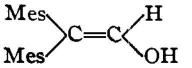
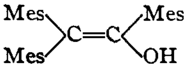
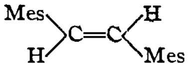
LIST OF COMPOUNDS STUDIED

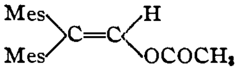
FIGURE 2

(1) $C_6H_5—C=CH_2$ styrene[9]

(2)

2,2-Dimesitilvinyl alcohol[10]

(3)

Trimesitylvinyl alcohol[11]

(4)

1,2-Dimesitylethylene[12]

(5)

2,2-Dimesitylvinyl acetate[13]

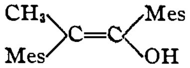
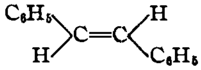
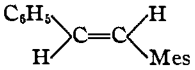
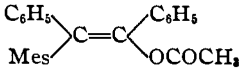
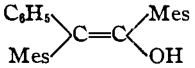
(6)

1,2-Dimesityl-1-propen-1-ol[14]

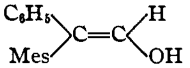
FIGURE 3

(1)

trans-Stilbene[15]

(2)

1-Mesityl-2-phenylethylene[16]

(3)

2-Mesityl-1,2-diphenylvinyl acetate[17]

(4)

1,2-Dimesityl-2-phenylvinyl alcohol[18]

(5)

2-Mesityl-2-phenylvinyl alcohol[19]

Summary

1. The ultraviolet extinction coefficient of symmetrical triphenylbenzene indicates that the molecule possesses a large amount of resonance energy. An explanation is offered for the non-coplanarity of triphenylbenzene (indicated by the X-ray evidence) as contrasted with biphenyl.

2. Ultraviolet extinction curves have been obtained for a number of substituted vinyl alcohols, where the crowding is so great as to permit only one aromatic ring to assume a position coplanar with the carbon-carbon double bond.

---

[9] Prepared in this laboratory. Similar results were obtained by A. Smakula, *Z. angew. Chem.*, **47**, 777 (1934).

[10] R. C. Fuson and S. P. Rowland, THIS JOURNAL, **65**, 992 (1943).

[11] R. C. Fuson, D. H. Chadwick and M. L. Ward, unpublished work.

[12] R. C. Fuson, E. C. Horning, M. L. Ward, S. P. Rowland and J. L. Marsh, THIS JOURNAL, **64**, 30 (1942).

[13] R. C. Fuson, P. L. Southwick and S. P. Rowland, *ibid.*, **66**, 1109 (1944).

[14] R. C. Fuson, J. Corse and C. H. McKeever, *ibid.*, **62**, 3250 (1940).

[15] A. Smakula, *Z. physik Chem.*, **155A**, 356 (1931).

[16] R. C. Fuson, J. J. Denton and C. Best, *J. Org. Chem.*, **8**, 64 (1943).

[17] R. C. Fuson, L. J. Armstrong, D. H. Chadwick, J. W. Kneisley, S. P. Rowland, W. J. Shenk and Q. F. Soper, THIS JOURNAL, **67**, 386 (1945).

[18] R. C. Fuson, L. J. Armstrong, J. W. Kneisley and W. J. Shenk, *ibid.*, **66**, 1464 (1944).

[19] R. C. Fuson, N. Rabjohn and D. J. Byers, *ibid.*, **66**, 1272 (1944).

URBANA, ILLINOIS RECEIVED NOVEMBER 8, 1945

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

Salts and Esters of Hydroxylamine-O-sulfonic Acid[1]

BY R. N. KELLER AND PETER A. S. SMITH[2,3]

In a previous communication[4] the amination of aromatic nuclei by means of hydroxylamine-O-sulfonic acid in the presence of aluminum chloride was reported

$$R—H + H_2N—O—SO_3H \xrightarrow{AlCl_3} R—NH_3{}^+HSO_4{}^-$$

At that time no attempt was made to explain the role of the aluminum chloride in the reaction. It was felt that the intermediate formation of the aluminum salt of hydroxylamine-O-sulfonic acid might be involved, since a recorded attempt[5] to prepare salts of this acid indicates that they are extremely unstable and reactive. We have therefore prepared a series of hydroxylamine-O-sulfonates and, although the aluminum salt could not be isolated, the properties of the sodium, silver, lead, ammonium, hydroxylamine, guanidine, pyridine and trimethylamine salts are recorded in this paper. Several of these salts were obtained in two forms, one which was relatively stable and one which deflagrated violently in a matter of minutes after preparation. Among the decomposition products of the salts were hydrazoic acid, hydroxylamine, and, in the case of ammonium hydroxylamine-O-sulfonate, hydrazine. These observations confirm and extend the original findings of Sommer, Schulz and Nassau[5] and support their explanation that NH (or $NH_2{}^+$) is an intermediate in the decomposition reaction. A discussion of the bearing of the chemical behavior of these salts on the mechanism of the amination reaction follows the experimental part.

In our original investigation[4] it was suggested that the low yields of aromatic amine obtained by amination with hydroxylamine-O-sulfonic acid might be improved by using a derivative of this

---

[1] Presented in part at the 107th meeting of the American Chemical Society, Cleveland, Ohio, April, 1944.

[2] From a thesis submitted to the Horace H. Rackham School of Graduate Studies in 1944 by Peter A. S. Smith in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[3] Allied Chemical and Dye Fellow, 1943-1944.

[4] R. N. Keller and Peter A. S. Smith, THIS JOURNAL, **66**, 1122 (1944).

[5] F. Sommer, O. F. Schulz and M. Nassau, *Z. anorg. allgem. Chem.*, **147**, 142 (1925).

TABLE I

SALTS OF HYDROXYLAMINE-O-SULFONIC ACID

Cation	Source of cation	Equivalent weight Calcd.	Equivalent weight Found	% purity	Dec. temp., °C.	Other analyses % Calcd.	Other analyses % Found
Na^{+}[a]	Hydroxide, methoxide, acetate, ethoxide	67.5	70.0	96.5	Indefinite, sinters *ca.* 150	Na 17.0	16.5
		67.5	71.8	94.5	Indefinite, sinters *ca.* 150	Na 17.0	16.9
						S 23.7	21.8
		67.5	69.3	97.5	Indefinite, sinters *ca.* 150	Na 17.0	16.5
						S 23.7	23.4
$C_5H_5NH^+$ (pyridinium)	Free base	96.0	98.5	97.6	*ca.* 30	S 16.7	16.8
NH_4^{+}[b]	Hydroxide	65.0	70.2	92.6	Sinters *ca.* 120	S 24.6	24.7
$(CH_3)_3NH^+$	Free base	86.0	87.2	98.6	103–105		
Pb^{++}	Acetate	107.5	135.8	79.4	75[c]	Pb 48.2	48.9
		107.5	134.0	80.3	66	Pb 48.2	47.8
Ag^+	Nitrate	110.0	119.0	92.5	Indefinite		
NH_3OH^+	Free base	73.1	75.0	97.5	63–66		
$(H_2N)_3C^+$ (guanidinium)	Thiocyanate, nitrate, acetate	86.0	88.0	97.5	50–55		
K^+	Thiocyanate, hydroxide, acetate	75.6	125.0	61.0	*ca.* 20		
Zn^{++}	Acetate	72.4	98.7	73.0	78		

[a] Several selected preparations. [b] The decomposed ammonium salt contained some hydrazine, detected with chlorauric acid. [c] The lead salt puffed suddenly, when allowed to stand, hurling the lid of the containing weighing bottle twenty feet.

acid more soluble in hydrocarbons. To this end an attempt has been made to prepare the methyl and ethyl esters of hydroxylamine-O-sulfonic acid by the reaction of methyl iodide with the silver salt and by direct acylation of hydroxylamine sulfate with ethyl chlorosulfonate. The crude products obtained did indeed appear to be the desired esters, but they proved to be no better aminating agents than the parent acid.

Experimental

Salts of Hydroxylamine-O-sulfonic Acid. General Procedure.—The stable salts were prepared by the following method with but slight modifications in individual cases. One-thousandth mole of the base or salt from which the cation was to come was dissolved in 15 ml. of absolute methanol and chilled to 0°; in some cases it was necessary to add a little water to achieve complete solution. The resulting solution was poured in a thin stream with stirring into a solution prepared from 0.001 mole of hydroxylamine-O-sulfonic acid and 15 ml. of ice-cold methanol. Where the desired salt did not precipitate under these conditions, benzene or ether was added; the preparation of the silver salt required the addition of petroleum ether as well. The products were filtered immediately, washed with alcohol and ether, and dried *in vacuo*. Celerity in these operations was essential in order to avoid alcoholysis of the hydroxylamine-O-sulfonate group. The yields of salts obtained in this manner varied between about 20 and 90%.

All salts were analyzed iodometrically by titrating the iodine liberated when they were dissolved in an ice-cold solution of potassium iodide acidified with hydrochloric acid, and allowed to stand one hour[5]

$$H_2N{-}O{-}SO_3H + 2I^- + H^+ \longrightarrow NH_4^+ + I_2 + SO_4^=$$

In addition, analyses were made for cation and/or sulfur where these were considered desirable. The iodometric equivalent weight is the most accurate criterion of the purity of the salts, however, since the most likely contaminant is the methyl sulfate of the cation, arising by methanolysis of the hydroxylamine-O-sulfonate group

$$M^+[O_3SO{-}NH_2]^- + CH_3OH \longrightarrow M^+[O_3SO{-}CH_3]^- + NH_2OH$$

It will be noticed that the methyl sulfate has almost exactly the same analytical figures for both cation and sulfur as does the hydroxylamine-O-sulfonate. Such analyses were therefore made for the most part to confirm the assumption that the only significant impurity was the methyl sulfate.

The decomposition points of the salts were determined by heating small samples in a capillary at the rate of 18° per minute.

The preparation of unstable forms of the sodium, ammonium, and hydroxylamine salts was accomplished either by mixing the reagents according to the above procedure as quickly as possible or by treating a suspension of hydroxylamine-O-sulfonic acid in dry ether with an alcoholic solution of the base (in the cases of ammonia and hydroxylamine). The analysis of these preparations was interrupted by deflagration on the balance pan, and for the most part no quantitative characterization of them could be made.

The potassium and hydrazine salts could not be obtained in stable form, and all attempts to prepare the aluminum, ferric, cupric, mercuric, magnesium, zinc and aniline salts in either form in a state of moderate purity by the wet method failed, apparently due to their high solubilities in the solvents used. When dry aluminum chloride was ground with hydroxylamine-O-sulfonic acid in equivalent amount, much hydrogen chloride was evolved, presumably due to a metathetical reaction forming some aluminum hydroxylamine-O-sulfonate. No pure substance was isolated from this mixture, but it was found to aminate benzene and toluene readily.

All preparations were tested for aminating power, both alone and together with an equal weight of aluminum chloride, by heating for half an hour under toluene. The diazotized aqueous extract of the reaction mixture was added to alkaline β-naphthol; the azo-dyes so produced showed the formation of toluidine in every case when aluminum chloride was used, but in no case without it. Determination of the yield of toluidine according to the previously described procedure[4] showed only about 2% yields.[6]

---

(6) The amination of toluene with hydroxylamine-O-sulfonic acid was attempted with a large variety of other substances as catalysts, following the procedure previously described for the case of aluminum chloride.[4] Of these, only anhydrous ferric chloride and boron trifluoride were found to effect the amination of toluene in detectable amount; the yield was about 2% with the former catalyst, only a trace with the latter. The catalysts found to be ineffective were: thionyl chloride, sulfuryl chloride, phosphoryl trichloride, phosphorus trichloride, phosphorus pentachloride, phosphorus pentoxide, an-

Decomposition of Potassium Hydroxylamine-O-sulfonate.—Freshly prepared potassium hydroxylamine-O-sulfonate was placed in a glass tube through which a slow current of air was passed and led through distilled water. In a few minutes after preparation the salt deflagrated, evolving a bluish cloud and becoming quite hot. A condensate which formed on the walls of the tube was identified as water. The white residue, which had fused, dissolved readily in water to give a strongly acid solution rich in sulfate, and presumably consisted of potassium pyrosulfate and/or bisulfate. The solution in which the vapors were caught was also strongly acid, but contained no detectable sulfate, showing that no solid had been carried over. The acidity was apparently due to hydrazoic acid, whose presence was detected by precipitation with silver nitrate, and by the pink color formed with ferric chloride. The presence of hydroxylamine was shown by the reduction of neutral auric chloride, but no reduction occurred in acid solution, showing that hydrazine was absent. No definite test for ammonia could be obtained with Nessler reagent.

Decomposition of Pyridinium Hydroxylamine-O-sulfonate.—The pyridine salt was decomposed by gentle warming in an open flask; a viscous, orange colored, transparent sirup remained. This was dissolved in ice-cold, dilute hydrochloric acid, treated with a slight excess of sodium nitrite and the excess of the latter removed with sulfamic acid. The resulting solution was added to one of β-naphthol in sodium hydroxide, whereupon a deep magenta color developed, turning yellow upon acidification. The colored material was extractable with ether from the neutralized solution, but evaporation of the extracts left only a very small amount of deep red crystalline solid[7] representing in no run more than a 2% yield. This material melted at 105–125° after several recrystallizations; further purification was not practical due to the very small amount of the sample. The abrupt and reversible color change from magenta to yellow on acidification agrees exactly with that reported for β-pyridylazo-β-naphthol,[7] however, and of the three aminopyridines, only the β-isomer can be diazotized and coupled in the usual manner. It is therefore reasonably certain that pyridine is aminated and that some β-aminopyridine is formed. No attempt was made to detect small amounts of α- or γ-aminopyridine.

Methyl Ester of Hydroxylamine-O-sulfonic Acid.—One gram of silver hydroxylamine-O-sulfonate was suspended in 15 ml. of absolute methanol and treated with 2 ml. of methyl iodide; reaction appeared to take place at once. After removal of the silver iodide by filtration with the aid of "sil-o-cel," the solution was rapidly concentrated *in vacuo*. The white crystalline crusts which formed were dried briefly in a vacuum desiccator and then assayed iodometrically. Equivalent weight of $CH_3OSO_2ONH_2$: calculated, 63.5; found, 98.6.

The obviously impure product was found to be free of silver and iodine. It was soluble in water and alcohol, but only sparingly soluble in other solvents. It melted at 120–130° without apparent decomposition, and the cooled melt still possessed strong oxidizing power.

Ethyl Ester of Hydroxylamine-O-sulfonic Acid.—Powdered hydroxylamine sulfate (6 g.) was covered with 10 ml. of ethyl chlorosulfonate and heated gradually to the boiling point of the latter. There was much foaming and evolution of hydrogen chloride, and the solid phase changed to a viscous sirup. After one hour, the mixture was cooled, the excess ethyl chlorosulfonate was decanted, and the pasty residue was pressed dry on a sintered glass filter and washed with light petroleum ether. The light tan, partially crystalline mass was completely soluble in water and in methanol, from which it could not be recovered. The solutions possessed strong and rapid oxidizing power, which slowly waned on standing. All attempts to purify this substance having failed, the crude material was analyzed both iodometrically and permanganometrically. For the latter titration the product was hydrolyzed to hydroxylamine salts by digestion with dilute sulfuric acid and then oxidized with ferric chloride.[8] Equivalent weight: calculated for $(C_2H_5OSO_2ONH_3)_2SO_4$ (sulfate of ethyl hydroxylamine-O-sulfonate), 95; found, permanganometric 101, iodometric 134.

Discussion

Although the experimental evidence presented here neither proves nor disproves any mechanism previously proposed by us for the amination reactions, it has suggested the following interpretation. The amination of pyridine in the decomposition of pyridine hydroxylamine-O-sulfonate is of significance because it is a case of amination of an aromatic ring by the cationoid agent NH (or NH_2^+) in the absence of any added catalyst. Benzene and toluene, however, which are far more easily attacked than pyridine by cationoid reagents, undergo no amination at all when heated with either hydroxylamine-O-sulfonic acid or one of its salts in the absence of a catalyst. We believe that this anomaly may be due to the ability of pyridine to form a salt itself with hydroxylamine-O-sulfonic acid, bringing pyridine and aminating agent into intimate molecular contact, and thus favoring the amination reaction over the other possible reactions of the active fragment. The fact that sodium hydroxylamine-O-sulfonate by itself does not aminate pyridine or toluene shows that the mere presence of a decomposable salt of hydroxylamine-O-sulfonic acid is not sufficient to bring about amination; and the fact that aluminum chloride does not noticeably increase the amount of amination of pyridine suggests that where intimate contact of aromatic nucleus and hydroxylamine-O-sulfonate ion is already achieved, further catalysis by aluminum chloride does not occur.

If the foregoing interpretation is accepted, the role of aluminum chloride in catalyzing the amination of benzene and toluene must be to bring the aminating agent and hydrocarbon into intimate molecular contact. Evidence in support of such a role is found in the observations that aluminum chloride as well as other aluminum salts form addition compounds (presumably coordination complexes) with aromatic hydrocarbons,[9] and that aluminum hydroxylamine-O-sulfonate is apparently formed from aluminum chloride and hydroxylamine-O-sulfonic acid, and is a good aminating agent.[10] It is interesting to

---

hydrous stannic chloride, anhydrous cupric chloride, mercuric chloride, aluminum ethoxide (in absolute ethanol), aluminum amalgam, aluminum sulfate, lithium chloride, hydrogen chloride, silicon tetrachloride, sulfuric acid and phosphoric acid.

(7) A. Binz and C. Räth, *Ann.*, **486**, 95 (1931).

(8) W. C. Bray, M. E. Simpson and A. A. MacKenzie, THIS JOURNAL, **41**, 1363 (1919).

(9) H. Campbell and D. D. Eley, *Nature*, **154**, 85 (1944).

(10) Additional confirmation of the views expressed has been obtained from two pilot experiments on the amination of benzylamine with hydroxylamine-O-sulfonic acid. When equivalent quantities of the two substances are mixed, a vigorous reaction takes place. Diazotization of the products and coupling with β-naphthol gives an intense red color, indicative of the formation of an aryl amine. No aluminum chloride was used in these experiments. Benzylamine was chosen because it contains a ring essentially the same as that of toluene in general reactivity, together with a salt-forming group in the same molecule.

note that the only catalysts which have been effective (ferric chloride, boron fluoride, and aluminum chloride)[6] for the amination reaction all show a strong tendency to form coördination complexes.

Summary

1. The sodium, ammonium, trimethylammonium, pyridinium, guanidinium, hydroxylammonium, lead, and silver salts of hydroxylamine-O-sulfonic acid have been prepared.

2. All of these substances were found to be more or less unstable, yielding various nitrogenous decomposition products suggesting the intermediate formation of the radical NH or NH_2^+.

3. An interpretation of the mechanism of the amination of aromatic rings by hydroxylamine-O-sulfonic acid and its catalysis by aluminum chloride has been suggested on the basis of the chemical behavior of these salts.

ANN ARBOR, MICHIGAN RECEIVED FEBRUARY 21, 1946

[CONTRIBUTION FROM THE CHEMICAL RESEARCH DIVISION, DEPARTMENT OF CHEMICAL ENGINEERING, TENNESSEE VALLEY AUTHORITY]

The System Ammonia–Phosphoric Acid–Water at 75°

BY J. C. BROSHEER AND J. F. ANDERSON, JR.

In an experimental study of the preparation of ammonium phosphate fertilizers there became apparent a need for reliable data on the solubility relationships in the system ammonia–phosphoric acid–water at temperatures up to 75°. The Russian investigators, Muromtsev,[1] Muromtsev and Nazarova,[2] and Volfkovich, Berlin and Mantsev,[3] have reported solubility measurements at 0, 25 and 50° that are consistent and apparently reliable. The data of D'Ans and Schreiner[4] at 25° and of Jänecke[5] at 0 and 25° agree fairly well with the data of the Russian investigators. Buchanan and Winner[6] have determined the solubilities of monoammonium and diammonium phosphates in water at temperatures up to 110.5 and 70°, respectively; their results for monoammonium phosphate agree well with the Russian data, but their results for diammonium phosphate appear to be low at 0 and 25° and slightly high at 50°. Although Jänecke[7] has reported solubilities in the system ammonia–phosphoric acid–water at high temperatures, as indicated by the temperature at which a trace of solid phase existed in experimental compositions in sealed glass bulbs, his measurements are not adequate to define the solubility relationships at 75°.

The present paper extends the data in the literature to include solubilities in the system ammonia–phosphoric acid–water at 75°. Presented also are a few measurements made at 60°. The solubilities were determined by analysis of the saturated liquid phases, and the compositions of solid phases were determined either by microscopic examination or by Schreinemakers'[8] method of residues.

Measurements

The materials were reagent grades of phosphoric acid, monoammonium phosphate, diammonium phosphate and aqua ammonia. The purity of the salts was such that recrystallization was demonstrably without effect on their solubility.

Equilibrium between the components was established in a bath maintained at 75.00 (or 60.00) ± 0.05°. The thermometer used was calibrated against a thermometer certified by the National Bureau of Standards. Although equilibrium apparently was reached within twenty-four hours, the charges were rotated in the bath for at least three days.

Most of the charges were held in 300-ml. glass-stoppered bottles, 51 mm. in diameter, that were rotated end over end at 2 r. p. m. in the bath. When equilibrium was attained, the bottles were returned to the vertical position until the charges had settled. Liquid-phase samples were transferred, in heated pipets, to weighing bottles which were immediately stoppered and cooled. Samples of the wet solid phase were transferred similarly in small glass thimbles that were manipulated by platinum wires.

Charges in which the vapor pressure of ammonia prevented accurate sampling from open bottles (last 8 equilibria, Table II) were placed in 200-ml. equilibration flasks of the design shown in Fig. 1. After introduction of the charge, arm A was sealed, and the flask was revolved in the bath with axis CE horizontal. When equilibrium was attained, the flask was rotated about arms A and B to bring tip E uppermost. Protective cap L was removed from tip E, and the sampling bulb (Fig. 1), with stopcock F open and bulb J evacuated, was seated and fastened on standard-taper joint D. Tip E, which extended into the bore of stopcock F, was broken by a momentary partial closing of F, and stopcock G was opened simultaneously. The liquid-phase sample thus was filtered through fritted-glass filter K and collected in bulb J. When sampling was complete, stopcock F was closed and the flask and sampling bulb were removed from the bath as a unit. The cooled sample bulb was separated from the flask, and both the liquid-phase and the wet solid-phase samples were weighed and analyzed.

Aliquots of hydrochloric acid solutions of the samples from either of the equilibration vessels were analyzed for ammonia by addition of alkali and distillation into standard acid; similar aliquots were analyzed for phosphoric acid by double precipitation as magnesium ammonium

---

(1) B. A. Muromtsev, *Kalii U. S. S. R.*, No. 1, 36-39 (1937).

(2) B. A. Muromtsev and L. A. Nazarova, *Bull. acad. sci. U. R. S. S.*, No. 1, 177-184 (1938).

(3) S. I. Volfkovich, L. E. Berlin and B. M. Mantsev, *Trans. Sci. Inst. Fertilizers Insectofungicides U. S. S. R.*, **153**, 228–241 (1940).

(4) J. D'Ans and O. Schreiner, *Z. physik. Chem.*, **75**, 95–107 (1910).

(5) E. Jänecke, *ibid.*, **127**, 71–92 (1927).

(6) G. H. Buchanan and G. B. Winner, *Ind. Eng. Chem.*, **12**, 448–451 (1920).

(7) E. Jänecke, *Z. physik. Chem.*, **A177**, 7–16 (1936).

(8) F. A. H. Schreinemakers, *ibid.*, **11**, 75 (1893).