which, acidified with hydrochloric acid, gave with xanthydrol solution a white precipitate insoluble in alcohol, evidently dixanthylurea.

Another experiment with 5.7 g. of bromine and 7.9 g. of anhydrous formic acid, twenty-four days of standing, 25.7 g. of aniline, etc., yielded 0.4 g. of material. This was extracted with cold concd. hydrochloric acid in an effort to remove the last portions of brominated aniline, then with alcohol and the residue from the evaporation of the alcohol was sublimed in the molecular still. The several fractions of the sublimate, recrystallized from alcohol, appeared to consist of mixtures of 4,4′-dibromo- and 2,2′,4,4′-tetrabromocarbanilide. They were brought together and heated with alcoholic ammonia for five hours at 140–150°. The residue from the evaporation of the alcohol was extracted with water, and the aqueous solution, acidified with hydrochloric acid, gave with xanthydrol a white precipitate, insoluble in alcohol, m. p. 260° dec., showing the same behavior alone and in mixed melting point as a known sample of dixanthylurea prepared according to the directions of Werner and Fearon.[9]

Twelve grams of bromine and 30.7 g. of anhydrous formic acid were allowed to stand together for two days. The mixture, bromine being at the bottom, was allowed to run slowly from a dropping funnel into a solution of 108.3 g. of aniline in 300 cc. of benzene which was stirred vigorously with a mechanical stirrer. There was no considerable heating. A large amount of white precipitate appeared but this did not impede the stirring. The mixture, made alkaline, steam distilled, extracted with ether, etc., as described, yielded 0.2644 g. of crude product. Calculated as pure carbanilide this corresponds to 1.73% of the bromine. Fractional sublimation in vacuum and fractional crystallization yielded one fraction which consisted of impure carbanilide and another which consisted largely of brominated carbanilides. The first of these, recrystallized several times from alcohol, from dilute alcohol, and from water, and twice micro-recrystallized from alcohol, yielded carbanilide, m. p. 233.5–234.0°, identified by mixed m. p. 234.0–234.5° with a known sample, m. p. 234.5–235.0°. The other principal fraction was refluxed gently for forty-five minutes with 2 cc. of aniline in order that the brominated carbanilides by a "urea dearrangement" might be converted into carbanilide. The excess aniline was driven off by steam distillation, and the residue, dissolved out by ether, weighed 0.0341 g. In the molecular still it yielded 0.0199 g. of sublimate, light brown in color, and 0.0074 g. of residual tar. The sublimate, which evidently contained some brominated aniline, after several recrystallizations yielded carbanilide, m. p. 234.0–234.5°, mixed m. p. 234.5–235.0°, known m. p. 234.5–235.0°.

Summary

Bromine reacts with formic acid to produce a substance which, in the presence of an excess of bromine, reacts with aniline to form derivatives of urea, namely, carbanilide and brominated carbanilides.

The intermediate substance, evidently capable of existence only in the presence of free bromine, is probably dibromo-dihydroxy-methane formed by the addition of bromine to dihydroxy divalent carbon, the tautomeric form of formic acid.

CAMBRIDGE, MASS. RECEIVED FEBRUARY 10, 1940

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[9] Werner and Fearon, *J. Chem. Soc.*, **117**, 1360 (1920).

[CONTRIBUTION NO. 219 FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Metal Pyridine Complex Salts. VI. Cobaltous and Nickelous Dipyridine Salts of Fatty Acids

BY TENNEY L. DAVIS AND ALBERT V. LOGAN

In the preceding paper of this series[1] experiments were reported which showed that the pyridine in the pyridine complex cupric, cobaltous and nickelous cyanates is held by greater forces of affinity than the pyridine in the corresponding complex thiocyanates. The greater forces of chemical affinity are evident both from the lower dissociation pressures of the complex cyanates and from the greater shrinkages which occur when the complex cyanates, as compared with the complex thiocyanates, are formed from their component salts and pyridine. The thiocyanate radical to a greater extent than the cyanate radical exhausts the total affinity of the metal atom and leaves less of it available for coördinative combination with pyridine. The effect is due solely to the difference between a sulfur and an oxygen atom at the far end of the acid radical which is attached to the metal by an electrovalent linkage.

In the present paper we wish to report experiments on the dipyridine cobaltous and nickelous salts of acetic, propionic, butyric, isobutyric and valeric acids. We have determined their dissociation pressures over the temperature interval between 15–20° and 85–90° and the volume changes which occur at 25° when the complexes are formed by the combination of their compo-

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[1] Davis and Logan, THIS JOURNAL, **58**, 2153 (1936).

TABLE I

DISSOCIATION PRESSURES, EXPERIMENTAL VALUES (MM. AT 20°)

	Cobaltous Dipyridine							
Acetate	41.0°	48.0°	60.5°	71.0°				
	3.7	6.5	14.0	24.0				
Propionate	30.0°	45.0°	55.0°	65.0°	70.0°	80.0°		
	4.0	9.7	17.0	32.0	44.0	82.0		
Butyrate	30.0°	43.6°	54.0°	60.0°	70.0°	80.0°		
	3.0	7.0	14.5	20.0	38.5	76.0		
Isobutyrate	26.2°	43.0°	51.0°	60.0°	71.0°			
	2.9	8.0	13.0	21.2	41.5			
Valerate	40.0°	50.0°	60.0°	70.0°				
	10.0	18.0	35.2	75.0				
	Nickelous Dipyridine							
Acetate	28.0°	40.0°	60.0°	70.0°	80.0°			
	1.0	1.5	3.0	7.4	16.5			
Propionate	30.0°	43.0°	48.0°	55.0°	60.0°	70.0°	80.0°	88.0°
	2.0	3.0	3.5	4.5	5.0	11.0	24.0	46.0
Butyrate	35.0°	45.0°	51.0°	60.0°	64.0°	70.0°	72.0°	80.0°
	1.8	2.5	3.0	4.0	5.0	8.0	10.0	18.0
Isobutyrate	18.0°	34.0°	50.0°	60.0°	70.0°	80.0°		
	1.2	1.9	3.2	4.5	9.5	19.5		
Valerate	15.0°	41.0°	50.0°	60.0°	70.0°	80.0°		
	2.7	5.6	7.0	9.0	21.0	44.0		

nent salts with pyridine. The results show the effect, upon the residual affinity of the metal atoms, of additional —CH_2— groups successively introduced into the acid radical.

Experimental Procedure

The dissociation pressures of the complexes were determined in the same way as in the earlier experiments of this series.[2]

Preparation of Compounds.—Cobaltous or nickelous carbonate was refluxed for several hours with the pure fatty acid, a small quantity of water was added, the solution was filtered and evaporated to dryness, and the crystalline residue was powdered and dried in vacuum over caustic potash for the removal of moisture and excess acid. When analysis showed that the material was the pure anhydrous salt, it was taken for the preparation of the complex.

The dry salts were converted into the complexes by treating them with chloroform and adding pyridine until everything went into solution. The lower members of the series of complex salts were found to be much less soluble in chloroform than the higher members, and a considerable excess of pyridine was found to be necessary to make them dissolve. The filtered solutions were allowed to evaporate in the hood, and the resulting crystals, dried between filter papers, were placed in a desiccator over caustic potash. The complex acetates and propionates were allowed to come to equilibrium with pyridine in an open vessel in the desiccator. When the same procedure was tried with the complex butyrates, isobutyrates and valerates, the crystals deliquesced and became wet with pyridine. The crystals of these complexes therefore were allowed to come to equilibrium, over caustic potash, with the pyridine which still adhered to their surfaces after they had been pressed between filter papers.

Cobalt was determined as sulfate, nickel as sulfate and sometimes by titration with potassium cyanide, and pyridine by the method of A. C. Houghton,[3] which we have used in earlier work and have found to be accurate to about 1%.

The five nickelous dipyridine complex salts consisted of bright greenish blue crystals. Cobaltous dipyridine acetate consisted of rose pink crystals, the propionate, butyrate and isobutyrate were more deeply colored, and the valerate crystallized in ruby red prisms.

Density Determinations.—The densities of the cobaltous and nickelous salts were determined by weighing in specific gravity bottles with dry benzene at 25°. Since it was expected that organic liquids would dissolve pyridine from the complexes, the densities of the latter were determined by using saturated solutions of the complexes in pyridine for the pycnometer liquids. The large effect of temperature on the solubility of the complex butyrates, isobutyrates and valerates in pyridine is probably the principal source of error in the determinations.

Experimental Results

The experimental data for the dissociation pressures, corrected for the expansion of mercury from 20°, are summarized in Table I. If these data are plotted on a semi-logarithmic chart, along with the data for the vapor pressure of pyridine (from our earlier experiments), they give good straight lines for the cobaltous complexes, lines which approach slowly at the higher tem-

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(2) Davis and Batchelder, THIS JOURNAL, **52**, 4069 (1930).

(3) A. C. Houghton, *Ind. Eng. Chem.*, **1**, 698 (1909).

TABLE II

DISSOCIATION PRESSURES AT 25° (MM. AT 20°)

Dipyridine	Acetate	Propionate	Butyrate	Isobutyrate	Valerate
Cobaltous	1.5	3.0	2.3	2.7	3.7
Nickelous	0.9	1.7	1.3	1.5	3.6

peratures toward the straight line which represents the vapor pressure of pyridine. The data for the nickelous complexes yield straight lines which bend in the neighborhood of 60° and resume their straightness with a different slope, lines which approach the pyridine line both at the higher and at the lower temperatures. The dissociation pressures at 25°, estimated from the graphs, are shown in Table II.

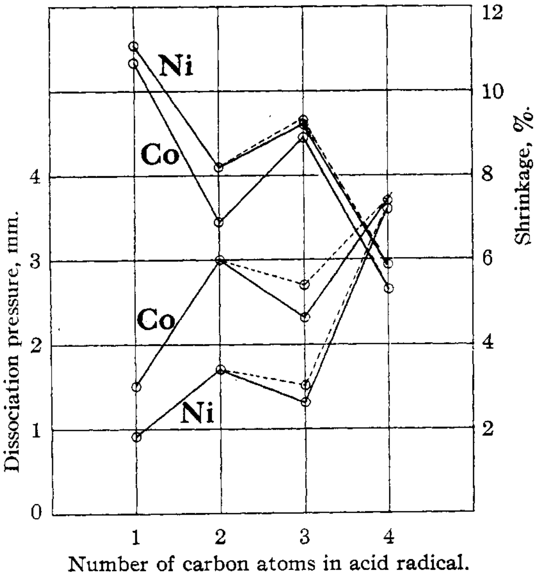

Fig. 1.—Dissociation pressures at 25° (lower), and shrinkages (upper) which occur at 25° during the formation of the complexes of cobaltous and nickelous dipyridine salts of fatty acids. (Dotted lines indicate isobutyrates.)

The results of analyses and of density determinations are summarized in Table III. In two cases the analytical figures represent single determinations; in all others they are averages of two check values.

The values reported for the densities are averages of two or of three determinations, and the "error" is the mean deviation from the average. From the densities and from our earlier data on the density of pyridine,[1] the molecular volumes were calculated and the contractions which occur when the simple salts combine with pyridine at 25° to form the dipyridine complexes were inferred. The decreases of volume per mole of complex are indicated in the last two columns of Table III.

Discussion of Results

From the positions of the dissociation pressure lines on a semilogarithmic chart (not reproduced), it is possible to conclude that, within the temperature range in which we have worked, the cobaltous dipyridine salts of the fatty acids are less stable at the higher temperatures. The nickelous compounds have a point of maximum stability in the neighborhood of 60°, and tend to decompose when they are warmed or cooled from that temperature. All of the nickelous and zinc pyridine complex salts which we have studied earlier have the remarkable property that they tend to decompose at low temperatures.

The greater forces of affinity which produce the greater decreases of volume during the formation of the complexes also result in the pyridine being more strongly bound to the metal and produce the lower dissociation pressures. The relationship is exhibited in the chart, Fig. 1, where the dissociation pressures at 25° and the volume-

TABLE III

ANALYSES, DENSITY DETERMINATIONS AND SHRINKAGES WHICH OCCUR AT 25° DURING THE FORMATION OF THE COMPLEXES

	Simple salt						Dipyridine complex				Volume decrease	
	Metal, %		Density at 25°		Metal, %		Pyridine, %		Density at 25°			
Cobaltous	Found	Calcd.	Average	Error	Found	Calcd.	Found	Calcd.	Average	Error	cc.	%
Acetate	33.17	33.31	1.7755	0.0005	17.45	17.59	46.61	47.17	1.4286	0.0003	28.0	10.7
Propionate	28.41	28.77	1.5475	.0003	16.21	16.24	43.41	43.54	1.3260	.0010	20.4	6.9
Butyrate	25.45	25.30	1.4011	.0012	15.26	15.08	40.11	40.21	1.3093	.0002	29.3	8.9
Isobutyrate	25.33	25.30	1.3509	.0007	15.25	15.08	40.09	40.21	1.2837	.0023	29.6	8.9
Valerate	22.63	22.58	1.3267	.0017	14.25	14.02	37.20	37.71	1.2342	.0050	18.9	5.3
Nickelous												
Acetate	33.24	33.22	1.7983	0.0004	17.34	17.53	46.88	47.21	1.4478	0.0025	28.8	11.1
Propionate	28.43	28.69	1.6163	.0003	16.23	16.18	43.44	43.56	1.3696	.0034	23.6	8.2
Butyrate	25.07	25.22	1.4476	.0006	15.01	15.02	40.30	40.44	1.3093	.0002	29.8	9.2
Isobutyrate	25.38	25.22	1.3617	.0000	14.89	15.02	40.33	40.44	1.2837	.0023	30.9	9.3
Valerate	22.49	22.51	1.3404	.0005	...	...	37.40	37.74	1.2499	.0009	21.3	5.9

decreases during formation at 25° are plotted as functions of the number of the carbon atoms in the acid radicals. Both curves show the saw-tooth pattern which is a characteristic representation of many of the properties of fatty acids.

The acid radicals which contain two and four carbon atoms use less of the total affinity of the metals than do the acid radicals which contain three and five carbon atoms, and the corresponding complexes hold their pyridine more firmly, having lower dissociation pressures, their formation being accompanied by greater shrinkages.

Except for the effect of odd and even numbers of carbon atoms, the general effect of increasing the number of carbon atoms in the acid radical appears to be to reduce the residual affinities of the metal atoms and to leave less available for combination with pyridine.

The effect of a fork in the carbon chain is small.

The nickel atom has greater chemical forces available for coördinative combination with pyridine at 25° than has the cobalt atom, for the nickelous complex salts are formed with greater volume decreases, and have lower dissociation pressures, than the cobaltous compounds.

Summary

The dissociation pressures of cobaltous and nickelous dipyridine acetate, propionate, butyrate, isobutyrate, and valerate have been determined over the temperature range from 15–20° to 85–90°.

The densities at 25° of the complexes and of their component salts have been determined, and the volume changes which occur at 25° during the combination of the simple salts with pyridine have been calculated. The complexes of which the formation is accompanied by the greater shrinkages have the lower dissociation pressures.

The effect of groups upon the residual affinities of the metal atoms is discussed.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE CITY COLLEGE, THE COLLEGE OF THE CITY OF NEW YORK]

Alkanolamines. IX. Reducing and Hydrolyzing Action of the Ethanolamines on the Dichloronitrobenzenes

BY CHESTER B. KREMER AND AARON BENDICH

In a preceding article of this series,[1] an account was given of the reactions occurring between the isomeric dichloronitrobenzenes and monoethanolamine as carried out in neutral solvents. When these reactions are carried out in the absence of neutral solvents, the course followed is quite different, the condensing ability of the amino alcohol is considerably decreased and there is substituted the tendency toward reduction, hydrolysis and the formation of addition compounds. The finding of a combination of these tendencies, together with condensation, in a single run, is not infrequent. Insofar as the reductions involved, not only are the starting materials reduced to various stages, but there is also noted the reduction of an expected end-product. Under certain circumstances, it is found that when a dichloronitrobenzene is treated with monoethanolamine in the presence of anhydrous sodium carbonate, there can be isolated from the reaction mixture: (1) the condensation product, (2) a reduced product of the dichloronitrobenzene, either the azo or amino derivative, (3) the reduced condensation product, (4) an hydrolysis product of the dichloronitrobenzene, and in some cases (5) addition compounds of the type $xC_6H_3NO_2Cl_2 \cdot yNH_2CH_2CH_2OH$ where x and y are usually 1 or 2.

In order to make this survey more complete, the action of diethanolamine and triethanolamine upon the isomeric dichloronitrobenzenes was also studied. The ability of these ethanolamines to reduce, hydrolyze and form addition products with the isomers is, in most cases, greater than that of monoethanolamine. While condensations are possible in the case of diethanolamine, there was no instance of such reaction during the course of this work. Condensations involving this amino alcohol do occur when the reaction takes place in a neutral solvent; but even here the tendency is not great.

The fact that good yields of amino products can be obtained in these reactions is of interest since mononitro compounds are not generally re-

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[1] Kremer and Bendich, THIS JOURNAL, 61, 2658 (1939).