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

HYDROXYLAMINE SALTS OF ORGANIC ACIDS[1]

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Although hydroxylamine has been known since 1868,[2] a careful search of the literature reveals records of only 18 organic salts of this base, and of these only nine have been fully described as to melting point, decomposition by heat, etc.[3]

The present writers have isolated 26 salts not previously described, have worked out further details concerning the benzoate and cinnamate and also studied the reaction of four other acids with hydroxylamine. The salts were prepared by simple neutralization in alcoholic solution. The three nitrobenzoates could not be obtained pure by this method, but double decomposition of hydroxylamine sulfate and the barium salts of the acids yielded the desired compounds.

The hydroxylamine was isolated by the method of Lecher and Hofmann[4] as modified by Houben.[5] Repetition of this procedure, not less than 50 times, has shown us that the somewhat elaborate apparatus prescribed is not essential, and in its place we have used successfully a hand-shaken flask, carrying a dropping funnel for admission of the ethylate and a calcium chloride exit tube. The accumulation of a large excess of sodium ethylate in the alcoholic suspension of the hydroxylamine hydrochloride is fatal to the preparation, for not only does the solution then remain per-

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[1] An abstract of a thesis submitted by Mary Peyton Ballard in partial fulfilment of the requirements for the degree of Master of Arts at the University of Cincinnati.

[2] Lossen, *Z. Chem.*, **1,** 551 (1865); *Ann.*, *Spl.*, **6,** 220 (1868).

[3] Formate. (a) Ssabanejew, *J. Russ. Phys.-Chem. Soc.*, **31,** 380 (1899). (b) Jones and Oesper, THIS JOURNAL, **42,** 517 (1909).

Acetate. (c) Lossen, *Ann.*, *Spl.*, **6,** 231 (1868). (d) Ref. 3 b, p. 518.

Mono-, di- and trichloro-acetate. (e) Jones and Werner, THIS JOURNAL, **39,** 417 (1917).

Oxalate. (f) Ref. 3 c, p. 231.

Tartrate. (g) Ref. 3 c, p. 233.

Picrate. (h) Ref. 3 g.

Fumarate. (i) Tanatar, *Ber.*, **29,** 1478 (1896). (j) Posner, *Ber.*, **36,** 4317 (1903).

Maleate. (k) Ref. 3 j. p. 4318.

Succinate. (l) Tanatar, *J. Russ. Phys.-Chem. Soc.*, **29,** 214, 319 (1897).

Cinnamate. (m) Posner, *Ann.*, **389,** 4 (1912).

Benzoate. (n) Ref. 3 a. (o) Gluud and Kempf, *J. Chem. Soc.*, **103,** 1532 (1913).

m-Aminobenzoate. (p) Ref. 3 a, p. 381.

m-Chlorobenzoate. (q) Ref. 3 o, p. 1533.

Succinamate. (r) Ref. 3 a.

Benzenesulfonate. (s) Piloty, *Ber.*, **29,** 1561 (1896).

Benzenesulfinate. (t) Jones and Whalen, THIS JOURNAL, **47,** 1353 (1925).

[4] Lecher and Hofmann, *Ber.*, **55,** 915 (1922).

[5] Houben, *J. prakt. Chem.*, **105,** 20 (1922).

manently alkaline, but the phenolphthalein undergoes change and the solution becomes bright yellow. In the early stages of our work the hydroxylamine was frozen out of its alcoholic solution, weighed, redissolved in alcohol and the equivalent quantity of organic acid added; the alcohol was removed in a vacuum and the residual salt was recrystallized. Part of the free acid was usually found mixed with the salt and its removal sometimes presented difficulties. Experience showed that the alcoholic solution of the hydroxylamine obtained from the filtration of the sodium chloride was pure enough for the preparation of the salts, and in most cases a slight deficiency of the acid was added directly to the filtrate and the hydroxylamine salt recovered from the solution.

The nitrogen content of organic hydroxylamine salts has usually been determined by combustion methods, though we have experienced difficulty with this procedure, as warm carbon dioxide decomposes some of the salts. There has been doubt as to the applicability of the Kjeldahl procedure to hydroxylamine salts except after modification.[6] The present writers have found the Kjeldahl-Gunning method absolutely reliable for the organic salts. The weighed samples were wrapped in filter paper, added to the sulfuric acid suspension of potassium sulfate, heated until the reaction was well under way and the copper sulfate was then added. The determination was finished in the usual manner. The well-known modifications designed for nitro bodies failed when applied to the three nitrobenzoates of hydroxylamine, but satisfactory results were obtained by Krüger's method.[7]

The hydroxylamine salts of fatty acids when heated above their melting points lose water and give rise to the corresponding hydroxamic acid:[8] $RCO_2H.NH_3O \longrightarrow RCO.NHOH + H_2O$. This dehydration often occurs at room temperature at rates varying from case to case, but the products recovered from the reaction of hydroxylamine on *n*-butyric, lactic, thioacetic and β-hydroxybutyric acids were viscous liquids, that we could not solidify; very soon after their isolation they gave deep red solutions with acidulated ferric chloride, indicating the presence of hydroxamic acid. The propionate and valerate underwent this change slowly at room temperature, becoming progressively more liquid. The other salts have shown no change in melting point after several months' standing, even though many of them were dried for days over phosphorus pentoxide preliminary to the analysis. The hydroxylamine salts of the acids of the aromatic series are stable for months at room temperature, and when heated undergo a totally different change since they give rise, not to hydroxamic acids, but to ammonium salts or to amides, that is, the dehydration products of the latter.

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[6] Dyer, *J. Chem. Soc.*, **67,** 811 (1895).

[7] Krüger, *Ber.*, **27,** 611, 1633 (1894).

[8] See Tanatar, however, for changes undergone by salts of dibasic acids [*Chem. Zentr.*, [II] **68,** 339, 659 (1897); *Ber.*, **29,** 1478 (1896)].

The nitrobenzoates are faintly yellow; the myristate became straw-colored after standing over calcium chloride for 12 hours. The other salts

TABLE I

Salt	M. p. °C.	Analysis, % of N		Recrystallized from	Soluble in	Insoluble in
		Calcd.	Found			
Propionate	56–57	13.00	12.84	A + E	W, A	C, E, L
Butyrate	oil	...	...	..	..	..
*iso*Bútyrate	98–99	11.57	11.59	G	W, A	E, L
Hydroxybutyrate	oil	...	...	..	..	..
Valerate	67	10.37	10.36	G	W, A	E, L
Lactate	oil	...	...	..	..	..
Glycolate	77–78	12.85	12.78	A + E	W, A	E, L
Myristate	69–70	5.36	5.38	L	A, B, C, E	W, L
Thio-acetate	oil	...	...	..	..	..
Benzoate[a]	113	9.03	8.89	A + E	W, A	B, E, L
o-Chlorobenzoate	104.5	7.39	7.25	B	W, A, B	E, L
m-Chlorobenzoate	144	7.39	7.27	A + E	W, A	B, E, L
p-Chlorobenzoate	130	7.39	7.21	A + E	A	W, E, L
o-Bromobenzoate	99	5.98	5.96	C	W, A	E
m-Bromobenzoate	139	5.98	5.96	A + E	W, A	E
p-Bromobenzoate	...	5.98	5.90	A + E	W, A	E
o-Aminobenzoate	95–96	16.46	16.27	C + A	W, A	B, C, E, L
o-Toluate	105	8.28	8.24	B	W, A, E	B, C
p-Aminobenzoate	103	16.46	16.39	B + A	W, A	B, C, E, L
m-Toluate	83	8.28	8.27	B	W, A, E	B, C
p-Toluate	128	8.28	8.19	C + A	W, A, E	B, C
o-Nitrobenzoate	133	14.00	14.00	A + E	W, A	W, E, L
m-Nitrobenzoate	137	14.00	14.00	A + E	W, A	B, E, L
p-Nitrobenzoate[b]	146	14.00	14.03	W	W, A	B, E, L
Cinnamate	119	7.73	7.65	A + E	W, A	E
Hydrocinnamate	84–85	7.65	7.60	B	W, A	E
Salicylate	141	8.19	8.03	T + A	W, A	T
Phenylacetate	83	8.28	8.48	B	W, A	E
Mandelate	125	7.56	7.54	A + E	W, A	E
Hippurate	68	13.20	13.16	C + A	W, A	B, C, E
o-Phthalate	134.5	12.07	12.04	A	W, A	E
Benzenesulfonate[c]	98–107	7.33	7.15	C + A	W, A	C

The abbreviations used in the columns of the solubility data are as follows: A, ethyl alcohol; B, benzene; C, chloroform; E, ether; T, toluene; W, water; L, ligroin; G signifies that no successful method of recrystallizing was found and the sample was thoroughly washed with ether, preparatory to analysis.

[a] Gluud and Kempf, Ref. 3 o, give the melting point of presumably the same salt as 121–122°. They reported no analysis. Three different preparations melted consistently at 114° and showed no change after standing for three months.

[b] The monohydrate of this salt separated from aqueous solution; m. p., 143°. Calcd. for $(NO_2)C_6H_4COOH.NH_3O.H_2O$: N, 12.85. Found: 12.70. A weighed sample lost the calculated weight of water after standing for ten days over phosphorus pentoxide, and the anhydrous salt gave the data recorded in the table.

[c] When heated gradually no evidence of fusion was observed below 120°. When the sample was plunged into a bath previously heated to 98°, the salt softened, and complete fusion was observed at 107°.

are colorless, most of them appearing as beautifully lustrous plates. The characteristics of the salts are summarized in Table I.

Summary

Twenty-eight salts of hydroxylamine with organic acids have been prepared and described. The Kjeldahl-Gunning and the Krüger methods have been successfully applied to the determination of the nitrogen content of these compounds.

CINCINNATI, OHIO

NEW BOOKS

Lehrbuch der Physik in Elementarer Darstellung. (A Text book in Physics presented in an elementary form.) By ARNOLD BERLINER. Third edition. Julius Springer, Linkstr. 23–24, Berlin W 9, Germany, 1924. x + 645 pp. 734 figs. 17 × 25 cm. Price, bound, 18.60 gold marks.

This is a comprehensive text in physics intended for students specializing in such fields as medicine and chemistry. It is well balanced in plan and covers the whole field in much more detail than do our ordinary American texts for college use. The book is written in an unusually clear style and the author has avoided involved sentence structure. The publishers have aided by printing the book so that various forms of type assist the reader in quickly comprehending the ideas. The illustrations consist of a large number of very simple, clear-cut drawings. A further attractive feature of the book is the stress laid on the biographical side of the subject. This is very neatly done in the body of the text and again in a chronological table at the end. As would be expected, there is considerable of the new physics included, such as the Einstein theory of relativity and Bohr's theory of atomic structure.

It seems to an American teacher that the book would have been more valuable if the material had been more carefully selected. There is too much obsolete physical apparatus described in detail; for instance, tangent galvanometers, influence machines, Atwood's machine, Sprengel's pump, Nernst's lamp, the cells of Daniell, Grove, Bunsen and Clark. Curiously enough, the electron (or 3-electrode vacuum) tube is not even mentioned, nor is there any discussion of the mercury-diffusion pump and rotating, mechanical, oil-sealed, vacuum pumps, which are used so extensively to back up these diffusion pumps. It is a pity that the electron theory of electricity should not be referred to in the discussion of electrostatics and electrodynamics but is postponed until cathode rays are taken up. In fact, all of the earlier treatment of electricity is purely the traditional one. To English-speaking readers it will be a bit of a shock that J. J. Thomson is referred to only once and then merely as the man who improved the cloud