influence of variation in the ion-size alone has been adequately demonstrated by the increase in the dissociation constant found to accompany the increase in size of the alkyl radical in the homologous series of symmetrically substituted tetraalkylammonium picrates and nitrates in ethylene chloride at 25°.[2b,3]

It has been the purpose of this investigation to determine the dissociation constants of a series of salts in ethylene chloride as solvent in which the electrical asymmetry of one of the ions is consistently varied in such a way that the effective ion-size remains substantially unchanged and thereby to obtain some indication of the specific influence of such a variation on the dissociation constant. Nine monosubstituted phenyltrimethylammonium perchlorates were used, namely, the ortho,

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(1) Present address: Department of Chemistry, University of Southern California, Los Angeles, California.

(2) (a) Gleysteen and Kraus, THIS JOURNAL, **69**, 451 (1947); (b) Tucker and Kraus, *ibid.*, **69**, 454 (1947); (c) Mead, Ramsey, Rothrock and Kraus, *ibid.*, **69**, 528 (1947); (d) Kline and Kraus, *ibid.*, **69**, 814 (1947). For summaries of previous results see C. A. Kraus, *Trans. Electrochem. Soc.*, **66**, 179 (1934); *J. Franklin Inst.*, **225**, 687 (1938); *Science*, **90**, 281 (1939).

(3) Mead, Fuoss and Kraus, *Trans. Faraday Soc.*, **32**, 594 (1936).

meta and para isomers of each of the substituents, chlorine, methoxy and methyl.

Experimental

Each of the perchlorates was obtained by metathesizing the corresponding quaternary methosulfate or halide with an excess of almost saturated aqueous sodium perchlorate. Alcohol was then added and the entire mixture filtered hot. On cooling the filtrate, the quaternary perchlorate precipitated. Purification of each salt consisted of several recrystallizations from 95% alcohol and finally from absolute alcohol.

Preparation of *o*, *m* and *p*-Methoxyphenyltrimethyl-, and *o*, *m* and *p*-Methylphenyltrimethylammonium Salts.—The method described by Groenewoud and Robinson[4] was used in the preparation of the *o*, *m* and *p*-isomers of methoxyphenyltrimethylammonium methosulfate and of methylphenyltrimethylammonium methosulfate from the corresponding primary amines. A comparison of melting points of the corresponding quaternary picrates with the values reported by Groenewoud and Robinson showed that each isomeric amine had been trimethylated. Groenewoud and Robinson proved the structure of their quaternary picrates by halide analysis of the corresponding quaternary ammonium halide. The methylation of *o*-toluidine did not give satisfactory yields by the above method. Instead, N-dimethyl-*o*-toluidine (1 mole, Eastman Kodak Co. White Label) and methyl iodide (3 moles) were allowed to react for three and one-half hours at 105° in a sealed bomb-tube. Solid *o*-methylphenyltrimethylammonium iodide was isolated by water extraction in 75% yield. The melting points obtained for the perchlorates and picrates prepared, along with those previously reported, are given in Table I.

Table I

Melting Points of Methoxy- and Methylphenyltrimethylammonium Salts

Methoxy salts	Found	Reported by G. and R.[4]	Reported by Zaki[5]
o-Picrate	125	125	.....
o-Perchlorate	220	.....	224.5
m-Picrate	132	133	.....
m-Perchlorate	153.5	.....	.....
p-Picrate	176	176.5	.....
p-Perchlorate	192.5	.....	.....
Methyl salts			
o-Picrate	112	113	.....
o-Perchlorate	202	.....	198–199
m-Picrate	109	108	.....
m-Perchlorate	124	.....	.....
p-Picrate	195	193–198	.....
p-Perchlorate	195	.....	.....

Preparation of *o*-, *m*- and *p*-Chlorophenyltrimethylammonium Salts.—*o*-Chloro-N-dimethylaniline, prepared as described by Van Duin,[6] was methylated with methyl iodide in very small yields even after allowing several days reaction time at different temperatures between 45 and 105°. Higher temperatures resulted in decomposition of the product. *Anal.* Calcd. for *o*-chlorophenyltrimethylammonium iodide: I(ionizable), 42.6. Found: I (ionizable), 42.8. However, a 75% yield of quaternary salt was obtained by allowing the *o*-tertiary amine (1 mole) and dimethyl sulfate (1.5 moles) to react for thirteen hours at 150° in a sealed tube. *Anal.* Calcd. for *o*-chlorophenyltrimethylammonium methosulfate: C, 42.7. Found: C, 42.9. The perchlorate prepared from this methosulfate had the same melting point, 184°, as that from the iodide.

m-Chloroaniline hydrobromide (1 mole) and methanol (1.4 moles) were heated for five and one-half hours at 145° in a sealed bomb-tube. Solid *m*-chlorophenyltrimethylammonium bromide was isolated by water extraction in a 58% yield. The same materials were used by Pfeiffer and Schneider[7] in their preparation of this salt. *Anal.* Calcd. for *m*-chlorophenyltrimethylammonium bromide: Br (ionizable), 31.9. Found: Br(ionizable), 32.0; melting point of perchlorate, 166.5°.

p-Chloro-N-dimethylaniline was prepared from *p*-chloroaniline by the same method as was used by Van Duin[6] for the ortho isomer. A 60% yield was obtained. Melting point was 34.0°, compared with the reported values, 35.5 and 32.8°.[8,9] The desired quaternary salt was obtained in 74% yield by refluxing the tertiary amine (1 mole) with methyl iodide (4 moles) in a small quantity of ether for nine hours. *Anal.* Calcd. for *p*-chlorophenyltrimethylammonium iodide: I(ionizable), 42.7. Found: I(ionizable), 42.8; melting point of perchlorate, 225.5°.

Solvents.—Ethylene chloride (Eastman White Label), dried with anhydrous calcium sulfate, was further purified by distilling twice through a three-foot, silvered column packed with glass spirals. Anhydrous conditions were maintained during distillation and storage by use of drying tubes containing calcium chloride and calcium sulfate. Adequate purity of each portion of solvent used was assured by its very low conductivity. This was found to be entirely negligible relative to that of the most dilute solutions used.

The conductance of solutions of only one of the salts, *o*-chlorophenyltrimethylammonium perchlorate, was determined in ethylidene chloride at 25°. This solvent was purified in the same way as was ethylene chloride.

Procedure.—The conductance cells and pipets were the same design as those used by Kraus and co-workers.[3,10] The cell constants were determined by the well-known comparison method using potassium chloride solutions prepared according to the directions of Jones and Bradshaw.[11] The cell constants of cells used were 0.2472 and 0.2325. Measurements were made with a shielded conductance bridge, built locally according to the specifications given by Shedlovsky,[12] in connection with a voltage amplifier and a variable oscillator. All measurements were carried out at a frequency of 2500 cycles/second. The temperature of the oil thermostat was maintained constant at 25° within 0.001°. The quantity (between 10 and 40 milligrams) of each of the quaternary perchlorates needed in preparing the initial solutions were weighed out on a Kuhlmann microbalance. A large quantitative balance (load capacity, 2000 g.) was used in weighing the conductance cells and weight-pipets. The quite volatile ethylidene chloride was cooled to about 0° in an oil-bath before making the solvent withdrawals preceding each successive dilution.

Results

The values of the dissociation constants (K) and of the limiting equivalent conductances (Λ_0) were obtained from the conductance measurements by the method of Fuoss and Kraus.[13] At least two independent series of measurements were made with each salt. The values of the concentration, c (in gram formula weights per liter), and the equivalent conductances (Λ) obtained in one series of measurements of each salt, along with the derived values of F/Λ and $c\Lambda f^2/F$, are given in Table I. In calculating these derived values, the

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(4) Groenewoud and Robinson, *J. Chem. Soc.*, 1694 (1934).

(5) Zaki and Fahim, *ibid.*, 270 (1942).

(6) Van Duin, *Rec. trav. chim.*, **51**, 878 (1932).

(7) Pfeiffer and Schneider, *Ber.*, **68A**, 50 (1935).

(8) Heidelberg, *ibid.*, **20**, 149 (1887).

(9) Evans, Watson and Williams, *J. Chem. Soc.*, 1348 (1939).

(10) Kraus and Fuoss, This Journal, **55**, 21 (1933).

(11) Jones and Bradshaw, *ibid.*, **55**, 1780 (1933).

(12) Shedlovsky, *ibid.*, **52**, 1793 (1930).

(13) Fuoss and Kraus, *ibid.*, **55**, 476 (1933); Fuoss, *ibid.*, **57**, 488 (1935).

TABLE II

CONDUCTANCE DATA AT 25°

$C \times 10^4$	Λ	$F/\Lambda \times 10^3$	$c\Lambda f^2/F \times 10^4$
A. In Ethylene Chloride			
o-Methoxy-			
4.750	29.60	30.12	76.45
1.348	42.47	21.95	39.08
0.5597	51.96	18.33	22.21
.2531	59.51	16.23	12.41
.09470	67.24	14.55	5.631
m-Methoxy-			
5.504	21.00	42.40	64.47
3.321	25.12	36.13	50.97
1.404	33.58	27.74	32.69
0.7978	39.78	23.73	23.54
.4281	47.03	20.32	15.88
p-Methoxy-			
3.956	23.74	38.43	57.32
1.854	30.76	30.32	38.95
0.8201	39.61	23.97	24.54
.3358	49.76	19.38	13.70
.1783	56.86	17.10	8.659
o-Methyl-			
8.920	19.32	45.73	88.56
4.223	25.20	36.10	63.48
1.718	33.92	27.54	39.92
0.8680	41.61	22.80	26.87
.2211	57.03	17.01	10.66
m-Methyl-			
11.56	16.77	52.12	94.89
6.624	20.53	43.63	75.23
2.529	28.79	32.13	47.49
0.5348	46.02	20.80	19.26
.2035	56.97	17.06	9.80
p-Methyl-			
8.824	18.76	47.09	85.67
6.217	21.26	42.17	73.69
2.665	28.61	32.25	49.18
0.6792	43.55	21.87	22.58
.3513	51.32	18.77	14.62
o-Chloro-			
9.562	17.55	50.20	85.98
3.967	24.07	37.88	58.06
1.601	32.75	28.56	36.57
0.9020	39.09	24.24	26.19
.3192	50.87	18.96	13.29
m-Chloro-			
6.502	16.29	55.72	62.65
2.059	25.05	37.36	35.95
0.7292	35.64	26.80	20.16
.2913	46.34	20.89	11.25
p-Chloro-			
5.887	16.01	57.13	57.69
3.121	20.41	45.55	42.71
1.627	26.01	36.29	30.58
0.8638	32.36	29.48	21.50
.3182	43.77	22.13	11.59
B. In Ethylidene Chloride			
o-Chloro-			
2.739	16.19	59.12	34.83
1.182	23.31	41.46	22.23
0.4631	34.38	28.40	13.86
.1301	56.05	17.54	6.53

dielectric constants of ethylene chloride and of ethylidene chloride of 25° have been taken as 10.23 and 10.2,[18] respectively, and the viscosities at 25° as 0.00780 and 0.00465 poise,[21] respectively. The substituted phenyltrimethylammonium salt is designated by the position and name of the particular substituent.

Since a strictly linear relationship is found in each case on plotting F/Λ against $c\Lambda f^2/F$, the graphs are not reproduced. Values of K and Λ_0 obtained from these graphs are given in Table II.

TABLE II

DISSOCIATION CONSTANTS AND LIMITING EQUIVALENT CONDUCTANCES AT 25°

Salt	$K \times 10^5$	Λ_0
A. In Ethylene Chloride		
$(o\text{-}CH_3OC_6H_4)(CH_3)_3NClO_4$	8.64	73.9
$(m\text{-}CH_3OC_6H_4)(CH_3)_3NClO_4$	3.99	75.2
$(p\text{-}CH_3OC_6H_4)(CH_3)_3NClO_4$	4.35	73.9
$(o\text{-}CH_3C_6H_4)(CH_3)_3NClO_4$	4.65	76.9
$(m\text{-}CH_3C_6H_4)(CH_3)_3NClO_4$	4.35	75.9
$(p\text{-}CH_3C_6H_4)(CH_3)_3NClO_4$	4.46	76.2
$(o\text{-}ClC_6H_4)(CH_3)_3NClO_4$	4.45	73.9
$(m\text{-}ClC_6H_4)(CH_3)_3NClO_4$	2.79	73.9
$(p\text{-}ClC_6H_4)(CH_3)_3NClO_4$	2.46	73.9
B. In Ethylidene Chloride		
$(o\text{-}ClC_6H_4)(CH_3)_3NClO_4$	0.452	123.5

Discussion

In comparison with the large variation found in the ionization constants of isomeric organic acids and bases which involve the rupture of covalent bonds (*e. g.*, substituted benzoic acids[14] and dimethylanilinium ions[15]), the influence of the position of a substituent on the extent of dissociation of these quaternary perchlorates is quite small. This difference is to be expected since the covalent bond (broken in ionization) is an integral part of the molecule whereas the electrostatic "bond" between the ion-pairs is not.

The distinctly greater values of the dissociation constants of the *o*-methoxy- and of the *o*-chloro-substituted salts relative to those of their meta and para isomers, may be attributed to the "proximity" or "ortho" effect known to account for the unique behavior of ortho substituted anilines in most of their reactions.[16] The fact that there is not a similar difference between the dissociation constant of the ortho methyl salt and those of its meta and para isomers indicates that the "prox-

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(14) Dippy and Page, *J. Chem. Soc.*, 357 (1938).

(15) Davies and Addis, *ibid.*, 1622 (1937); Davies, *ibid.*, 1865 (1938).

(16) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 204.

imity" effect is not to be ascribed solely to bulk or steric hindrance. The much weaker polar nature of the methyl group compared to that of the methoxy and chloro substituents indicates that the "proximity" effect here is due primarily to electrostatic interaction between the methoxy and chloro substituent and the neighboring polar group, $N(CH_3)_3^+$. The accepted interpretations of these interactions show that a decrease in the intensity of the positive charge on the nitrogen results. This would thereby weaken the electrostatic attraction between the positive and negative ions and thus produce an increase in the dissociation constant.

Since apparently the electrostatic influence of a substituent in the ortho position predominates over any steric (or screening) effect, it seems probable that an interpretation of the effect of a substituent in the meta or para position may likewise be found in the influence of its polar nature on the electrical asymmetry of the ion. That the effective volumes (or sizes) of the positive ions of these nine salts in ethylene chloride is substantially the same is shown by the nearly constant values of their limiting equivalent conductances. It is therefore assumed that the relative intensities of the positive charge on the nitrogen is the principal factor determining the relative values of the dissociation constants of these salts. The greater the intensity of this positive charge the smaller will be the value of the dissociation constant. An evaluation of these relative intensities for the meta and para isomers of the three substituents may be deduced[17] from a consideration of the inductive (−I) and the tautomeric (+T) effects of the methoxy and chloro substituents in the meta and para positions, and of the weak inductive effect (+I) of the methyl substituent in either of these positions. The smaller dissociation constants found for the *m*- and *p*-chloro salts compared to those of the corresponding methyl and methoxy salts is expected on account of an over-all greater displacement of electrons away from the nitrogen in the chloro substituted ions. In fact the small positive inductive effect, +I, of the methyl substituent causes a relatively small displacement of electrons toward the nitrogen. Both the tautomeric (+T) and inductive (−I) effects participate in determining the influence of the methoxy substituent When in the para position the tautomeric effect is known to predominate over the inductive effect, thereby producing a resultant displacement of electrons toward the nitrogen (substantially equivalent to that of the methyl substituent); whereas, when it is in the meta position the competition between the tautomeric effect and the inductive effect causes a small displacement (relative to that of chlorine) away from the nitrogen. It is thus seen that the relative magnitudes of the dissociation constants of the meta and para substituted salts are qualitatively accounted for by the effect of the three substitutents on the intensity of the positive charge on the nitrogen.

The much smaller value of the dissociation constant obtained for *o*-chlorophenyltrimethylammonium perchlorate in ethylidene chloride, CH_3-$CHCl_2$, at 25° (0.452×10^{-4}) relative to that in ethylene chloride (4.45×10^{-4}) is noteworthy in view of the fact that the value of the dielectric constant of ethylidene chloride at 25°[18] is the same, within one-tenth of a unit, as that accepted for ethylene chloride,[19] namely, 10.23. Fuoss and Kraus[20] have derived the relation

$$K^{-1} = \frac{4\pi N}{1000}\left(\frac{e^2}{DkT}\right)^3 Q(b)$$

in which K is the dissociation constant; N, Avogadro's number; e, the electronic charge; D, the dielectric constant; T, the absolute temperature and Q (b), a function of b, equal to $e^2/aDkT$ in which a is the mean effective distance of closest approach between a positive and negative ion. They have shown that the dissociation constant of tetraisoamylammonium nitrate in dioxane–water mixtures, having dielectric constants at 25° ranging from 2.38 to 38.0, varies with the dielectric constant in satisfactory accord with this relation. The function, $Q(b)$, is of such a nature that the dissociation constant of a given salt should be smaller in that solvent in which the parameter a is smaller, provided the other factors, D and T, are the same. From this it follows that the mean distance of closest approach of the *o*-chlorophenyltrimethylammonium ion to the perchlorate ion is considerably less in ethylidene chloride than it is in ethylene chloride. An interpretation of this difference in terms of the known differences in dipole moments and/or polarizabilities of these two solvents is not warranted on the basis of the present results. Further work is in progress.

The greater value of Λ_0 obtained for *o*-chlorophenyltrimethylammonium perchlorate in ethylidene chloride is quite precisely that expected from Walden's rule, ($\Lambda_0\eta$ = constant). The viscosities of ethylidene chloride and ethylene chloride at 25° are 0.00465 and 0.00780 poise,[21] respectively. The effective volumes of the free ions of this salt are therefore substantially the same in these two solvents.

Summary

The dissociation constants and Λ_0 values of the ortho, meta and para isomers of chloro-, methoxy- and methylphenyltrimethylammonium perchlorates in ethylene chloride at 25° have been derived from conductance measurements by the Fuoss–Kraus method.

Likewise the dissociation constant and Λ_0 value of *o*-chlorophenyltrimethylammonium perchlorate

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(17) Hammett, *J. Chem. Soc.* p. 186–196.

(18) Unpublished value of 10.2 obtained by Dr. M. T. Rogers of Michigan State College (personal communication).

(19) Smyth, Dornte and Wilson, THIS JOURNAL, **53**, 4253 (1931); White and Morgan, *J. Chem. Phys.*, **5**, 661 (1937).

(20) Fuoss and Kraus, THIS JOURNAL, **55**, 1019 (1935).

(21) "International Critical Tables," Vol. VII, 213.

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 $N(CH_3)$ 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°.

LOS ANGELES, CALIF. RECEIVED JUNE 9, 1947

[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,[1] 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.[2]

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[3]

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 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[4] 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 ±1.5°.

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

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(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.

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