[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

Complex Ions. VIII. Pyridine–Silver Ions

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It is of interest to compare the complex ions formed from silver ion and pyridine with the ammine–silver ions.[1] Koch[2] and Britton and Williams[3] have determined the dissociation constant of the ion $Ag(C_5H_5N)_2^+$ on the assumption that this is the only pyridine–silver ion. Under their conditions a monopyridine ion would be unimportant. The constants are not in very good agreement, but great accuracy is not claimed.

In this investigation the solubilities of silver iodate, silver sulfate and silver bromate in pyridine solutions have been measured. Preliminary calculations of the iodate results gave rapidly increasing dissociation constants for the most dilute solutions when it was assumed that only the dipyridine complex ion was formed. Assumption of the existence of the ion $AgPy^+$ as well as $AgPy_2^+$, where Py stands for C_5H_5N, led to a satisfactory interpretation of all of the solubility data.

Materials.—Silver sulfate and silver iodate were prepared by precipitation as previously described, except that the iodate was dried at 110°. Silver bromate was prepared by slow precipitation from silver nitrate and potassium bromate. Analysis gave 45.70% silver; calculated 45.75%.

Pyridine of "practical" grade was refluxed over barium oxide for several hours and distilled through a Widmer column. A fraction having a boiling-point range of 0.2° was taken. Pyridine solutions were usually made by weighing the pure pyridine and water. In some cases the weighed pyridine was diluted to known volume, and the density was determined so that the molality could be calculated

Other chemicals were of analytical reagent grade.

Solubility Determinations.—The solubility of silver iodate in pyridine solutions of known molality was determined essentially as previously described for the solubility in ammonia,[4] except that the pyridine was not determined. The temperature was 25 ± 0.05°. The results are shown in the first two columns of Table I.

TABLE I

SOLUBILITY OF SILVER IODATE IN PYRIDINE SOLUTIONS

Py, total m	$AgIO_3$ $m \times 10^3$	Ag^+ $m \times 10^5$	$AgPy_2^+$ $m \times 10^3$	Py, free m	$K_2 \times 10^5$
0.0497	1.082	3.064	0.905	0.0477	7.70
.0547	1.180	2.819	1.004	.0525	7.73
.0571	1.232	2.704	1.057	.0549	7.72
.0997	2.084	1.637	1.911	.0957	7.84
.1013	2.130	1.603	1,960	.0973	7.74
1075	2.244	1.526	2.072	.1032	7.85
.1493	3.089	1.128	2.916	.1433	7.94
.1498	3.122	1.117	2.950	.1437	7.82
.2018	4.173	0.852	4.00	.1936	7.99
.2061	4.189	.849	4.01	.1979	8.28
.3026	6.27	.584	6.10	.2903	8.08
.409	8.46	.445	8.28	.3924	8.28
.409	8.47	.445	8.29	.3925	8.28
.516	10.66	.361	10.48	.494	8.42
.516	10.72	.360	10.54	.495	8.37
.728	15.05	.267	14.86	.698	8.75
.853	17.62	.232	17.43	.818	8.90

The silver ion molality was calculated from the iodate ion molality (assumed equal to the total iodate molality), the ionic strength, and the solubility product for silver iodate[4] (p. 2672). The difference between the total silver and silver ion molalities was taken as the sum of the molalities of two complex ions, $AgPy^+$ and $AgPy_2^+$. Because of the small solubility of silver iodate, the second is more important than the first. Therefore the data of Table I were used for the calculation of K_2, the equilibrium constant for the reaction

$$AgPy_2^+ \rightleftarrows Ag^+ + 2Py$$

$$K_2 = [Ag^+][Py]^2/[AgPy_2^+] \qquad (1)$$

Activity coefficients should cancel approximately from Equation 1.

To correct for the relatively small amount of the monopyridine ion, $AgPy^+$, the instability constant, k_1, of this ion, determined as described below, was used.

$$k_1 = [Ag^+][Py]/[AgPy^+] = 1.0 \times 10^{-2} \qquad (2)$$

Simultaneous equations were set up allowing the calculation of the molalities of free pyridine and the ion $AgPy_2^+$. These molalities are given in Table I, together with the corresponding values of K_2.

The solubilities of two somewhat more soluble silver salts, the sulfate and the bromate, in pyridine were determined to obtain more favorable data for the calculation of k_1. For silver sulfate the procedure was essentially as described previously.[1b] For silver bromate the procedure was like that for iodate except that ammonium molybdate was used as a catalyst in the titration.[5]

The results for silver sulfate are given in Table II. As the ion $AgPy^+$ was present in larger molality than the ion $AgPy_2^+$, the molality of the latter was calculated by means of Equation 1 with $K_2 = 7.8 \times 10^{-5}$. Since k_1 was needed for the calculation of K_2, an approximation method in-

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(1) (a) Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, Denmark, 1941, p. 130; (b) Vosburgh and McClure, THIS JOURNAL, **65**, 1060 (1943).

(2) Koch, *J. Chem. Soc.*, 2053 (1930).

(3) Britton and Williams, *ibid.*, 798 (1935).

(4) Derr, Stockdale and Vosburgh, THIS JOURNAL, **63**, 2672 (1941).

(5) Kolthoff and Sandell, "Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1943, p. 624.

volving also the data of Table IV was used for finding mutually consistent values for the two constants. The molalities of the ion AgPy$^+$ and the uncombined pyridine could then be calculated, and finally k_1.

TABLE II

SOLUBILITY OF SILVER SULFATE IN PYRIDINE SOLUTIONS

Py, total m	Ag_2SO_4 $m \times 10^3$	Ag^+ $m \times 10^3$	$AgPy^+$ $m \times 10^3$	Py, free $m \times 10^3$	$k_1 \times 10^3$
0.01475	31.82	52.3	9.5	1.65	9.1
.02075	33.29	51.9	11.0	2.35	11.1
.03607	37.68	51.0	16.1	3.53	11.2
.05492	42.79	50.3	20.5	4.8	11.8

Before attempting to measure the solubility of silver bromate in pyridine solutions, its solubility in water and potassium nitrate solutions was determined. The solubility of silver bromate has been measured by Hill,[6] Reedy,[7] and Dalton, Weymouth and Pomeroy,[8] the results being 8.29, 8.31 and 8.06 millimoles per 1000 g. of water, respectively, at 25°. The first two agree within the precision of the second, and the result in this investigation was only a little lower, 8.27×10^{-3} m. The solubility results with this preparation were more consistent among themselves than those obtained with a preparation of lower solubility in a previous investigation.[1b] The effect of potassium nitrate on the solubility agreed with that found by Dalton, Weymouth and Pomeroy. The results are given in Table III, and can be calculated by means of the equations

$$K_{\text{S.P.}} = [Ag^+][BrO_3^-]f^2 = 5.60 \times 10^{-5} \quad (3)$$

$$-\log f = 0.5056\sqrt{\mu}/(1 + \sqrt{\mu}) + 0.104\mu \quad (4)$$

TABLE III

SOLUBILITY OF SILVER BROMATE IN POTASSIUM NITRATE SOLUTIONS

KNO_3, m	$AgBrO_3$, m	μ	$K_{\text{S.P.}} \times 10^5$
	0.00827	0.00827	5.61
0.0477	.00949	.0572	5.59
.1002	.01027	.1105	5.50
.401	.01304	.414	5.62

The solubility of silver bromate in pyridine solutions is given in Table IV. The calculation of the silver ion molality was made by means of Equations 3 and 4 and that of k_1 by the method used for the silver sulfate data. The value of k_1 used in the calculations for the silver iodate data (Table I) was the mean of the values in Tables II and IV, $k_1 = 1.0 \times 10^{-2}$.

Discussion.—The values for K_2 in Table I increase with the pyridine molality in the more concentrated solutions. However, they show only erratic variations for total pyridine molalities up to 0.1 m, and the value adopted, $K_2 = 7.8 \times 10^{-5}$, is the average for the more dilute solutions. The constants of Britton and Williams[3] increase with the pyridine concentration also. Their average value, determined at 15°, when corrected to 25° by the temperature coefficient data of Koch[2] is 7.0×10^{-5}. Koch's value for K_2 seems to be about 11×10^{-5} at 25°, but is a little uncertain because the temperature for the accepted average value is not given.

TABLE IV

SOLUBILITY OF SILVER BROMATE IN PYRIDINE SOLUTIONS

Py, total m	$AgBrO_3$ $m \times 10^3$	Ag^+ $m \times 10^3$	$AgPy^+$ $m \times 10^3$	Py, free $m \times 10^3$	$k_1 \times 10^3$
0.00597	9.80	7.08	2.09	2.63	8.9
.00827	10.32	6.76	2.44	3.59	9.9
.01273	11.49	6.14	3.22	5.25	10.0
.01564	12.34	5.76	3.72	6.20	9.6

It is probable that the increase in K_2 is the effect of some uncontrolled variable which varies appreciably only in the more concentrated solutions. The dielectric constant of the medium might be one such variable. Another possibility is the activity coefficient of the pyridine, which was taken as unity in all calculations.

The assumption of the existence of two complex pyridine–silver ions gives a satisfactory interpretation of the solubility data, whereas the assumption of the dipyridine ion alone was unsatisfactory. This is to be expected by analogy with the ammines.

It is interesting to compare the constants for the pyridine complexes with those for the ammines. The constant k_2 may be defined in terms of the constants used above by the equation $k_1k_2 = K_2$. The ratio of k_1 to k_2 for pyridine is 1.3 as compared with 3 for ammonia. The monopyridine ion is more important relatively than the monammine. The ratio of k_1 for ammonia to k_1 for pyridine is 4×10^{-2}, while the ratio of the ionization constants of the two bases is about 10^{-4}. This comparison emphasizes the lack of relationship between basic strength and stability of silver complex ions which was pointed out by Britton and Williams.

Summary

The solubilities of silver iodate, silver sulfate and silver bromate in dilute pyridine solutions have been determined.

The results have been interpreted in terms of two complex ions, AgPy$^+$ and AgPy$_2^+$, with dissociation constants k_1 and K_2 equal to 1.0×10^{-2} and 7.8×10^{-5}, respectively.

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(6) Hill, THIS JOURNAL, **39**, 218 (1917).

(7) Reedy, *ibid.*, **43**, 1440 (1921).

(8) Dalton, Weymouth and Pomeroy, *ibid.*, **46**, 60 (1924).