Summary

It has been shown by means of linear expansion measurements in different directions in single crystals of sodium nitrate that the gradual transition occurring between 150 and 278° is most marked in the direction of the *c* axis and was not detected along the *a* axis. This is interpreted as indicating a separation of the layers of nitrate ions resulting from the change in the eigenfunctions caused by the rotation of the ion. The angle α is calculated to be 45°34′ at 280° as compared with α = 45°35′ obtained from the x-ray data by Kracek, Posnjak and Hendricks.

KEARNY, NEW JERSEY
RECEIVED AUGUST 24, 1932
PUBLISHED FEBRUARY 9, 1933

[CONTRIBUTION FROM THE PHYSICO-CHEMICAL INSTITUTE OF THE UNIVERSITY OF ROSTOCK]

Anomalous Electrolytes. I. The Electrical Conductivity of Solutions of Iodine and Cyanogen Iodide in Pyridine[1]

BY L. F. AUDRIETH[2] AND E. J. BIRR

It has often been shown that substances which are usually designated as non-electrolytes, with reference to water as solvent, may in suitable media exhibit salt-like properties and yield conducting solutions. This anomalous behavior has been ascribed either to (1) a transformation of a *pseudo*-salt into a true salt, or (2) to reaction of the solute with the solvent with the resultant formation of solvated compounds of greater or lesser stability which conduct the electric current. Thus nitro compounds have been found to yield conducting solutions in ammonia[3] and in hydrazine,[4] whereas iodine and the cyanogen halides have been found to act as electrolytes in such solvents as liquid sulfur dioxide, arsenious chloride and sulfuryl chloride.[5]

In the first paper of this series the results of a preliminary investigation concerning the nature of solutions of iodine and cyanogen iodide in pyridine, as revealed by a study of their electrical conductivity, are presented.

Experimental

Materials.—The solvent, Pyridin purissimum Kahlbaum, was dried over solid potassium hydroxide and then distilled repeatedly from a solution of cadmium per-

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[1] It is with pleasure that the authors acknowledge their indebtedness to Professor Paul Walden for his interest and encouragement and for his kindness in placing at their disposal the facilities of the laboratory.

[2] University of Illinois, Urbana, Illinois. National Research Council Fellow at the University of Rostock, 1931–1932. The aid of a fellowship grant from the National Research Council, Washington, D. C., is gratefully acknowledged.

[3] Franklin and Kraus, *Am. Chem. J.*, **23**, 279 (1900); **27**, 191 (1905); Franklin, *Z. physik. Chem.*, **69**, 272 (1909).

[4] Hilgert, Thesis, Rostock, 1932.

[5] Walden, *Z. physik. Chem.*, **43**, 385, 409, 423, 445 (1903).

chlorate in an atmosphere free from carbon dioxide and water vapor. The first and final fractions were always rejected. This procedure sufficed to give a highly purified and anhydrous pyridine whose specific conductivity varied from $\kappa_{25°} = 2.0$ to 7.0×10^{-8}.

Iodine was purified by sublimation from a mixture of pure and dry sodium iodide and iodine. Cyanogen iodide was also purified by sublimation.

Apparatus.—For details of the apparatus employed in carrying out the conductivity measurements reference is made to the original articles.[6] All measurements were carried out at 25°. The conductivity cell which had been employed previously in a study of the conductivity of salts in pyridine[7] was used in the present investigation. The cell constant, $K_c = 0.0824$, was found to have remained unchanged as indicated by a recheck against standard potassium chloride solutions and by comparison with other cells.

(a) **Iodine in Pyridine.**—Iodine dissolves in pyridine to give a brown solution. Addition of water to such a solution, either immediately or after the solution has stood for some time, results in the precipitation of a rather unstable complex compound possessing the formula, $C_5H_5N \cdot I_2$.[8] Since iodine solutions in pyridine are brown, pyridine has been designated as an "active" solvent and one in which "the reactivity (of iodine) is increased by virtue of its coördinative linkage."[9] Thus, iodine in pyridine reacts with silver saccharide to precipitate silver iodide, a reaction which does not take place, or only very slowly, in solvents in which iodine dissolves to give a violet solution.[9]

Both freshly prepared solutions and those which have aged are decolorized by shaking with mercury.

An investigation of such solutions with respect to their electrical conductivity[10] revealed the fact that these undergo rapid change with time. The conductivity increases rapidly during the first hour and then very slowly over a time interval of 100–150 hours. To follow this change more carefully, accurately weighed amounts of iodine were dissolved in pyridine and the change in conductivity with respect to time investigated. Several typical runs are noted in Table I. The concentrations in moles per liter, C, and the dilutions in liters per mole, V, are noted. κ represents the specific conductivity, λ the molecular conductivity calculated on the basis of iodine dissolved as I_2. All values were corrected for the specific conductivity of the solvent, $\kappa_{\text{solv.}}$, which was measured each time before the addition of the iodine. The time in hours is noted.

It is clearly evident from the data in Table I that the character of iodine solutions in pyridine changes profoundly on standing. This fact had already been surmised by Ley and Engelhardt,[11] also by Getman,[12] who

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[6] Walden, Ulich and Birr, *Z. physik. Chem.*, **131**, 1 (1927); Ulich, *ibid.*, **115**, 377 (1925).

[7] Walden, Audrieth and Birr, *ibid.*, [A] **160**, 337 (1932).

[8] Waentig, *ibid.*, **68**, 513 (1910).

[9] Feigl and Bondi, *Monatsh.*, **49**, 417 (1928); **53/54**, 508 (1929).

[10] Mathews [*J. Phys. Chem.*, **9**, 650 (1905)] reports the specific conductivity of a saturated solution of iodine in pyridine to be $\kappa = 1.14 \times 10^{-3}$.

[11] Ley and Engelhardt, *Z. physik. Chem.*, **74**, 55 (1910).

[12] Getman, THIS JOURNAL, **50**, 2883 (1928).

TABLE I

CHANGE IN CONDUCTIVITY OF SOLUTIONS OF IODINE IN PYRIDINE WITH TIME, $t = 25°$

(1) $C = 0.0032$, $V = 311$, $\kappa_{\text{solv.}} = 6.9 \times 10^{-8}$			(2) $C = 0.00648$, $V = 154.4$, $\kappa_{\text{solv.}} = 3.34 \times 10^{-8}$		
Time	$\kappa \times 10^{-5}$	λ	Time	$\kappa \times 10^{-5}$	λ
0.08	2.453	7.66	0.16	3.58	5.33
.25	4.801	14.98	.33	19.83	30.63
.58	11.3	35.34	.66	20.4	31.5
.83	11.53	35.97	1.00	20.62	31.85
4.42	11.95	37.32	1.33	20.75	32.04
6.00	12.16	37.96	18.33	22.18	34.26
22.00	12.65	39.52	22.00	22.38	34.55
29.75	12.72	39.71	26.75	22.52	34.75
46.9	12.80	39.98	118.0	22.89	35.35

observed a difference in the absorption spectrum of freshly prepared and older solutions of iodine in pyridine.

Since the λ-values obtained were extraordinarily high it was deemed advisable to carry out several series of measurements at higher dilutions in order to determine the character of the conductivity curve. The following method was employed.

Stock solutions of iodine in 100 cc. of pyridine were prepared and then kept in a thermostat at 25° for one hundred hours to permit the reaction to come to equilibrium. Fifty cc. of pyridine was then pipetted into the conductivity cell and the specific conductivity of the solvent determined. The various concentrations were then prepared by the addition of definite volumes of stock iodine solution to the solution in the cell. The results of three such series of measurements are presented in Table II in which the molar conductivities, λ, and the concentrations, C, are noted.

TABLE II

MOLAR CONDUCTIVITIES OF IODINE SOLUTIONS IN PYRIDINE, $t = 25°$

$C \times 10^{-5}$	λ	$C \times 10^{-5}$	λ
0.0000	132.0	34.38	62.0
4.059	103.5	36.94	59.6
7.814	91.1	42.36	60.7
8.71	90.9	52.9	61.1
16.02	77.1	104.5	53.9
16.77	76.9	224.2	48.4
18.01	73.0	240.8	47.8
22.95	70.5		

At high dilutions a constant conductivity value was quickly attained, but at higher concentrations the solutions revealed a gradual increase toward a constant maximum value. Above dilutions of 5000 liters excellent agreement between the various series of runs was obtained, but with increasing concentrations the final values often showed considerable divergence. The more dilute the original stock solution, the more rapidly were the equilibrium values approached.

By plotting the experimentally determined λ_v-values against the square root of the concentration and extrapolating to infinite dilution (which is permissible since values above 5000 liters lie on a straight line), the surprising value of approximately 130–2 is obtained. This value for the limiting conductivity is about twice as great as might be expected on the basis of a simple dissociation of the iodine molecule into a positive and a negative ion. Such a value might have appeared logical had chemical interaction between solvent and solute resulted in the formation of two molecules of pyridonium iodide, $C_5H_5N\cdot HI$, from one molecule of iodine. However, pyridine solutions of iodine, even after standing for a month, still precipitate the insoluble complex, $C_5H_5N\cdot I_2$, on the addition of water, and are still largely decolorized by shaking with mercury. Such a reaction can, therefore, not be considered as an explanation for the observed phenomena.

There is only one other possibility and this involves the formation of a ternary electrolyte. In order to explain the experimental findings the following equilibrium must be set up:

$$\mathrm{Py} + \mathrm{I_2} \rightleftharpoons \underset{(A)}{\mathrm{Py\cdot I_2}} \rightleftharpoons \underset{(B)}{\mathrm{IPy^+}} + \mathrm{I^-} \rightleftharpoons \underset{(C)}{\mathrm{Py^{++}}} + 2\mathrm{I^-} \qquad (1)$$

$$2[\mathrm{Py\cdot I_2}] \rightleftharpoons \underset{(D)}{\mathrm{IPy^+}} + \mathrm{I\cdot PyI_2^-} \qquad (2)$$

Equation (I) explains satisfactorily (1), the transformation of the pyridine–iodine complex, a non-electrolyte, into a true salt, *iodipyridonium iodide*[13] (A to B); (2), the extremely labile character of the equilibrium in that the addition of water, and of mercury, drives the reaction to the left with the removal of iodine; (3), the extremely high value for the limiting conductivity, λ_∞, which can only be explained by the formation of a ternary electrolyte (C); (4), the displacement of the equilibrium to the right with decreasing concentration of iodine. Since electrophoresis of such iodine–pyridine solutions (0.02–0.03 *M*) results in the migration of the colored ion to the anode, it is very probable that the transformation of the pseudo-salt involves the intermediate formation of polyiodides, that is, the reaction is a stepwise process as indicated by Equation (2). It is therefore highly probable that solutions of iodine in pyridine contain in equilibrium with one another the various forms A, B, C and D. Dilution shifts this equilibrium to the right with formation of the ternary electrolyte (C), whereas the forms A, B and D predominate in more concentrated solutions.

(b) Cyanogen Iodide in Pyridine.—Clark and Streight[14] have already

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[13] In a publication entitled "Über eine neue Klasse von Verbindungen des positiv einwertigen Jods" (Verlag Hirzel, Leipzig, 1932), which has just come to the attention of the authors, Carlsohn describes the preparation and properties of a whole series of salts of the two hypotheticl bases, I(Py)OH and I(Py)OH. Our theory that the rapid change in conductivity of solutions of iodine and cyanogen iodide in pyridine is due to the formation of quaternary iodipyridonium salts is further substantiated by these findings of Carlsohn.

[14] Clark and Streight, *Trans. Roy. Soc. Canada*, [3] **22**, 323 (1928).

shown that solutions of cyanogen iodide in pyridine conduct the electric current. Electrolyses of 0.1 *M* solutions result in the discharge of cathodic iodine. They ascribe the conductivity of the cyanogen halides to the formation of quaternary pyridonium salts.[14]

An investigation of solutions of cyanogen iodide in pyridine with respect to their electrical conductivity revealed the fact that these too, like the iodine–pyridine solutions, suffered an increase in conductivity on standing. Dilute solutions of cyanogen iodide are at first colorless, but become on standing successively yellow, orange, red-brown and finally deep red-brown. The results of three series of measurements, in which the change in conductivity was observed, are given in Table III.

TABLE III

CHANGE IN CONDUCTIVITY OF SOLUTIONS OF CYANOGEN IODIDE IN PYRIDINE WITH TIME, $t = 25°$

(3) $C = 0.00538$		(4) $C = 0.00352$		(5) $C = 0.00626$	
Time (hrs.)	$\kappa \times 10^{-5}$	Time	$\kappa \times 10^{-5}$	Time	$\kappa \times 10^{-5}$
0.33	0,143	1.00	0.4637	1.58	0.710
.58	.247	1.83	1.109	2.40	1.176
1.00	.456	17.33	7.308	5.00	3.351
3.08	2.212	23.25	7.785	6.83	4.556
4.13	3.72	26.12	7.925	8.00	5.031
5.70	5.67	42.12	8.561	10.66	5.668
7.83	6.245			23.80	7.626
23.83	8.411			29.42	8.186
32.00	8.897			47.00	9.48
50.08	9.74			54.43	9.90
98.83	10.8			72.50	10.81
119.00	11.26			77.70	11.02
				126.00	11.77

The change in conductivity again is due to the formation of an electrolyte. It seems quite probable that a similar sort of reaction mechanism may be postulated for solutions of cyanogen iodide in pyridine as in the case of iodine. However, the transformation of the pseudo-salt into an electrolyte proceeds much more slowly and is further-complicated by side reactions.[15] It is of interest to note that the conductivity values for solutions of cyanogen iodide in pyridine are much lower than those of corresponding concentrations of iodine in this solvent. This fact further supports the formation of an iodipyridonium cyanide,[16] possibly also of a corresponding

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(15) Interaction of pyridine with an ethereal solution of cyanogen bromide results in the formation of an extremely unstable addition compound which can be obtained in crystalline form. This substance breaks down rapidly to give a variety of ill-defined decomposition products [Shimidzu, *Chem. Zentr.*, I, 2202 (1927)].

(16) Iodine monochloride also dissolves in pyridine to give a solution whose conductivity increases rapidly upon standing. The process of solution is, however, accompanied by very apparent decomposition. It is highly probable that the rapid increase in conductivity may here also be ascribed to the formation of a quaternary pyridonium salt. This assumption is further supported by the fact that the addition of pyridine to a solution of iodine monochloride in ether results in the formation of a crystalline compound, C_5H_5N ClI [see Pictet and Krafft, *Bull. soc. chim.*, [3] **7**, 73 (1892)].

ternary electrolyte. Cyanides are much weaker salts in pyridine than are iodides.[7]

Summary

Both iodine and cyanogen iodide dissolve in pyridine to give solutions whose electrical conductivity increases with time to give maximum values. The experimental evidence indicates that reaction between solvent and solute results in the primary formation of a non-conducting addition compound which in time changes over to a true quaternary pyridonium salt. In the case of iodine the extraordinarily high value for the molecular conductivity at infinite solution can only be explained by the formation of a ternary salt.

ROSTOCK, GERMANY

RECEIVED AUGUST 31, 1932
PUBLISHED FEBRUARY 9, 1933

[CONTRIBUTION FROM THE PHYSICO-CHEMICAL INSTITUTE OF THE UNIVERSITY OF ROSTOCK]

Electric Moments of Hydrazine and its Derivatives[1]

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In a discussion of the structure of azo compounds as revealed by the measurement of their dipole moments, Bergmann, Engel and Sandor[3] arrive at the conclusion that hydrazo compounds probably also possess a *trans*-configuration, first, because azotoluene and hydrazotoluene form mixed crystals, and, second, because the former has a zero electric moment and must therefore possess a structure of highest symmetry. While their statement "that only similarly constituted substances can form mixed crystals" is not a question for dispute, it nevertheless seemed highly improbable that a definite comparison between the structures of these two classes of compounds, based on this one observation, was permissible. That hydrazo compounds might easily assume the *trans*-configuration in solid mixtures in which this form is forced upon it by the symmetry of the other component is very probable. That they should prefer this structure exclusively, say in dilute benzene solution, seemed questionable in view of the fact that the $>\mathrm{N—N}<$ linkage in hydrazo compounds permits free rotation, that is, theoretically allows a variety of positions of the substituents with respect to each other, whereas the positions of groups in azo compounds with —N=N— linkage is presumably fixed.

That this objection to Bergmann's postulation is correct is conclusively

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[1] The authors acknowledge with pleasure their indebtedness to Professor Paul Walden for his kindness in placing at their disposal the facilities of the laboratory.

[2] University of Illinois, Urbana, Illinois. National Research Council Fellow at the University of Rostock, 1931–1932. The aid of a fellowship grant from the National Research Council, Washington, D. C., is gratefully acknowledged.

[3] Bergmann, Engel and Sandor, *Ber.*, **63**, 2572 (1930).