Acknowledgments.—Several of the gel preparations were kindly supplied by the Shell Development Company and the Standard Oil Development Corporation and the remaining ones were prepared by M. M. Stewart of these laboratories. Grateful acknowledgment is also accorded to Dorothy Diener, Bernice Good and Sybil Cumming for assistance in the accumulation of experimental data.

Summary

Physical data on the microstructure of a series of ten amorphous silica and silica–alumina gels have been obtained from studies of low temperature gas adsorption, porosity and small angle X-ray scattering. Good correlations are obtained between (1) the mean pore diameter calculated from the specific micropore volume and the specific surface and the mean pore diameter calculated according to a capillary condensation theory of isotherm analysis, (2) the average particle size and the specific surface and (3) the pore to particle size ratio and the porosity factor. It is concluded that the over-all correlations which are found indicate the validity of the assumptions necessary in the data interpretation at least for the materials which have been studied.

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[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, NAVAL RESEARCH LABORATORY]

The Preparation of Nitrite Salts of Alkyl Amines[1]

BY JOHN K. WOLFE[2] AND KENNETH L. TEMPLE[3]

Alkyl ammonium nitrite salts have been prepared by the reaction of the amine hydrochloride with sodium nitrite[4] or silver nitrite,[5] the amine sulfate with barium nitrite, or the amine with nitrogen sesquioxide,[6] all of these reactions being carried out in aqueous solution. The present study outlines a new method of preparation, employing the amine, sodium nitrite, solid carbon dioxide, methanol and a small amount of water. Sodium carbonate precipitates as the reaction proceeds, leaving a methanol solution of the nitrite. The general reaction, using a primary amine as the example, can be represented by the equation

$$2RNH_2 + CO_2 + H_2O + 2NaNO_2 \longrightarrow 2RNH_2{\cdot}HNO_2 + Na_2CO_3$$

The reaction between the amine and carbon dioxide in methanol in the absence of water formed a white powder which precipitated at about $-20°$ and corresponded to the formula $(RNH_2)_2{\cdot}CO_2$. These substances could be filtered and isolated at room temperature but they sublimed readily. Compounds of this type have been previously observed and identified.[7]

This white powder reacted with sodium nitrite and water in the presence of methanol to produce the ammonium nitrite.

This method has been applied successfully to isopropylamine, diisopropylamine, diisobutylamine and triethylamine, with a yield of about 75% of the nitrite in each case.

The use of methanol instead of water as the solvent permits the use of a lower temperature, thus decreasing the formation of nitrosamines and the decomposition of unstable nitrites. The evolution of carbon dioxide gas during the preparation excludes oxygen and thus tends to prevent the formation of nitrates.

Table I summarizes the various reaction conditions studied. Sodium nitrite is superior to potassium nitrite since potassium carbonate separates in a flocculent condition and is much harder to filter. Absolute ethanol, acetone and isopropanol are inferior to methanol as a solvent, undoubtedly due to the higher solubility of sodium nitrite in methanol. The yield of sodium carbonate is fairly constant in all of the cases in which methanol was used. The yield of sodium carbonate is probably a better measure of the extent of the nitrite reaction than is the yield of the nitrite, since in many cases the nitrites are difficult to isolate.

This new method of synthesis was tried for higher molecular weight amines, whose nitrite salts are not water soluble, and quite low yields were obtained. It was found that some of these nitrites had been described in the literature and were prepared in aqueous solution but the yields reported were often quite low and the methods were poorly described. Dicyclohexylammonium nitrite, a compound not previously described, was prepared in this study in 98% yield and the experimental method used in its preparation is described as an example. Dicyclohexylaminenitrite is easily converted to the N-nitrosamine by warming in dilute acid solution. A comparison of these two materials shows the expected chemical behavior.

A study of the alkyl ammonium nitrite salts which have been investigated indicates that, in general, the salts of primary amines of low molecular weight and the salts of tertiary amines are

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[1] The opinions or assertions contained in this paper are the authors' and are not to be construed as official or reflecting the views of the Navy Department.

[2] Present address: General Electric Research Laboratory, Schenectady, N. Y.

[3] Present address: Rutgers University, New Brunswick, N. J.

[4] Van der Zande, *Rec. trav. chim.*, **8**, 205 (1889).

[5] Neogi, *J. Chem. Soc.*, **99**, 1252 (1911).

[6] Bamberger and Muller, *Ber.*, **21**, 847 (1888).

[7] Hayashi, *Abst. Bull. Inst. Phys. Chem. Res.* (*Tokyo*), **11**, 133 (1932).

TABLE I

PREPARATION OF AMINE NITRITE SALTS BY NEW METHOD

Amine	Inorg. nitrite	Solvent	Moles solvent / Moles nitrite	Time, hr.	Na_2CO_3, % yield	Nitrite salt, % yield
Di-isopropylamine	$NaNO_2$	MeOH	7.5	3.5	76	76
Di-isopropylamine	KNO_2	MeOH	12.5	4.5	48[a]	15
Di-isopropylamine	$NaNO_2$	AbsEtOH	10.3	18	56[a]	43
Di-isopropylamine	$NaNO_2$	Acetone	82	8	61[a]	19
Di-isopropylamine	$NaNO_2$	*i*-PrOH	26.6	3.5	28[a]	20
Di-isobutylamine	$NaNO_2$	MeOH	15	3.5	74	66.5
Triethylamine	$NaNO_2$	MeOH	12.5	3.5	75	68
Mono-isopropylamine	$NaNO_2$	MeOH	10	4	75	74

[a] Contained unreacted inorganic nitrite.

hygroscopic while the salts of primary amines of high molecular weight and the salts of secondary amines are not hygroscopic. The salts of highly branched secondary amines appear to be the most stable.

Experimental[8,9]

The following method was used in the preparation of the nitrite salts: A mixture of 200 mesh C. P. sodium nitrite, water and methanol was placed in a three-necked two-liter round-bottom flask fitted with dropping funnel and Hershberg stirrer. The stirred mixture was cooled to 0° by the addition of solid carbon dioxide and the amine was then added over a period of one and one-half to two hours, a temperature of 0-5° being maintained by the addition of solid carbon dioxide. Stirring was continued for about two hours, sufficient methanol being added to wash the foam from the sides of the flask. The precipitated sodium carbonate was filtered at room temperature and washed well with methanol.[10] The solvent was removed from the filtrate under reduced pressure and the solid product recrystallized from a suitable solvent.

The molecular weight of each of the nitrites was determined by boiling a weighed sample of the nitrite with an excess of 0.5 *N* sodium hydroxide solution until the free amine was volatilized and then titrating the residual alkali with standard acid.

Diisopropylammonium Nitrite.—One mole of diisopropylamine (boiling at 81–85°), one mole of sodium nitrite, 0.5 mole of water and 300 ml. of methanol gave 80 g. of sodium carbonate. The solution of the solid nitrite in 500 ml. of anhydrous isopropanol, filtered to remove sodium nitrite, gave 112 g. of nitrite when cooled to −40°. The melting point of 136–7° was unchanged by recrystallization from acetone and ethyl acetate.[11]

Anal. Calcd. for $C_6H_{16}O_2N_2$: C, 48.6; H, 11.0; N, 18.9; mol. wt., 148. Found: C, 48.7; H, 11.5; N, 18.6; mol. wt., 147.

Diisobutylammonium Nitrite.—The salt obtained from 0.5 mole of diisobutylamine (boiling at 136–140°), 0.5 mole of sodium nitrite, 0.25 mole of water and 300 ml. of methanol was dissolved in 250 ml. of isopropanol. By cooling the solution to −40°, 58.6 g. of colorless plates melting at 145–146° was obtained.

Anal. Calcd. for $C_8H_{20}O_2N_2$: C, 54.5; H, 11.5; N, 15.9; mol. wt., 176. Found: C, 54.7; H, 11.2; N, 15.6; mol. wt., 174.5.

Triethylammonium Nitrite.—One mole of triethylamine (boiling at 88–90°), one mole of sodium nitrite, 0.5 mole of water and 500 ml. of methanol gave 81 g. of sodium carbonate. Removal of the methanol in an atmosphere of dry carbon dioxide at a temperature not exceeding 25° gave one hundred grams of light tan crystals melting at 94–97° with decomposition. The product turned brown on standing at room temperature for a few hours but was stable when stored at −40° over calcium chloride in a vacuum desiccator. A solution of 2 g. of the salt in 400 ml. of absolute ether gave white silky needles when cooled to −60°. These needles melted at 96.5–98° in a sealed tube.[12]

Anal. Calcd. for $C_6H_{16}O_2N_2$: mol. wt., 148. Found: mol. wt., 146, 147.

Isopropylammonium Nitrite.—The reaction of one mole of isopropylamine (boiling at 31–35°), one mole of sodium nitrite, 0.5 mole of water and 470 ml. of methanol gave a methanol solution which was evaporated under reduced pressure in an atmosphere of carbon dioxide, the temperature being maintained below 25°. The white crystalline product weighed 79 g. and melted at 47–49°. This substance is very hygroscopic and turns brown when stored in a vacuum desiccator at room temperature, but is stable in a dry atmosphere at −40°. Recrystallization of the product from a solution of four parts of ethyl acetate and one part of isopropanol, by cooling the solution to −60°, gave white crystals which melted at 49–50° in a sealed tube.

Anal. Calcd. for $C_3H_{10}O_2N_2$: mol. wt., 106. Found: mol. wt., 107.

Di-cyclohexylammonium Nitrite [$(C_6H_{11})_2NH \cdot HNO_2$].—Ten milliliters (9.1 g., 0.045 mole) of di-cyclohexylamine (Monsanto) were mixed with 400 ml. of water, an excess of concentrated hydrochloric acid was added and the mixture was heated almost to boiling to dissolve the salt formed. The solution was adjusted to *p*H 8 with ammonium hydroxide. Solid C. P. sodium nitrite (150 g.) was added, the mixture was stirred at 0° for one hour and the precipitate was filtered and dried. The yield was 11.2 g. (98%) of light tan crystals melting at 176–178° with decomposition. Recrystallization from methanol yielded colorless plates melting at 178–180° with decomposition. Acidification of this product produced the characteristic nitric oxide odor.

Anal. Calcd. for $C_{12}H_{24}N_2O_2$: C, 58.8; H, 11.8; N, 13.7. Found: C, 58.6; H, 11.7; N, 14.0.

N-Nitroso-Di-cyclohexylamine [$(C_6H_{11})_2NNO$].—A sample of dicyclohexylamine acetate (m. p. 115–116°) was warmed with an aqueous solution of acetic acid and sodium nitrite. The insoluble precipitate was filtered and recrystallized from acetone, yielding colorless crystals of nitrosamine melting at 104–105°.

Anal. Calcd. for $C_{12}H_{22}N_2O$: C, 68.5; H, 10.5. Found: C, 68.6, 68.8; H, 10.3, 10.5.

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[8] The authors wish to acknowledge the help of Miss Nyla Mack of the Chemistry Division, NRL, for some of the analyses.

[9] All melting points are corrected.

[10] The identity of the precipitate was established by X-ray diffraction examination, performed by Ens. Birks of the Physical Optics Division of NRL, and by comparison with an authentic sample of anhydrous sodium carbonate.

[11] Van der Zande[4] reported a melting point of 140°. The authors find that the melting point depends on the rate of heating, approaching 140° in a rapidly heated bath.

[12] Neogi [*J. Chem. Soc.*, **99**, 1252 (1911)] and Ray [*ibid.*, **101**, 216 (1912)] reported that this compound forms yellow prisms decomposing at 75°.

A mixed melting point of the nitrosamine with dicyclohexylammonium nitrite showed the normal depression and wide range. N-Nitroso di-cyclohexylamine failed to give nitric oxide fumes on treatment with cold hydrochloric acid.

Summary

1. A new method is described for the preparation of alkyl ammonium nitrites from amines, employing sodium nitrite, carbon dioxide and methanol. The nitrites of isopropylamine, diisopropylamine, diisobutylamine and triethylamine have been prepared.

2. Alkyl ammonium nitrite salts of primary amines of low molecular weight and the salts of tertiary amines are in general hygroscopic while the salts of secondary amines are not hygroscopic.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE JOHNS HOPKINS UNIVERSITY]

The Selective Degradation of Certain Pyrryl Polycarboxylic Esters[1,2]

BY ALSOPH H. CORWIN AND J. LLOYD STRAUGHN[3]

Publication of a method for the conversion of Knorr's pyrrole (2,4-dimethyl-3,5-dicarbethoxypyrrole) into 2-carboxyl-3,5-dicarbethoxy-4-methylpyrrole[4] opened the way for the preparation of many new pyrrole derivatives from this substance, providing that methods for selective degradations of the new acid could be found. The present paper describes these selective degradations. Knorr's pyrrole is already one of the most readily available substitution products of pyrrole. The numerous additional substances that can be prepared from it by transformations recorded below make it the most versatile of all pyrrole derivatives in the number and variety of chemical individuals which can be prepared from it.

Mechanism of Formation of 2-Carboxyl-3,5-dicarbethoxy-4-methylpyrrole.—When Knorr's pyrrole is chlorinated with sulfuryl chloride in glacial acetic acid, best yields of the desired acid are obtained if the reaction is performed at as low a temperature as possible. The use of 5% acetic anhydride lowers both the freezing point of the solution and its water content and increases the yield of acid by 5–10%. Increasing the temperature of the reaction, on the other hand, lowers the yield of acid and increases the yield of aldehyde. This observation suggests that the aldehyde represents a by-product of the reaction and not an intermediate in the formation of the acid. This conclusion was confirmed by attempting to halogenate the aldehyde under the conditions of the reaction. No acid could be obtained and the aldehyde was recovered unchanged. When the same reaction was tried using 2-dichloromethyl-3,5-dicarbethoxy-4-methylpyrrole, however, 45% of acid and 36% of aldehyde could be obtained. These results show that the dichloromethylpyrrole can be an intermediate in the reaction and that any of it which is converted to aldehyde in the course of the reaction will not yield acid.

It is possible to convert benzal chloride and acetic acid to benzaldehyde and acetyl chloride.[5] The analogous reaction in the pyrrole series can be represented schematically as

$$RCHCl_2 + CH_3COOH \longrightarrow RCHO + CH_3COCl + HCl$$

It is easily demonstrated that this reaction proceeds at 50° but not rapidly at 17°. At the higher temperature hydrogen chloride is given off and the distillate contains acetyl chloride, as shown by its reaction with aniline to form acetanilide. The dichloromethylpyrrole is best prepared by chlorination in chloroform, to avoid the possibility of aldehyde formation.

It follows from the observations recorded above that the aldehyde is not an intermediate in the formation of the acid, that the dichloro- and trichloro-pyrroles are intermediates and that reaction conditions should be directed toward the stabilization of the dichloromethylpyrrole.

The Stability of Pyrryl-carboxylic Acids.—By methods outlined below several pyrrylcarboxylic acids were prepared which had one methyl group and various combinations of three electron attracting groups, either carboxyl or carboxylic ester groups. None of these acids could be decarboxylated smoothly by the usual methods. When combinations were tried which contained only two electron attracting groups, however, decarboxylation took place smoothly. This behavior is analogous to that found in the benzene series in which electron releasing groups, such as phenolic hydroxyl groups, facilitate decarboxylation and the addition of electron attracting groups, such as carboxyl, to phenolic compounds hinders decarboxylation.[6] Because of this situation, further reactions were directed toward preparation and degradation of derivatives of methyldicarboxyl pyrroles.

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(1) Studies in the Pyrrole Series, XX; Paper XIX, Erdman and Corwin, THIS JOURNAL, **69**, 750 (1947).

(2) This paper is taken from the doctoral dissertation of John Lloyd Straughn, The Johns Hopkins University.

(3) Present address, Department of Chemistry, Western Maryland College, Westminster, Md.

(4) Corwin, Bailey and Viohl, THIS JOURNAL, **64**, 1267 (1942).

(5) Jacobsen, German Patent 11494 (1879), See *Frdl.*, **1**, 24 (1888).

(6) A close analogy is afforded in the resorcylic acids. 2,6-Dihydroxybenzoic acid decomposes in the range of 150–170° while the addition of a carboxyl group in the 3 position increases the stability so that the material melts at 312° without marked decomposition. See Senhofer and Brunner, *Wien. Akad. Ber.*, **80**, 504 (1879), and Brunner, *Ann.*, **351**, 320 (1907).