The presence of glycol aldehyde is due to the cleavage of the hexose-2,3-enediol or that of a triose-1,2-enediol. It is also conceivable that the formic acid in these reactions may arise from the cleavage of the ethene diol molecule into two molecules of hydroxymethylene.

COLUMBUS, OHIO

THE DISSOCIATION PRESSURES OF CERTAIN METAL PYRIDINE THIOCYANATES

BY TENNEY L. DAVIS AND HOWARD R. BATCHELDER

The determination of the dissociation pressures of the compounds of pyridine with metal thiocyanates is part of an investigation of the affinities by which pyridine and similar nitrogen bases are linked in their complex compounds. Of two compounds, such as nickelous tetrapyridine thiocyanate and cobaltous tetrapyridine thiocyanate, for example, which have the same molecular constitution and differ only in the metal which they contain, the one which has the lower dissociation pressure of pyridine is evidently the one in which the pyridine is attached more firmly to the metal. Since the pyridine is supposed to be attached to the coördination valence of the metal, it is to be expected that the order of the metals with reference to their affinity for pyridine will be the same in the series of the salts of one acid as in the series of the salts of another. By comparison, also, of the dissociation pressures of the corresponding pyridine derivatives of different salts of the same metal, it is possible to estimate the effect of the acid radical—for one acid will occupy more or less of the affinity of the metal than another acid and will leave less or more of the affinity available for combination through the coördination valences.

We have worked with cobaltous, cupric, nickelous and zinc pyridine thiocyanates. The compounds were prepared and purified by the methods which had been used earlier for the chloroform-soluble metal pyridine cyanates.[1] Dissociation pressures were measured by starting with a mixture of pyridine with the most highly pyridinated compound of the metal thiocyanate, evacuating the space above it and allowing to come to equilibrium, noting the pressure, then pumping off a small amount of pyridine, again allowing to come to equilibrium and again noting the pressure, and so on, until the pyridine was completely removed from the substance. Thus we were able to be certain that none of the intermediate pyridine complexes escaped us, and that the dissociation pressures of all of the compounds, from that which existed in the presence of an excess

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

of pyridine to that which existed in the presence of the non-pyridinated metal thiocyanate, were actually observed.

Cobaltous thiocyanate forms compounds only with two and with four molecules of pyridine, while cobaltous cyanate forms compounds with two, with four and with six molecules—a fact which suggests that the affinity of pyridine for the metal in the thiocyanate series is probably less than in the cyanate series. Studies on the dissociation pressures of the metal pyridine cyanates which are now going on in this Laboratory will throw further light upon the matter.

Description of the Compounds

Cobaltous tetrapyridine thiocyanate[2] separates from chloroform in pink crystals which are moderately soluble in chloroform and more readily soluble in a mixture of chloroform and pyridine. Its solutions in organic solvents undergo the same color changes under the same conditions as solutions of cobaltous hexapyridine cyanate. After a week of exposure to the open air, it is converted entirely into deep blue cobaltous dipyridine thiocyanate.

Cupric dipyridine thiocyanate[3] is a green powder, less soluble in chloroform than the cobalt compound and more readily soluble in chloroform if an excess of pyridine is present. It loses pyridine to form the mono-pyridine compound, not previously reported, somewhat paler green in color and somewhat less soluble in chloroform than the dipyridine compound. When warmed in a vacuum, it yields black cupric thiocyanate.

Nickelous tetrapyridine thiocyanate[4] crystallizes from chloroform containing an excess of pyridine in blue crystals which resemble crystals of hydrated copper sulfate. When the chloroform solution is distilled or when the crystals are exposed to the air, the substance is converted into a pale blue powder of nickelous dipyridine thiocyanate,[5] sparingly soluble in chloroform. When the tetrapyridine compound is moistened with pyridine, or exposed for a long time to an atmosphere saturated with pyridine, it yields blue-violet crystals of a substance, not heretofore reported, which contains seven molecules of pyridine, possibly nickelous tetrapyridine thiocyanate with three molecules of pyridine of crystallization. The dissociation pressure curve of this substance is parallel to and only slightly lower than the vapor pressure curve of pure pyridine, and is of markedly different slope from those of the other nickelous thiocyanate pyridine complexes.

[2] Reitzenstein, Z. anorg. Chem., 18, 253 (1898); 32, 304 (1902); Sand, Ber., 36, 1436 (1903).

[3] Litterscheid, Arch. Pharm., 239, 336 (1901); 240, 74 (1902); Spacu, Bull. Soc. Stiinte Cluj, 1, 284 (1924).

[4] Grossmann, Ber., 37, 559 (1904).

[5] Rosenstein and Cohn, Z. anorg. Chem., 27, 284 (1901).

Zinc tetrapyridine thiocyanate[6] crystallizes in fine white needles from chloroform and pyridine mixture, in which it is moderately soluble. When moistened with pyridine and allowed to stand, it forms a cake of crystals from which the pyridine is removed with difficulty.

TABLE I
ANALYSES

Substance	Metal, % Calcd.	Metal, % Found
Cobaltous monopyridine thiocyanate	23.30	...
Cobaltous dipyridine thiocyanate	17.70	17.32, 17.71
Cobaltous tripyridine thiocyanate	14.31	...
Cobaltous tetrapyridine thiocyanate	12.00	11.97, 11.92
Cobaltous pentapyridine thiocyanate	10.34	...
Cupric monopyridine thiocyanate	24.58	24.92, 25.02
Cupric dipyridine thiocyanate	18.83	18.80
Cupric tripyridine thiocyanate	15.26	...
Nickelous monopyridine thiocyanate	23.10	...
Nickelous dipyridine thiocyanate	17.62	17.51, 17.35
Nickelous tripyridine thiocyanate	14.24	...
Nickelous tetrapyridine thiocyanate	11.95	12.14, 12.04
Nickelous pentapyridine thiocyanate	10.29	...
Nickelous hexapyridine thiocyanate	9.04	...
Nickelous heptapyridine thiocyanate	8.06	8.46, 8.27
Nickelous octapyridine thiocyanate	7.27	...
Zinc tripyridine thiocyanate	15.60	...
Zinc tetrapyridine thiocyanate	13.13	13.61, 13.63
Zinc pentapyridine thiocyanate	11.33	...

The substances were analyzed for metal—cobalt, nickel and zinc being determined as sulfate, copper as oxide. Results are shown in Table I, where the calculated values for the substances containing one more and one less molecule of pyridine than the found substances are included for comparison.

Measurement of Dissociation Pressures

The apparatus consisted of an ordinary closed-arm manometer mounted on a transparent millimeter scale and sealed to a side-arm, parallel to the arm of the U of the manometer, to the lower extremity of which a 50-cc. Erlenmeyer flask containing a few grams of the substance to be studied had been sealed. As near as practicable beyond this side-arm a tube carrying a glass stopcock was sealed on and inclined upward in such a manner that the Erlenmeyer flask and manometer and side-arm could be immersed completely in the bath while the stopcock remained above the cover of the bath. The apparatus was set up in a 4-liter beaker filled with distilled water, fitted with a tin cover and an electric stirrer, and having an electric light mounted behind it to illuminate the scale. The cover served to prevent excessive evaporation and provided a support from which to suspend the apparatus and the thermometer. Heat was supplied by a micro-burner and, with adequate protection from drafts, it was easy to maintain the temperature constant for several hours within a tenth of a degree. In preliminary ex-

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[6] Grossmann and Hünseler, Z. anorg. Chem., **46,** 361 (1905).

periments in which the manometer was outside of the bath, it was found that pyridine distilled into the manometer and that the observed pressure was the vapor pressure of pyridine. The above-described simple apparatus was found to avoid the difficulty. A tube containing phosphorus pentoxide for the absorption of pyridine was inserted between the stopcock and the pump, for it was found that the pyridine, by dissolving in the oil of the pump, otherwise reduced the pump's efficiency.
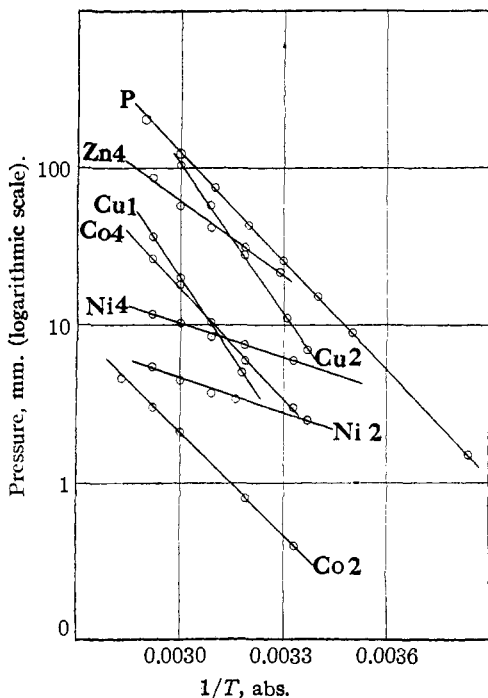
After the apparatus was assembled, the flask containing the substance having been sealed on, a cubic centimeter or more of pyridine was introduced through the stopcock by means of a capillary dropper, for the purpose of providing enough pyridine to displace all of the air in the system and to insure the presence of the most highly pyridinated compound. The bath was then brought to the desired temperature, the apparatus evacuated, the stopcock closed and readings were taken at intervals until it was apparent that equilibrium had been attained. In each series of experiments, the complete removal of air was confirmed and the accuracy of the apparatus was checked by comparison of the equilibrium pressure when some pyridine was in the flask with the reported vapor pressure of pyridine at that temperature. The pump was then again operated for a short time and a second equilibrium attained checking the first. After this the pump was operated for a longer time, removing pyridine, until it was evident either from a color change or from a sudden decrease in pressure that a change in the substance was taking place. The stopcock was then closed, readings taken as

Fig. 1.—Dissociation pressures of metal pyridine thiocyanates. P, pyridine (vapor pressure); Co 4, cobaltous tetrapyridine thiocyanate; Co 2, dipyridine; Cu 2, cupric dipyridine; Cu 1, monopyridine; Ni 4, nickelous tetrapyridine; Ni 2, dipyridine; Zn 4, zinc tetrapyridine.

before, and the system again pumped out enough to displace the equilibrium, and so on, until the equilibrium pressure after two successive pumpings was the same. The system was then brought to equilibrium at a different temperature or it was evacuated until the compound of next lower pyridine content began to decompose, and the process was repeated. Observed pressures were corrected to 20° to take account of the expansion of the mercury and glass of the manometer.

The results are conveniently summarized by the chart, Fig. 1, in which the logarithm of the pressure is plotted against the reciprocal of the absolute temperature.

The curves for the dissociation pressures of cobaltous tetra- and dipyri-

dine thiocyanates are practically parallel to each other and to the curve for the vapor pressure of pyridine, which indicates that the affinities of cobaltous dipyridine thiocyanate and of cobaltous thiocyanate for pyridine are practically constant over the temperature range of our observations.

The curves of the cupric compounds approach the pyridine curve at the higher temperatures—and the affinities of cupric thiocyanate and of cupric monopyridine thiocyanate for pyridine decrease with increasing temperature. The curve of cupric dipyridine thiocyanate intersects the pyridine curve at about 70°, at which point the dissociation pressure of the complex and the vapor pressure of pyridine are both equal to 170 mm. Above this temperature the dipyridine compound decomposes spontaneously into cupric monopyridine thiocyanate and pyridine.

The nickelous compounds, on the other hand, show increased affinities for pyridine at the higher temperatures. The curve of nickelous tetrapyridine thiocyanate intersects the pyridine curve at about −3°, and the substance spontaneously decomposes below that temperature. We find that the higher pyridinated compound, when cooled in a freezing mixture, does in fact decompose to produce the lower pyridinated one, but have not been able to measure the vapor pressure at the low temperature.

The affinity of zinc thiocyanate for pyridine decreases with decreasing temperature and disappears at about 20°. A sample of zinc tetrapyridine thiocyanate cooled to −13° showed a pressure of 1.5 mm., which corresponds very closely to the vapor pressure of pyridine at that temperature.

We are not acquainted with any other complex salts which show the remarkable property, exhibited by the nickelous and zinc pyridine thiocyanates, of decomposing when they are cooled.

Reading from the chart, Fig. 1, we get the values for the dissociation pressures at the even temperatures which are shown in Table II.

TABLE II

DISSOCIATION PRESSURES (MM. OF MERCURY AT 20°)

Temp., °C	20	30	40	50	60	70	80
$Co(NCS)_2 \cdot 4Py$	1.9	3.4	6.0	10.6	18.0	27.0	44.0
$Co(NCS)_2 \cdot 2Py$	...	0.5	0.8	1.3	2.1	3.0	4.7
$Cu(NCS)_2 \cdot 2Py$	5.1	12.0	27.0	58.0	106.0	..	..
$Cu(NCS)_2 \cdot Py$	...	3.4	5.0	10.1	20.0	36.0	..
$Ni(NCS)_2 \cdot 4Py$	5.0	6.1	7.5	9.8	10.5	12.0	..
$Ni(NCS)_2 \cdot 2Py$	2.3	2.7	3.3	3.9	4.6	5.2	..
$Zn(NCS)_2 \cdot 4Py$	...	21.5	31.0	42.0	57.0	100.0	..

Summary

The dissociation pressures of cobaltous tetra- and dipyridine thiocyanates, of cupric di- and monopyridine thiocyanates, of nickelous tetra- and dipyridine thiocyanates, and of zinc tetrapyridine thiocyanate have been measured at temperatures between 20 and 80°.

The affinity which holds the pyridine in the cobaltous compounds is practically constant over the temperature range 20 to 80°. In the cupric compounds it decreases at the higher temperatures, while in the nickelous and zinc compounds it decreases at the lower temperatures.

CAMBRIDGE, MASSACHUSETTS

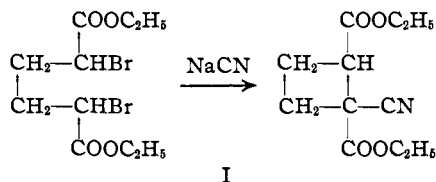[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

RING CLOSURES IN THE CYCLOBUTANE SERIES. II. CYCLIZATION OF α,α'-DIBROMO-ADIPIC ESTERS

BY REYNOLD C. FUSON, OSCAR R. KREIMEIER AND GILBERT L. NIMMO

A new method of effecting the closure of the cyclobutane ring has been reported by Fuson and Kao,[1] who obtained diethyl 1-cyanocyclobutane-1,2-dicarboxylate (I) from diethyl α,α'-dibromo-adipate by treatment with sodium cyanide in absolute alcohol.

$$
\begin{array}{ccc}
\text{COOC}_2\text{H}_5 & & \text{COOC}_2\text{H}_5 \\
| & & | \\
\text{CH}_2\text{—CHBr} & \xrightarrow{\text{NaCN}} & \text{CH}_2\text{—CH} \\
| & & | \quad | \\
\text{CH}_2\text{—CHBr} & & \text{CH}_2\text{—C—CN} \\
| & & | \\
\text{COOC}_2\text{H}_5 & & \text{COOC}_2\text{H}_5 \\
& \text{I} &
\end{array}
$$

The method has now been tried with other esters of α,α'-dibromo-adipic acid and of β-methyl-α,α'-dibromo-adipic acid. The present article is a report of these experiments.

Since the weight of substituents is known to influence the ease of ring closure, attempts have been made to extend the closure method to α,α'-dibromo-adipic esters in which the alkyl groups were large. For this purpose diphenyl α,α'-dibromo-adipate and di-β-naphthyl α,α'-dibromo-adipate were prepared. The diphenyl ester was prepared from α,α'-dibromo-adipyl chloride by treatment with sodium phenoxide. A somewhat better yield was obtained by heating the acid chloride with phenol. The dinaphthyl ester was prepared by heating α,α'-dibromo-adipyl chloride with β-naphthol.

As was to be expected, these esters could not be studied in ethyl alcohol solutions because of rapid ester interchange. Attempts to replace the absolute alcohol by acetone, ethers, acetonitrile and other solvents led to negative results. Attempts to use other metal cyanides in these solvents were likewise fruitless.

The influence of substituents in the adipic acid chain was then examined. Diethyl α,α'-dibromo-β-methyl adipate (II) was heated for twenty-four hours with powdered sodium cyanide in absolute alcohol.

[1] Fuson and Kao, THIS JOURNAL, 51, 1536 (1929).