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The Dissociation Pressures of Certain Metal Pyridine Cyanates

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The dissociation pressures of the pyridine complexes of cobaltous, cupric, nickelous and zinc thiocyanates have been reported in an earlier paper.[1] In an effort to gain a better understanding of the factors which influence the magnitude of the residual affinities of the metal atoms manifested through their coördination valences, we have now determined the dissociation pressures of the pyridine cyanates of the same four metals. It appears that the substitution of an oxygen atom in place of the sulfur at the remote end of the acid radical considerably increases the residual affinity of the metal atom. The complex cyanates have lower dissociation pressures than the corresponding thiocyanates containing the same number of pyridine molecules. A general similarity, but not a complete parallelism, exists between the dissociation pressures of the two series. Pyridine nickelous and pyridine zinc cyanates have the same extraordinary property as the pyridine thiocyanates of these metals, namely, the property of decomposing more readily at lower temperatures.

TABLE I

DISSOCIATION PRESSURES (MM. OF MERCURY AT 20°)

Temp., °C.	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	100
$Co(NCO)_2 \cdot 2Py$	...	...	...	...	...	...	...	...	1.1	...	1.8	...	2.8	...	3.9	5.9
$Co(NCO)_2 \cdot 4Py$	...	...	...	...	1.1	...	2.8	...	5.4	...	12.3	...	24.6	...	39.4	...
$Co(NCO)_2 \cdot 6Py$	5.8	...	10.0	...	15.9	...	25.7	...	44.0	...	66.2	...	...	...	...	...
$Cu(NCO)_2 \cdot 2Py$	...	...	...	...	1.0	...	1.9	...	3.5	...	5.9	...	9.9	...	16.2	...
$Cu(NCO)_2 \cdot 3Py$	...	0.7	...	2.1	...	6.4	11.9	18.8	35.6	...	...	...	...	...	...	...
$Cu(NCO)_2 \cdot 6Py$	7.0	10.0	13.4	18.4	26.5	...	49.6	69.3	92.5	...	...	...	...	...	...	...
$Ni(NCO)_2 \cdot 4Py$	...	...	1.0	...	1.2	...	1.4	...	1.6	...	1.8	...	2.1	...	2.3	2.6
$Ni(NCO)_2 \cdot 6Py$	...	5.0	...	...	6.4	...	7.3	...	8.4	8.9	9.5	11.3	14.3	16.7	20.2	30.5
$Zn(NCO)_2 \cdot 2Py$	...	0.5	...	...	...	...	0.8	...	0.9	...	...	...	1.2	...	1.4	1.6

The dissociation pressures were measured in the same way as was done with the thiocyanates, except that an absorption tower filled with fragments of pumice sprinkled with phosphorus pentoxide and moistened with concd. sulfuric acid was found to be more satisfactory than a U tube for the removal of pyridine from the vapors which were pumped from the apparatus. The method made possible the detection of all of the complexes of each metal cyanate with pyridine, existing between 20 and 100°, and the results suggested a simple means for the preparation of the new cupric tripyridine cyanate in the pure state for analysis. The other complex cyanates, except cobaltous tetrapyridine cyanate,[2] have been described in the first paper of this series.[3] We have also made a more careful study of the dissociation, in solution, of cobaltous hexapyridine cyanate which was discussed in the same paper.

Dissociation Pressures.—The dissociation pressures as determined by experiment are indicated in Table I. The chart, Fig. 1, in which the logarithm of the pressure is plotted against the reciprocal of the absolute temperature, supports a number of interesting conclusions, parallel to the inferences which were made in the case of the thiocyanates.

The curves of cobaltous di- and hexapyridine cyanates are roughly parallel to each other and to the curve of the vapor pressure of pyridine, as were those of cobaltous di- and tetrapyridine thiocyanates, and indicate that the affinities of cobaltous cyanate and cobaltous tetrapyridine cyanate for pyridine are substantially constant over the temperature range of our observations. Cobaltous tetrapyridine cyanate, on the other hand, decomposes more readily at the higher temperatures and exists only within a limited temperature range.

The curves of cupric di-, tri- and hexapyridine cyanates approach the pyridine curve at the higher temperatures, and indicate that the affini-

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[1] Davis and Batchelder, THIS JOURNAL, **52**, 4069 (1930).

[2] Described by Ripan, *Bull. soc. Stiinte Cluj*, **3**, 176 (1927). We have prepared it by warming the bottom of an evacuated vessel which contained, one above the other on suitable supports, two watch glasses containing mixtures of the hexapyridine and dipyridine compounds. The pyridine driven off from the lower sample was absorbed by the upper. The finally homogeneous contents of the lower watch glass was found by analysis to be cobaltous tetrapyridine cyanate.

[3] Davis and Logan, THIS JOURNAL, **50**, 2493 (1928).

ties of cupric cyanate and cupric di- and tripyridine cyanates for pyridine, like those of the thiocyanates, decrease with increasing temperature.

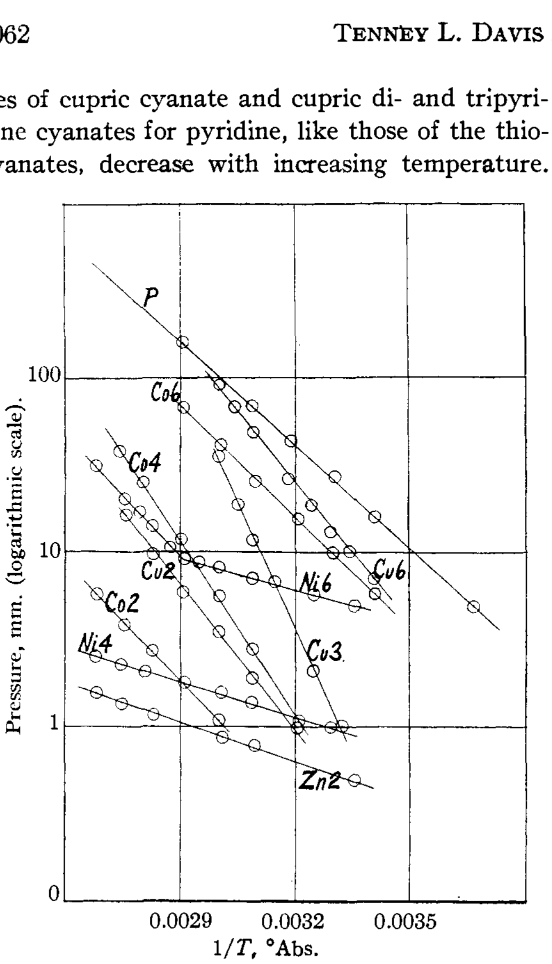

Fig. 1.—Dissociation pressures of metal pyridine cyanates: P, pyridine (vapor pressure); Co6 cobaltous hexapyridine cyanate; Co4 tetrapyridine; Co2 dipyridine; Cu6 cupric hexapyridine; Cu3 tripyridine; Cu2 dipyridine; Ni6 nickelous hexapyridine; Ni4 tetrapyridine; Zn2 zinc dipyridine.

The curve of cupric hexapyridine cyanate intersects the vapor pressure curve of pyridine at about 72°; above this temperature the substance breaks down into pyridine and cupric tripyridine cyanate.

Zinc dipyridine and nickelous tetrapyridine cyanates hold their pyridine with affinities which cecrease at the lower temperatures, Nickelous dexapyridine cyanate shows a change in its characteristics at about 70°. Above this temperature it holds its pyridine with an affinity which remains practically constant as the temperature is increased. Below 70° its curve approaches the vapor pressure curve of pyridine; it intersects it at about −8°, and below that temperature the substance decomposes into pyridine and nickelous tetrapyridine cyanate. The two forms of nickelous hexapyridine cyanate change into each other rather slowly, and the change is reversible. At temperatures near the transition point the vapor pressure apparatus needed two hours or more to come to equilibrium. With other substances fifteen or thirty minutes was sufficient.

The dissociation pressures of metal pyridine thiocyanates and cyanates of similar constitution are compared with one another in Table II. If the same data were plotted in a semi-logarithmic chart, it would appear that the curves of the corresponding compounds are not really parallel, although those of the cobaltous dipyridine and nickelous tetrapyridine compounds are nearly so.

Cupric Tripyridine Cyanate.—This substance was prepared by heating cupric hexapyridine cyanate in a closed apparatus at 75° in such a manner that the pyridine which separated was able to drain off. When the material appeared dry, it was removed, powdered and set aside in a desiccator which contained, in separate vessels, stick caustic and cobaltous hexapyridine cyanate to maintain about the right vapor pressure of pyridine. The crystalline material had a deeper blue color than cupric dipyridine cyanate.

Anal. Calcd. for $Cu(NCO)_2 \cdot 2Py$: Cu, 20.85; for $Cu(NCO)_2 \cdot 3Py$: Cu, 16.53; for $Cu(NCO)_2 \cdot 4Py$: Cu, 13.70. Found: Cu, 16.60, 16.65, 16.75.

Dissociation of Cobaltous Hexapyridine Cyanate in Chloroform Solution.—Pink cobaltous hexapyridine cyanate dissolves in chloroform to form a deep blue solution which evidently contains the dipyridine compound. Earlier determinations of the boiling points of such solutions gave anomalous results. We have now made careful repetition of the experiments. Between 0.2 and 0.5 g. of cobaltous hexapyridine cyanate was dissolved in 73.77 g. of purified dry chloroform, b. p. 61.10–61.16° at 758 mm., and 15 cc. of the solution was pipetted into the boil-

TABLE II

DISSOCIATION PRESSURES (MM. OF MERCURY AT 20°)

Temp., °C.	20	30	40	50	60	70	80	90	100
Cobaltous tetrapyridine thiocyanate	1.9	3.4	6.0	10.6	18.0	27.0	44.0	...	...
Cobaltous tetrapyridine cyanate	...	...	1.1	2.8	5.4	12.3	24.6	39.4	...
Cobaltous dipyridine thiocyanate	...	0.5	0.8	1.3	2.1	3.0	4.7	...	...
Cobaltous dipyridine cyanate	...	...	...	...	1.1	1.8	2.8	3.9	...
Cupric dipyridine thiocyanate	5.1	12.0	27.0	58.0	106.0	...	...	...	...
Cupric dipyridine cyanate	...	...	1.0	1.9	3.5	5.9	9.9	16.2	...
Nickelous tetrapyridine thiocyanate	5.0	6.1	7.5	9.8	10.5	12.0	...	...	...
Nickelous tetrapyridine cyanate	...	1.0	1.2	1.4	1.6	1.8	2.1	2.3	2.6

ing point apparatus. The results reported in Table III are calculated by taking the boiling point elevation for chloroform as 36.6° per gram molecule of solute in 100 g. of solvent.

TABLE III

DISSOCIATION IN CHLOROFORM SOLUTION

$Co(NCO)_2 \cdot 6Py$, g.	Observed ΔT, °C.	Expected ΔT if no dissociation	Apparent number of molecules
0.2197	0.095	0.01785	5.32
.2197	.085	.01785	4.76
.4964	.216	.03985	5.42
.4964	.208	.03985	5.22

If dissociation to pyridine and cobaltous dipyridine cyanate is complete, then five molecules would be present in the solution. The results agree with five molecules within the experimental error. They indicate complete dissociation in boiling chloroform solution, and correct and supersede the earlier report of Davis and Logan.

Dissociation in Diphenyl.—Cobaltous hexapyridine cyanate dissolves in melted naphthalene, diphenyl, diphenylamine, camphor, *n*-butyl carbamate, acetamide, acetanilide, phenol, resorcinol, benzoic acid and salicylic acid to yield blue solutions which turn pink more or less rapidly after they freeze. The solution in diphenyl turns pink most rapidly, suggesting that the substance at ordinary temperature dissociates less in that solvent than in the others. The solution in acetamide requires several hours or a day after cooling before the pink color reappears.

Preliminary experiments showed that pyridine dissolved in diphenyl behaved normally in its effect upon the freezing point, and the dissociation of cobaltous hexapyridine cyanate in diphenyl at temperatures slightly below the melting point of diphenyl, m. p. 68.8–68.9° corr., was accordingly determined by the freezing point method. The results reported in Table IV are calculated by taking the freezing point depression for diphenyl as 80° per gram molecule of solute in 100 g. of diphenyl.

TABLE IV

DISSOCIATION IN DIPHENYL SOLUTION

$Co(NCO)_2 \cdot 6Py$, g.	Observed ΔT, °C.	Expected ΔT if no dissociation	Apparent number of molecules	Dissociation constant
0.0586	0.441	0.0906	4.68	3.63×10^{-5}
.1143	.812	.1820	4.46	20.2×10^{-5}
.1560	1.073	.2470	4.34	47.0×10^{-5}

Eight grams of diphenyl was used in each experiment. The results indicate, as would be expected, that the dissociation is less in the more concentrated solutions. The dissociation constants shown in the last column, calculated on the assumption that cobaltous hexapyridine cyanate dissociates directly into the dipyridine cyanate and four molecules of pyridine, disagree so widely as to indicate that the assumption is false. We believe that cobaltous tetrapyridine cyanate is an intermediate in the dissociation and is present in the solution. Results of experiments in which cobaltous tetrapyridine cyanate and pyridine were dissolved together in diphenyl, and the freezing points of the solutions determined, are shown in Table V.

TABLE V

DISSOCIATION IN DIPHENYL SOLUTION

$Co(NCO)_2 \cdot 4Py$, g.	Pyridine, g.	Observed ΔT, °C.	Apparent number of molecules	% Dissociation of Co compound	Dissociation constant
0.0436	0.0150	0.441	2.68	84.0	0.0100
.0605	.0321	.725	2.514	75.7	.01785
.0850	.0293	.812	2.46	73.0	.01737
.1160	.0400	1.073	2.34	67.0	.02393
.0612	.0539	0.973	2.335	66.7	.02310
.0609	.0605	1.056	2.345	67.0	.0285
.0397	.1136	1.558	1.95	47.5	.0325
				Average	.0219

Eight grams of diphenyl was used in each experiment. The results indicate, as would be expected, that an excess of pyridine retards the dissociation. The dissociation constants shown in the last column, calculated on the assumption that the tetrapyridine compound dissociates into the dipyridine compound and two molecules of pyridine are of the same order of magnitude but show a tendency to increase in the cases where the more pyridine is present.

Summary

The dissociation pressures of cobaltous hexa-, tetra- and dipyridine cyanates, of cupric hexa-, tri- and dipyridine cyanates, of nickelous hexa- and tetrapyridine cyanates and of zinc dipyridine cyanate have been determined at temperatures between 20 and 100°.

The affinities which hold the pyridine in the nickelous and zinc compounds decrease at the lower temperatures.

The dissociation of cobaltous hexapyridine cyanate in boiling chloroform, and the dissociations of this substance and of cobaltous tetrapyridine cyanate in diphenyl solution at about 68°, have been measured.

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