

(5 to 6 equivalents) of sodium hydroxide, filtering and evaporating the filtrate to 300 cc. The resulting phenylmercuric hydroxide, filtered off and dried, weighed 32 g. (86% yield) and melted at 226–227°.

*Anal.* Calcd. for  $C_6H_5HgOH$ : Hg, 68.07. Found: Hg, 67.93.

Recrystallization of this product from water did not produce any observable further purification.

A saturated solution measured at about 25° with a Coleman pH meter, Model 3B, gave values in the range pH 7.0 to 7.5. The solubility of phenylmercuric hydroxide at 0° per 100 cc. was found to be 0.52 g. in water, 0.48 g. in 0.0185 *N* sodium hydroxide and 0.36 g. in 1 *N* sodium hydroxide.

The previously reported solubility of phenylmercuric chloride in alkali was also observed in this Laboratory.

These observations indicate that phenylmercuric hydroxide is a very weak base but does not ionize as an acid. The solubility of the chloride in alkali is then explained by the formation of the moderately soluble and almost completely undissociated free base. In agreement with this, at least when an excess of sodium chloride is added, a solution of the hydroxide titrated with standard perchloric acid, using phenolphthalein as an indicator, requires 0.98 equivalent of the acid. Similarly, a solution of basic phenylmercuric nitrate,  $C_6H_5HgNO_2 \cdot C_6H_5HgOH$ , with phenolphthalein as indicator, requires an amount of sodium hydroxide equivalent to the nitrate present.

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## Polarographic Behavior of Some Organic Compounds

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In order to answer some questions about the polarographic behavior of some sulfur and halogen compounds in the literature, the reducibility of the compounds described below was measured.

### Experimental

A Leeds and Northrup Electrochemograph equipped with the cell arrangement described by Furman, Bricker and Whitesell<sup>2</sup> was used for the polarographic measurements. The work was done at room temperature (24 to 25°). The capillary was a 10-cm. length of selected marine barometer tubing and had the following characteristics:  $m = 0.8173$  mg. per second;  $m^2/t^{1/2}$  was 1.22 in acid solutions and 1.17 in neutral and alkaline solutions at the potential where the diffusion current started; the head of mercury was 46.5 cm. Oxygen was removed from all solutions polarographed by passing purified nitrogen for fifteen minutes. Polarograms were taken at  $1/30$  sensitivity unless otherwise indicated.

The buffer solutions used were prepared by dissolving 0.25 mole of the first material in 600 ml. of distilled water neutralizing with a concentrated solution of the second material to the desired pH measured against the glass electrode, and diluting to 1000 ml.: acetate pH 4 and 5, acetic acid and sodium hydroxide; phosphate pH 6, 7, 8, 11 and 12, potassium dihydrogen phosphate and sodium hydroxide; acetate pH 7 and 8, ammonium hydroxide and acetic acid; borate pH 8 and 11, boric acid and sodium hydroxide; ammonia pH 9 and 10, ammonium hydroxide and hydrochloric acid; tartrate pH 11, tartaric acid and sodium hydroxide; 0.25 *M* potassium chloride was made up directly. In all cases, polarograms of the buffers showed no appreciable amount of reducible material before buffer breakdown.

(1) Present address: Sun Chemical Corporation, New York 13, N. Y.

(2) Furman, Bricker and Whitesell, *Ind. Eng. Chem., Anal. Ed.*, **14**, 333 (1942).

Dibenzyl sulfoxide, benzmorpholide and benzthiomorpholide were supplied in pure form by Robert Brown and Dr. Gregg Dougherty and were not further purified. Carbon tetrabromide was prepared by the procedure of Brisco, Peel and Rowlands<sup>3</sup> from bromoform and hypobromite. The sample was kept in a desiccator over calcium chloride to slow down decomposition. Paragon carbostyryl was recrystallized three times from 50% ethanol and dried in a vacuum over concentrated sulfuric acid. Standard solutions of these materials were made as follows:—carbostyryl, 1.0 mg. per ml. in 20% ethanol; benzmorpholide, 1.0 mg. per ml. in 5% ethanol; benzthiomorpholide, 0.50 mg. per ml. in 15% ethanol; dibenzyl sulfoxide, 1.0 mg. per ml. in 15% dioxane; carbon tetrabromide, 2.0 mg. per ml. in 30% ethanol. The solutions polarographed were made by mixing 10.0 ml. of buffer with 5.0 ml. of standard solution, adding maximum suppressor if necessary, and diluting to 25.0 ml.

Preliminary experiments showed that amounts of organic solvents such as ethanol or dioxane up to about 6% by volume could be tolerated without any appreciable effects on the pH of the buffer or the half-wave potentials. It was further found that about 1% by volume of organic solvent was helpful in that the residual current was almost eliminated.

### Results

It was found that carbostyryl (2-hydroxyquinoline) was reducible, but reasonable waves were found only in the borate buffer of pH 8 and potassium chloride. In both cases, the half-wave potential was estimated to be  $-1.9$  volts vs. the saturated calomel electrode, but there is some uncertainty since the buffer decomposition wave came very soon after the reduction wave. This behavior was most unexpected by comparison with the relatively low half-wave potentials for 8-hydroxyquinoline.<sup>4</sup>

Carbon tetrabromide was found to be reducible, but in all cases the buffer decomposition overlapped and made a measurement impossible. This was not out of line with the reported measurements on carbon tetrachloride.<sup>5</sup>

TABLE I  
POLAROGRAPHIC REDUCTION OF BENZTHIOMORPHOLIDE  
0.48 mmolar in 2% ethanol

Buffer	pH	$E_{1/2}$ , v. vs. S. C. E.	$I$ , ma.
Acetate	4.0	-1.16	3.92
Acetate	5.0	1.16	3.68
Acetate	7.0	1.55	3.92
Acetate	8.0	1.57	4.00
Phosphate	8.0	1.64	3.60
Borate	8.0	1.71	3.04
Ammonia	9.0	1.56	3.84
Ammonia	10.0	1.62	3.76
Tartrate	11.0	1.59	2.56*
Phosphate	11.0	1.69	2.80
Borate	11.0	1.70	3.12
Phosphate	12.0	1.64	2.48
Potassium chloride	..	1.60	3.28

\* Wave formation poor.

(3) Brisco, Peel and Rowlands, *J. Chem. Soc.*, 1766 (1929).

(4) Zan'ko, *Dokladi Akad. Nauk. URSR*, 27-35 (1940); Caruthers, *Ind. Eng. Chem., Anal. Ed.*, **18**, 412 (1942); Stone and Furman, *ibid.*, **16**, 696 (1944).

(5) Matheson and Nichols, *Trans. Electrochem. Soc.*, **73**, 193 (1938).

Neither dibenzyl sulfoxide or benzmorpholide were reducible under the conditions used, but benzthiomorpholide was reducible with the results listed in Table I. Concentration studies in acetate buffer of pH 4.0, phosphate buffer of pH 8, and borate buffer of pH 11.0 showed that while half-wave potentials were essentially constant, current-concentration ratios were not constant, but decreased with increasing concentration. On this basis together with the data in Table I, it is apparent that the formation of complex units between solvent, buffer and compound is of enough importance so that comparisons of measurements in different buffers are frequently of no value.

By comparing the diffusion coefficient calculated by means of the Ilkovic equation using  $n = 4$  in potassium chloride,  $5.8 \times 10^{-6}$  cm.<sup>2</sup> per sec., with the value  $4.81 \times 10^{-6}$  cm.<sup>2</sup> per sec. found by the Northrop-Anson technique<sup>6</sup> for sodium anthraquinone- $\beta$ -sulfonate in the same medium, it seemed reasonable that four electrons were involved in the reduction and that N-benzyl morpholine was the reduction product. Further experiments are being made to test this point.

(6) Northrop and Anson, *J. Gen. Physiology*, **12**, 543 (1929).

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## The Uronic Acid Component of Mucoitinsulfuric Acid

By M. L. WOLFROM AND F. A. H. RICE\*

Sulfuric acid, acetic acid and D-glucosamine have been identified as hydrolytic products of the various types of mucoitinsulfuric acids.<sup>1,2</sup> By analytical methods a uronic acid is readily detectable as a further component but its exact nature has not been precisely determined. Levene and López-Suárez,<sup>3</sup> by oxidative hydrolysis with nitric acid of the funis mucoitinsulfuric acid (from the Whartonian jelly of umbilical cords) isolated a crystalline potassium salt of saccharic acid for which they recorded a potassium analysis but no optical rotation. Such a reaction is not diagnostic for glucuronic acid, since glucose itself gives saccharic acid on nitric acid oxidation. We report herein the exact identification by an unequivocal method, of D-glucuronic acid as the uronic acid component of the mucoitinsulfuric acid from pig gastric mucosa. This was accomplished by application of the previously reported<sup>4</sup> procedure of oxidative hydrolysis with sulfuric acid and bromine. D-Glucosaccharic acid was isolated from

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(1) P. A. Levene, "Hexosamines and Mucoproteins," Longmans, Green and Co., London, 1925.

(2) M. Stacey, *Advances in Carbohydrate Chem.*, **2**, 161 (1946).

(3) P. A. Levene and J. López-Suárez, *J. Biol. Chem.*, **36**, 115 (1918).

(4) M. L. Wolfrom and F. A. H. Rice, *THIS JOURNAL*, **68**, 532 (1946).

the reaction mixture as its crystalline potassium acid salt, identified by analysis and optical rotation. Under similar but non-oxidative hydrolytic conditions, no D-glucosaccharic acid was isolable.

### Experimental

The sodium mucoitinsulfate (S, 6.06%) employed in this work was prepared from commercial pig gastric mucin and was the same material for which extensive analytical data have already been reported.<sup>5</sup> An amount of 1.00 g. of this substance was dissolved at 0° in a mixture of 5 ml. of concentrated sulfuric acid (sp. gr. at 15.56°/15.56° 1.84), 2 ml. of water and sufficient bromine to saturate the solution. The temperature of the reaction mixture was maintained at 0° for four days. Further quantities of bromine were added at intervals to maintain it in excess. After aeration to remove bromine, the mixture was poured slowly onto 200 ml. of ice and water and the sulfuric acid was neutralized in the cold by the addition of solid barium carbonate. The precipitated barium sulfate was removed by filtration and triturated with 20 ml. of 1% aqueous potassium hydroxide and again filtered. The combined filtrates were neutralized with acetic acid and concentrated under reduced pressure at 30–40° to yield a sirup. The sirup was treated with 50 ml. of a 1% solution of hydrogen chloride in methanol, filtered and concentrated under reduced pressure to a sirup. This sirup was extracted with 15 ml. of absolute ethanol, filtered and the solvent removed under reduced pressure. The residual sirup was dissolved in 2 ml. of water and the solution neutralized to ca. pH 7 with solid potassium bicarbonate. After the addition of 2 ml. of glacial acetic acid the solution was allowed to stand overnight in the icebox. Crystals formed that had the characteristic appearance of potassium acid saccharate when viewed under the microscope. These were removed by filtration and recrystallized by dissolving in 1 ml. of aqueous potassium bicarbonate (calcd. amt.) and adding an equal volume of glacial acetic acid; yield 48 mg.,  $[\alpha]_D^{20} + 10^\circ$  (*c*, 1.9 as dipotassium salt). The optical rotation was determined by solution in water containing an equivalent (to phenolphthalein) quantity of potassium bicarbonate and was in agreement with the value,  $[\alpha]_D^{20} + 10^\circ$ , previously found<sup>4</sup> for potassium D-glucosaccharate when polarized under like conditions.

*Anal.* Calcd. for C<sub>6</sub>H<sub>8</sub>O<sub>8</sub>K: K, 15.75. Found: K, 15.72.

The crystalline material was therefore identified as potassium acid D-glucosaccharate.

On repeating the above described hydrolysis of sodium mucoitinsulfate, but omitting the bromine, no potassium acid D-glucosaccharate was isolable.

(5) M. L. Wolfrom, D. I. Weisblat, J. V. Karabinos, W. H. McNeely and J. McLean, *ibid.*, **65**, 2077 (1943).

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## NEW COMPOUNDS

### Methyl Isoselenourea Sulfate<sup>1</sup>

To 50 ml. of a 25% solution of cyanamide (kindly supplied by the American Cyanamid Company) 2–3 drops of 12 M hydrochloric acid were added and a current of hydrogen selenide passed through the solution until the selenourea began to crystallize. The selenourea solution was cooled in an ice-bath and the compound filtered and

(1) Published by permission of the Director, North Dakota Agricultural Experiment Station.