[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY]

A FURTHER STUDY OF THE NEUTRAL AMMONIUM SALTS OF SOME ORGANIC ACIDS AND THEIR SUBSTITUTED DERIVATIVES

Eighth Communication[1]

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This work is a continuation of the investigation which has been in progress in this Laboratory on the preparation and properties of the neutral ammonium salts of organic acids and their substituted derivatives. The salts described in this paper were, with slight modifications in several instances, prepared by the same general method as was used in the previous investigations, that is, by passing dry ammonia into solutions of the acids in those anhydrous organic solvents in which their salts were found to be insoluble. When it was found that an acid and its ammonium salt were both soluble in a certain solvent, the solution of the ammonium salt was poured into an excess of another solvent in which the salt was insoluble. In several cases it was necessary to evaporate the solutions nearly to dryness before the salts crystallized. In the case of acetyl *m*-aminobenzoic acid, it is insoluble in all the common organic solvents that do not react with ammonia and its solubility in water is very slight. It is soluble in concd. ammonium hydroxide. The neutral ammonium salt was thus prepared by dissolving the acid in concd. ammonium hydroxide, evaporating the solution to dryness, and then passing ammonia into an alcoholic suspension of the residue.

Of the neutral salts described in this paper none has been previously prepared except those of phenoxyacetic acid[2] and 2,5-dichlorobenzene sulfonic acid.[3] They were prepared by neutralizing an aqueous solution of the acid with ammonium hydroxide. The ammonium 1,2,4-dinitro benzoate was described in a previous paper,[4] but we have determined its solubilities and recorded them in this work.

Solubility determinations were made of only the stable salts by the analytical method. By this method the salt, in excess, was stirred with the solvent at a definite temperature until equilibrium was reached. The excess of salt was allowed to settle and the clear liquid decanted off into a weighed evaporating dish and immediately weighed. When the solvent had completely evaporated the evaporating dish was again weighed. From the differences in weight the amount of salt soluble in the solvent at the given temperature could be calculated. All the solubility determi-

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[1] For a list of the previous papers on this subject see THIS JOURNAL, **40**, 683 (1918).

[2] Fritzsche, *J. prakt. Chem.*, [2] **20**, 269 (1879).

[3] Lesimple, *Z. Chem.*, **4**, 226 (1868).

[4] McMaster and Wright, THIS JOURNAL, **40**, 683 (1918).

nations were carried out at 20°, which temperature was maintained in an automatic water thermostat. A large test-tube was used to hold the solubility mixture and was fitted at the top with a mercury seal to prevent the absorption of water vapor from the air by the solvent. This seal was constructed by sinking a piece of glass tubing (a 25mm. section of a large test-tube) into a cork containing a glass bearing for the stirrer. The space between the tube and the bearing was then filled with mercury. A second tube, smaller than the first, was then tightly fastened to the stirring rod by means of a cork so that when the stirrer extended to the bottom of the test-tube, the second tube fitted within the bearing and the large tube at the same time dipped below the surface of the mercury. In this manner the contents of the test-tube could be sealed against contact with air and at the same time the solution thoroughly stirred at about 200 r.p.m. It was found by experiment that 20 minutes was sufficient to bring the

TABLE I

PROPERTIES AND ANALYSES OF NEUTRAL AMMONIUM SALTS

Acid	Stability in		Nitrogen	
	dry air	moist air	Calc.	Found
	(+ = stable;	− = unstable)	%	%
Iodo-acetic	−	−	6.89	6.90
Phenoxyacetic	+	+	8.28	8.29
p-Nitrophenylacetic	+	+	14.14	14.08
β-Bromopropionic	−	−[a]	8.23	7.98
α-Bromo-*n*-butyric	−	−[a]	7.61	7.48
o-Iodobenzoic	+	−	5.28	5.30
p-Iodobenzoic	−	−	5.28	5.24
o-Methoxybenzoic	+	+	8.28	9.32
Acetyl *m*-aminobenzoic	−	−	14.28	14.19
Acetyl *p*-aminobenzoic	−	−	14.28	14.30
5-Nitrosalicylic	+	+	14.00	14.00
α-Naphthalenesulfonic	+	−	6.22	6.28
β-Naphthalenesulfonic	+	+	6.22	6.26
2,5-Dichloro-benzenesulfonic	+	+	5.74	5.70
4-Nitrochloro-benzene-2-sulfonic	+	+	11.00	11.00

[a] Deliquescent.

TABLE II

SOLUBILITIES OF NEUTRAL AMMONIUM SALTS

Acid	Solvent		
	Water	CH_3OH	C_2H_5OH
Phenoxyacetic	13.03	3.97	0.44
p-Nitrophenylacetic	7.41	15.14	1.82
o-Iodobenzoic	67.11	184.10	63.37
o-Methoxybenzoic	38.25	17.85	4.82
1,2,4-Dinitrobenzoic	62.70	21.39	3.85
5-Nitrosalicylic	4.43	4.41	1.96
α-Naphthalenesulfonic	45.91	34.45	9.22
β-Naphthalenesulfonic	11.71	8.33	2.53
2,5-Dichloro-benzenesulfonic	11.30	20.15	2.59
4-Nitrochloro-benzene-2-sulfonic	4.72	2.76	0.96

solution to equilibrium with the salt. The solubilities so found are expressed in grams of salt per hundred grams of solvent.

In the preceding tables are recorded several of the properties, the results of analysis and the solubilities of the neutral ammonium salts of the acids listed.

Summary

Fifteen neutral ammonium salts of organic acids have been prepared by the action of dry ammonia on solutions of the respective acids.

The stabilities in dry and moist air and some of the solubilities have been determined.

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REDUCTION OF SEMICARBAZONES

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Introduction

The Skita method of reduction with colloidal platinum as catalyst, as shown in a previous communication from this Laboratory,[1] is of service in converting semicarbazones to the corresponding semicarbazides where other methods of reduction have produced only negative results.[2] Certain semicarbazones, such as glyoxylic acid semicarbazone[3] and benzal semicarbazone,[4] are readily reduced with sodium amalgam without molecular cleavage, but it has been quite definitely determined that reduction in the desired way with sodium amalgam succeeds only when an electronegative radical is joined to the carbon of the C=N complex. From the experiments described in this paper it appears probable that catalytic reduction with colloidal platinum is of general application in the conversion of semicarbazones to the corresponding semicarbazides.

Conditions have been established for obtaining excellent yields of semicarbazides with a minimum amount of platinum; for example, carvone semicarbazone and hexanone semicarbazone can be reduced with a yield of 80% where the semicarbazone and 10% platinic chloride solution are employed in the ratio of 10 g. to 1 cc. It is necessary in the case of camphor and fenchone, terpene ketones of similar structure, to employ for the reduction of their semicarbazones a much larger amount of platinic chloride. Camphor

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[1] Neighbors, Foster, Clark, Miller and Bailey, This Journal, **44**, 1557 (1922).

[2] Rupe and Oestreicher, *Ber.*, **45**, 30 (1912).

[3] Darapsky and Prabhakar, *Ber.*, **45**, 2625 (1912). Bailey and Read, This Journal, **36**, 1751 (1914).

[4] Kessler and Rupe, *Ber.*, **45**, 26 (1912).