[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA.]

THE NITROSULFONIC ACIDS OF *p*-XYLENE.

BY WILLIAM J. KARSLAKE AND RALPH C. HUSTON.

Received April 3, 1914.

1. Introduction.

Nolting and Kohn[1] record the preparation of an aminosulfonic acid of *p*-xylene to which they ascribe the formula:

$$C_6H_2\overset{1,4}{(CH_3)_2}\overset{6}{NH_2}\overset{2}{SO_3H}$$

This acid was prepared by reducing with ammonium sulfide, or with tin and hydrochloric acid, the solution resulting from the treatment of *p*-xylenesulfonic acid with red, fuming nitric acid. The nitro-acid was not isolated, nor were any of its derivatives prepared.

Guy G. Frary[2] describes a nitrosulfonic acid of *p*-xylene which he prepared by nitrating *p*-xylenesulfonic acid with nitric acid (sp. gr. 1.60) in the cold. The potassium, sodium, calcium, barium, strontium, magnesium, copper, and zinc salts were prepared and of these the potassium, barium, copper, and zinc salts were analyzed. Most of these were prepared from the crude acid solution and were purified with difficulty. Frary assigned the formula $C_6H_4\overset{1,4}{(CH_3)_2}\overset{6}{NO_2}\overset{2}{SO_3H}$ to the acid, in spite of the fact that an attempt to reduce it to the amino acid with ammonium sulfide proved unsuccessful. Attempts to prepare the sulfonchloride from the free acid, or from its potassium salt, resulted in the formation of a reddish brown oil which failed to solidify under water, and which did not crystallize from organic solvents. Somewhat better success attended the attempts to prepare the sulfonchloride of the nitrosulfonic acid by nitrating the sulfonchloride of *p*-xylene with nitrosulfuric acid. Two nitrosulfonchlorides were obtained, one in quantities large enough for analysis, the other, and more soluble one, in an insufficient quantity. The first melted at 109.5° and gave an amide melting at 179°. The second melted at 56–57° and gave an amide melting at 199–200°.

With the hope of obtaining a more thorough knowledge of the nitrosulfonic acids of *p*-xylene, the following research was undertaken. The problem was attacked in two ways, the initial material in each case being "Kahlbaum's" *p*-xylene. In one series of experiments *p*-xylene was sulfonated, and various methods of nitration were tried on the sulfonic acid or on its chloride. In the other series, a nitro group was introduced into *p*-xylene and the nitro-*p*-xylene treated with different concentrations of sulfuric acid or with chlorosulfonic acid.

---

[1] *Ber.*, **19**, 141 (1886).

[2] An unpublished Master's Thesis, State University of Iowa, 1909.

2. Experimental.

Sulfonation of p-Xylene.—*p*-Xylene may be sulfonated by means of strongly fuming sulfuric acid.[1] 500 g. of *p*-xylene, in a glass stoppered bottle, were treated with 650 g. of fuming sulfuric acid (25% anhyd.). The acid was added in small portions at a time, the mixture being constantly shaken. Considerable heat was evolved. On standing over night about three-fourths of the *p*-xylene dissolved. 75 g. more of the acid were added and the mixture turned three hours in a rotater, at the end of which time sulfonation was complete. The light brown syrupy mass was poured into an equal volume of water (1075 cc.) and allowed to stand over night. The separated acid was filtered off by suction and dried on porous plates. Yield, 770 g. The mother liquor yielded, on being heated two hours and cooled, a second crop of crystals which weighed 220 g., making a total of 990 g. of the crude sulfonic acid. A third crop of crystals, which tended to come down in radiating tufts, was obtained from the mother liquor. This latter compound was not studied further.

Nitration of p-Xylenesulfonic Acid.—The crude crystals of *p*-xylenesulfonic acid, which contained some sulfuric acid, were nitrated in the cold with fuming nitric acid, or with nitrosulfuric acid. In some cases the nitrating agent was added to the crude solution of sulfonic acid, no previous precipitation being made. The best yield was obtained by the following method: 100 cc. of the syrupy solution produced by the sulfonation of *p*-xylene were treated with nitric acid (sp. gr. 1.51), drop by drop, until 45 cc. had been added. The containing flask was cooled in ice. The reaction proceeded smoothly with evolution of red fumes. The solution was allowed to stand over night. After being evaporated on the water bath until red fumes ceased to be evolved, it was poured into 600 cc. of water. A small amount of dinitro-*p*-xylene was filtered off and the solution again evaporated to 110 cc. An equal volume of saturated potassium chloride solution was added and the mixture allowed to stand two days. The potassium salts were then filtered off and air dried. Yield, 64 g.

Action of Phosphorous Pentachloride on the Potassium Salts of the Nitrosulfonic Acids.—Frary's failure to obtain crystalline sulfonchlorides by the action of phosphorous pentachloride on the crude potassium salts of the nitrosulfonic acids is hard to understand. In this investigation eleven experiments, in which the dry potassium salts were treated with phosphorous pentachloride under different conditions, were made. All of the experiments yielded two sulfonchlorides, one melting at 109.5° and a more soluble one melting at 60°, while four of the eleven yielded, in addition, a third sulfonchloride, in very small amounts, which melted at 75°. The best yields were obtained under the following conditions: 150 g. of the crude, powdered potassium salts of the nitrated sulfonic acid, dried

---

[1] Fittig and Glinzer, *Ann.*, **136**, 305 (1865); Jacobson, *Ber.*, 10, 1009 (1877).

at 110°, were treated with 200 g. of phosphorous pentachloride. Heat was evolved and the whole mass slowly liquefied. After standing two hours the containing flask was heated one hour on a water bath. The heavy oily liquid was poured into ice water, washed thoroughly, and allowed to stand under ice water two days. It did not solidify but became granular in appearance and of the consistency of a thick paste. After the water was drained off the paste was dissolved in 1000 cc. of ether and dried over calcium chloride. Most of the ether was distilled off and the residue transferred to a beaker. Crystals began to form almost immediately although very slowly. After standing ten days the crystals were filtered off by the aid of a suction pump and washed with a mixture of ether and petroleum ether. Yield, 10 g. From this batch of crystals, upon recrystallization from ether and petroleum ether, there were obtained two sulfonchlorides; 9.6 g. of one which gave a melting point of 109.5° and 0.2 g. of a slightly more soluble one which melted at 74.5°. (In one case the separation of the two sulfonchlorides was made mechanically.) The mother liquor from the first crop of crystals was placed in an ice box for three weeks, when a second crop of crystals was filtered off. This crop gave, on recrystallization, 2.3 g. of the sulfonchloride melting at 109.5° and 3.1 g. of a decidedly more soluble sulfonchloride of the same crystalline form which, after repeated recrystallization, melted at 60°. A third crop of crystals of the sulfonchloride melting at 60° was obtained. Yield, 10.4 g. The remaining 14 g. of reddish oil did not yield crystals on standing three months. When treated with ammonium hydroxide it gave an amide which melted, after seven crystallizations from alcohol and water, at 147°, a close agreement with the melting point of *p*-xylene-sulfonamide.

Total yield of the nitrosulfonchloride melting at 109.5° = 11.9 g.
Total yield of the nitrosulfonchloride melting at 75.0° = 0.2 g.
Total yield of the nitrosulfonchloride melting at 60.0° = 13.5 g.

An attempt to increase the rate of precipitation of the low melting nitrosulfonchloride by dissolving the oil in ether, shaking with dilute ammonium hydroxide, neutralizing with hydrochloric acid, drying and evaporating, was not successful.

Recrystallization of the crude potassium salts from alcohol did not increase the yield of nitrosulfonchlorides to an appreciable extent.

Attempts to nitrate the sulfonchloride of *p*-xylene by means of nitric acid, nitrosulfuric acid, or diacetyl-orthonitric acid[1] met with only limited success. In all trials but one, only one sulfonchloride, and that in small quantities, was produced, *i. e.*, the one melting at 109.5°. In one case a very small yield of the sulfonchloride melting at 60° was isolated. A rather large excess of nitrosulfuric acid gave the best results.

---

[1] *Ber.*, **35**, 2526 (1902).

Sulfonation of Nitro-p-xylene.—*p*-Xylene was nitrated[1] in the cold with fuming nitric acid (sp. gr. 1.60). The nitro-*p*-xylene was purified by steam distillation.

Attempts to sulfonate this compound with concentrated or fuming sulfuric acid at room temperature, or at the temperature of boiling water were unsuccessful. Either no appreciable reaction took place, or a violent reaction set in which changed the reacting mixture to a charred mass.

Chlorosulfonic acid has been found to be an effective reagent in producing the sulfonic acids[2] and the sulfonchlorides[3] of aromatic nitro derivatives. Speaking generally, the nitro derivatives of the aromatic hydrocarbons, when heated with two or more mols of chlorosulfonic acid, produce sulfonchlorides, sulfonic acids, and sulfones. If the heating is omitted, little or no reaction takes place. F. von Heyden Nachfolger[4] found that the —SO_2Cl group took the meta position to the nitro group, there being formed at the same time smaller amounts of the ortho and para derivatives.

Of five experiments made, the one with the following proportions of reacting substances and the conditions here described gave the best results: 100 g. of nitro-*p*-xylene, which had been purified by two distillations with steam and dried over calcium chloride, were added, drop by drop, to 480 g. of chlorosulfonic acid, surrounded by ice. The dark red mixture, placed in a flask, the neck of which was fitted with a calcium chloride tube to protect from atmospheric moisture, was allowed to stand over night. When it was heated on the water bath hydrochloric acid was given off. The heating was continued, with occasional shaking for twelve hours, at the end of which time the evolution of hydrochloric acid gas had practically ceased. When cool the mixture was poured slowly into 2 liters of ice water. This caused the separation of a semi solid brown precipitate which, on standing one hour, solidified in the bottom of the vessel. The solid was filtered off and treated with 1 liter of ether, in which it dissolved, leaving a small amount of tarry residue. The tarry residue was filtered from the solution and the latter dried over calcium chloride. After standing two days the addition of 300 cc. of petroleum ether caused the separation of more tarry matter. After standing five hours longer the solution was filtered from the tarry matter and the calcium chloride. 500 cc. of ether was distilled off and the concentrated solution placed in a beaker, where crystals, which tended to adhere to the sides of the beaker, began to form immediately. The evaporation was continued in a current of dry air until the volume of the solution was reduced to 100 cc. The

---

[1] Jannasch, *Ann.*, **176**, 55 (1875).

[2] Armstrong, *Ber.*, **4**, 356 (1871).

[3] Dr. F. von Heyden Nachfolger, D. R. P. 89,997; *Frdl.*, **4**, 38 (1899).

[4] *Loc. cit.*

crystals were filtered off by suction and washed with a mixture of ether and petroleum ether. After recrystallization from ether and petroleum ether they weighed 23 g. One gram of them, recrystallized five times from petroleum ether, gave a constant melting point of 74.5–75.5°. The evaporation of the mother liquor was continued for five days. More crystals separated and at the same time a heavy oil formed in the bottom of the beaker. This second crop of crystals was filtered off and subjected to fractional crystallization. From it was recovered 6.3 g. of the sulfonchloride, m. p. 74.5°, and 10 g. of the more soluble sulfonchloride, mentioned in previous experiments, m. p. 60°. The mother liquor from the second crop of crystals was placed in the ice box and allowed to stand three weeks. It yielded a third crop which weighed 18 g. (crude) and which melted after repeated crystallizations at 60°. The remaining 10 g. of tarry matter, which probably contained some sulfone and *p*-xylenesulfonchloride, did not yield crystals when allowed to stand three weeks at low temperature.

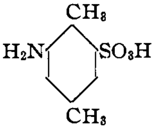
In some of the experiments the crude sulfonchloride, m. p. 74.5°, was recrystallized from pure petroleum ether. While it was more difficultly soluble in pure petroluem ether than in the mixed solvent, fewer crystallizations were necessary. The tarry impurity, being practically insoluble in petroluem ether, was left on the sides and bottom of the beaker after the sulfonchloride was dissolved.

Determination of Configuration.—In order to determine the configuration of the three crystalline nitrosulfonchlorides, they were hydrolyzed to the corresponding sulfonic acids. These were in turn subjected to the reducing influence of ammonium sulfide in alcoholic solution, or of stannous chloride in hydrochloric acid.

The acid from the sulfonchloride, m. p. 60°, yields, by either method, an aminosulfonic acid of *p*-xylene containing one molecule of water of crystallization. It crystallizes in clusters of very fine white needles which are quite difficultly soluble in cold water. When heated above 200° it begins to char but does not melt even when heated as high as 320°. A temperature of 160° is required for complete dehydration. An analysis gave the following results:

Calc. for $C_8H_{11}O_3NS.H_2O$: H_2O, 8.21%; S, 14.6%; found: H_2O, 8.12%; S, 14.43%.

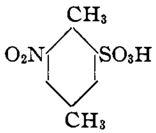
The properties of the above acid resemble very closely those of the aminosulfonic acid of *p*-xylene prepared by Nolting and Kohn[1] to which they assign the formula



---

[1] *Ber.*, **19**, 143 (1886).

and they are considered identical. The nitrosulfonic acid from which it was prepared must then have the formula,



The nitrosulfonic acid derived from the sulfonchloride melting at 109.5° is not reduced when hydrogen sulfide has been passed through its ammoniacal alcoholic solution for fifteen hours.[1] The unchanged nitrosulfonic acid was identified by means of its barium salt.

Different results were obtained when 5 g. of this acid were treated with three mols (12 g.) of stannous chloride and a slight excess of hydrochloric acid and then warmed for forty-eight hours on the hot plate. The tin was precipitated with hydrogen sulfide, filtered off, and the solution evaporated to dryness on the water bath. The residue was dissolved in water and boiled with barium carbonate. On filtering off the excess of the latter, a considerable amount of *p*-xylidine was found in the filtrate. On standing over night about 0.3 g. of barium sulfate settled out. A small amount of the barium salt of the unchanged nitrosulfonic acid was obtained on evaporation. These results indicate that the nitrosulfonic acid in question, upon being reduced under the conditions given, is at once hydrolyzed to *p*-xylidine and sulfuric acid. Nolting and Kohn[2] mention the occurrence of a small amount of a soluble acid in the mother liquor of 6-amino-1,4-dimethylbenzene-2-sulfonic acid which was oxidizable to *p*-xyloquinone. It is very probable that their soluble acid (?) was simply the hydrochloride of *p*-xylidine which would be readily oxidizable to the quinone.[3] A more thorough study of the conduct of this acid toward reducing agents is now being carried on.

The nitrosulfonic acid from the sulfonchloride melting at 74.5° is readily reduced, either by ammonium sulfide or by stannous chloride and hydrochloric acid. The aminosulfonic acid comes down in clusters of fine prismatic plates or needles, which are slightly less soluble than the aminosulfonic acid already described. The sodium salt crystallizes in small soluble white plates which contain no water of crystallization.

Calc. for $C_8H_{10}O_3NSNa$: Na, 10.32%; found: Na, 10.28% and 10.36%.

The barium salt comes down in readily soluble, long prismatic plates containing seven molecules of water of crystallization.

Calc. for $(C_8H_{10}O_3NS)_2Ba.7H_2O$: H_2O, 19%; Ba, 20.7%; found: H_2O, 19.12% and 19.22%; Ba, 20.48% and 20.36%.

---

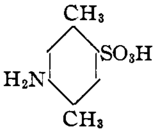
[1] It will be remembered that Frary was unsuccessful in an attempt to reduce this acid with hydrogen sulfide.

[2] *Loc. cit.*

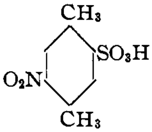
[3] Nolting, *Ber.*, 18, 2667 (1885).

These salts are identical in properties with the sodium and barium salts of 5-amino-1,4-dimethylbenzene-2-sulfonic acid described by Nolting and Kohn.[1] In order to better identify the acid, *p*-xylidine was sulfonated and the barium salt of the acid was decomposed with the calculated amount of sulfuric acid. On filtering off the barium sulfate and evaporating, the aminosulfonic acid came down in well formed needle-like plates which resembled closely in appearance those formed by the reduction of the nitrosulfonic acid.

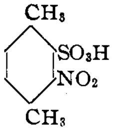
To further verify the identity of the acids, 1 g. of the one resulting from the reduction of the nitrosulfonic acid was oxidized with chromic acid. 0.54 g. of *p*-xyloquinone (phlorone) melting at 124–124.5° was obtained. The acid is then identical with the one which Nolting and Kohn[2] prepared by sulfonating *p*-xylidine and must have the formula



The acid from which it was formed by reduction must then have the formula



Since the nitrosulfonchloride, m. p. 60°, yields, on hydrolysis, 6-nitro-1,4-dimethylbenzene-2-sulfonic acid, and since the nitrosulfonchloride melting at 74.5° yields, on the same treatment, 5-nitro-1,4-dimethylbenzene-2-sulfonic acid, it follows that the nitrosulfonchloride melting at 109.5° must yield, on hydrolysis, 3-nitro-1,4-dimethylbenzene-2-sulfonic acid,



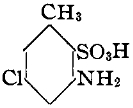
The fact that the acid was not reduced by hydrogen sulfide in ammoniacal alcoholic solution favors this formula, since the protective influence of two groups ortho to the nitro group would naturally be great. It is further shown that the phenyl ester is produced more slowly from the nitrosulfonchloride melting at 109.5° than from either of the other nitrosulfonchlorides. Finally, the very fact that the aminosulfonic acid which is formed by reducing this acid with stannous chloride and

---

[1] *Ber.*, **19**, 141 (1886).

[2] *Loc. cit.*

hydrochloric acid, is readily hydrolyzed in the presence of acids to *p*-xylidine, favors the assigned formula. Traube[1] has shown that the chloroaminotoluenesulfonic acid, of the formula



is readily hydrolyzed in acid solution to the corresponding chloroaminotoluene. It is readily seen that the relative position of the methyl, sulfo- and amino groups are the same in both acids.

Derivatives of 6-Nitro-1,4-dimethylbenzene-2-sulfonic Acid.

The Sulfonchloride, $C_6H_2(CH_3)_2NO_2.SO_2Cl$.—This compound is more soluble in a mixture of ether and petroleum ether than either of the other nitrosulfonchlorides of *p*-xylene. It forms regular rhombohedral prisms which show a tendency to form clusters and have a slight amber shade, even after repeated recrystallizations. It is readily soluble in ether, chloroform, carbon tetrachloride, benzene, and carbon disulfide; and less soluble in petroleum ether. When dissolved in a mixture of ether and petroleum ether and evaporated at ordinary temperatures, it tends to settle out as an oil. It is best crystallized from this mixed solvent at a temperature of about 10°. When heated under water it melts to an oil and is slowly hydrolyzed. M. p. 60–61°.

Calc.: Cl, 14.2%; S, 12.82%; N, 5.61%; found: Cl, 14.26%; 14.3%; S, 12.66%; N, 5.54%, 5.48%.

The Acid, $C_6H_2(CH_3)_2NO_2.SO_2OH.H_2O$.—Ten grams of the sulfonchloride was boiled one and one-half hours with 150 cc. of water under a reflux condenser. The solution was decolorized by boiling with animal charcoal, and evaporated to a thick syrup. On cooling, the acid crystallized out in plates. It was filtered off by suction, washed twice with concentrated hydrochloric acid, in which it was rather insoluble, and dried over sodium hydroxide. The acid was a bitter taste and is very hygroscopic. It is soluble in alcohol, but insoluble in ether, chloroform, carbon tetrachloride, benzene, and carbon disulfide. When heated to 128° it begins to char and does not melt even when heated to 200°. It loses its water of crystallization readily at 100°.

Calc.: H_2O, 7.23%; acid hydrogen, 0.401%; N, 5.62%; found: H_2O, 7.04%, 7.15%; acid hydrogen, 0.392%; N, 5.66%, 5.58%.

The Amide, $C_6H_2(CH_3)_2NO_2SO_2NH_2$.—The sulfonchloride was treated with excess of ammonium hydroxide and heated. It melted to an oil which was soon decomposed, a flocculent precipitate being formed. The mixture was evaporated almost to dryness and the residue washed repeatedly with water. It was then dissolved in alcohol. An equal volume

---

[1] *Ber.*, 26, 579 (1893).

of water was added and the solution set aside to crystallize. The amide comes down in clusters of fine prismatic plates, which are readily soluble in alcohol, ether, and chloroform, but insoluble in water. It melts at 172–173°.

Calc.: S, 13.91%; N, 12.17%; found: S, 13.84%; N, 11.81%, 12.16%.

The Anilide, $C_6H_2(CH_3)_2NO_2SO_2HNC_6H_5$.—The sulfonchloride was dissolved in carbon tetrachloride and treated with excess of aniline. A precipitate settled at once. The solvent was evaporated, the precipitate washed with hydrochloric acid (1 : 1), dissolved in 10% sodium hydroxide, and reprecipitated with hydrochloric acid. The anilide was filtered off and recrystallized from 50% alcohol. It forms clusters of fine, hard, flat needles which melt at 143–144° and are soluble in alcohol, ether, chloroform, and carbon tetrachloride, but insoluble in water.

Calc.: S, 10.46%; N, 9.07%; found: S, 10.44%; N, 9.05%.

The Phenyl Ester, $C_6H_2(CH_3)_2NO_2SO_3C_6H_5$.—This is best prepared by the Reverdin[1] method: 1 g. of phenol was mixed with an equal weight of pyridine and treated with 2.65 g. of the sulfonchloride. This dissolved with evolution of heat. The solution was warmed on the water bath for five minutes. On cooling, it solidified to a granular mass, which was washed with water and dissolved in hot alcohol. The phenyl ester crystallizes from alcoholic solution in clusters of fine needle-like plates which melt at 117–118°. It is fairly soluble in chloroform, carbon tetrachloride, and benzene, but insoluble in water.

Calc.: S, 10.4%; N, 4.56%; found: S, 10.18%, 10.29%; N, 4.53%.

Sodium Salt, $C_6H_2(CH_3)_2NO_2SO_3Na.2H_2O$.—6-Nitro-1,4-dimethylbenzene-2-sulfonic acid, in solution, was just neutralized with sodium hydroxide solution (litmus). The sodium salt comes down in tree-like clusters of very soluble prismatic plates. It is soluble in hot alcohol. This salt may also be prepared by treating a concentrated solution of the acid with a saturated solution of sodium chloride. It loses its water of crystallization at 108°.

Calc.: H_2O, 12.8%; Na, 7.96%; found: H_2O, 12.69%; Na (as sulfate), 7.79%.

Potassium Salt, $C_6H_2(CH_3)_2NO_2SO_3K.H_2O$.—A solution of the acid was neutralized with 10% potassium hydroxide solution (litmus). On standing, the potassium salt came down from the concentrated solution in clusters, or rosets, of readily soluble, colorless prismatic plates. It is slightly less soluble in alcohol than the sodium salt. It is readily precipitated from a concentrated solution of the acid on the addition of saturated potassium chloride solution.

Calc.: H_2O, 6.24%; K, 14.53%; found: H_2O, 6.34%; K (as sulfate), 14.26%.

Calcium Salt, $[C_6H_2(CH_3)_2NO_2SO_3]_2Ca.4H_2O$.—A solution of the acid

---

[1] *Ber.*, **35**, 1443 (1902).

was boiled with precipitated calcium carbonate. The excess of calcium carbonate was filtered off and the solution evaporated. The salt came down in tree-like clusters of colorless crystals. It is less soluble than the calcium salt of the 3-nitrosulfonic acid and slightly more soluble than that of 5-nitrosulfonic acid. It is slightly soluble in alcohol. A temperature of 200° for ten hours is necessary to effect complete dehydration.

Calc.: H_2O, 12.58%; Ca, 7.01%; found: H_2O, 12.45%; Ca (as sulfate), 6.97%.

Barium Salt, $[C_6H_2(CH_3)_2NO_2SO_3]_2Ba.2H_2O$.—This salt was prepared from a solution of the acid and barium carbonate after the same manner as the calcium salt. It came down in small, colorless nodules which showed a tendency to adhere to the sides of the beaker. It is slightly soluble in hot alcohol. One of its two molecules of water of crystallization is given up at 150°. A temperature of 200° for six hours is required to drive off the second molecule.

Calc.: H_2O, 5.68%; Ba, 21.69%; found: H_2O, 5.67%; Ba (as sulfate), 21.71%.

Silver Salt, $C_6H_2(CH_3)_2NO_2SO_3Ag.H_2O$.—The acid, in solution, was treated with a little more than the calculated amount of silver nitrate, and boiled. The small amount of silver chloride was filtered off and the solution evaporated. The silver salt came down in clusters of fine needle-like plates. It is less soluble than the silver salt of the 3-nitrosulfonic acid and slightly more soluble than the silver salt of the 5-nitrosulfonic acid. It is very slightly soluble in alcohol. When exposed to the light, the crystals slowly decompose and darken in color. They lose their water of crystallization readily when heated above 100°.

Calc.: H_2O, 5.07%; Ag, 30.39%; found: H_2O, 4.91%; Ag (as metal), 30.43%.

Derivatives of 3-Nitro-1,4-dimethylbenzene-2-sulfonic Acid.

The Sulfonchloride, $C_6H_2(CH_3)_2NO_2SO_2Cl$.—This crystallizes from a mixture of ether and petroleum ether in clear rhombohedral prisms which melt at 109.5–110.5°. It is less soluble in ether, chloroform, carbon tetrachloride, benzene, and petroleum ether, than either of the isomeric sulfonchlorides. When boiled with water it slowly decomposes, but does not melt.

Calc.: Cl, 14.2%; S, 12.82%; N, 5.61%; found: Cl, 14.32%, 14.26%; S, 12.81% 12.72%; N, 5.66%.

The Acid, $C_6H_2(CH_3)_2NO_2SO_2OH$.—Ten grams of the sulfonchloride were boiled with 150 cc. of water three hours and twenty minutes under a reflux condenser. On evaporation of the solution to a syrup, the acid crystallized out in clusters of elongated plates. After being dried over sodium hydroxide it melts when heated to 100°. When heated twenty-four hours at 108° it first melts and then hardens and becomes crystalline. When thus dehydrated it melts between 143° and 145° with partial decomposition. Like the 6-nitrosulfonic acid it is less soluble in concentrated hydrochloric acid than in water, fairly readily soluble in alcohol but insoluble in ether, chloroform, carbon tetrachloride, carbon disulfide, benzene and petroleum ether. It is deliquescent.

Calc.: H_2O, 7.23%; acid hydrogen, 0.401%; N, 5.62%; found: H_2O, 7.08%; acid hydrogen, 0.396%; N, 5.57%.

The Amide, $C_6H_2(CH_3)_2NO_2SO_2NH_2$.—One gram of the sulfonchloride was treated with an excess of ammonium hydroxide, warmed, and allowed to stand over night. As this treatment did not decompose the crystals, the mixture was heated three hours on a hot plate. On evaporation, the amide came down in fine flat, shiny needles which, after recrystallization from 50% alcohol, melted at 191–192°. It closely resembles the amide of the 6-nitrosulfonic acid in its solubilities.

Calc.: S, 13.91%; N, 12.17%; found: S, 13.8%, 13.86%; N, 12.21%.

The Anilide, $C_6H_2(CH_3)_2.NO_2.SO_2HNC_6H_5$.—The details of the preparation were the same as those described for the preparation of the anilide of the 6-nitrosulfonic acid. It crystallizes from 50% alcohol in long, flat needles which melt at 181.5–182.5°. It is insoluble in water and slightly less soluble in organic solvents than the anilide previously described. The crystals retain a slight bluish tinge after ten recrystallizations.

Calc.: S, 10.46%; N, 9.07%; found: S, 10.37%; N, 9.06%.

The Phenyl Ester, $C_6H_2(CH_3)_2.NO_2.SO_3C_6H_5$.—The sulfonchloride dissolved more slowly in the pyridine-phenol mixture than did the 6-nitro-1,4-dimethylbenzene-2-sulfonchloride, solution being complete after the mixture had been heated fifteen minutes on the water bath. The ester comes down from alcoholic solution in well formed colorless prisms which show a slight tendency to adhere to the sides of the beaker. It melts sharply between 83° and 83.5° and resembles the phenyl ester of 6-nitro-1,4-dimethylbenzene-2-sulfonic acid as regards its action towards solvents.

Calc.: S, 10.4%; N, 4.56%; found: S, 10.47%; N, 4.51%.

Sodium Salt, $C_6H_2(CH_3)_2.NO_2.SO_3Na.2H_2O$.—This salt comes down in clusters of small, light yellow prismatic plates. Its solubility in water and in alcohol resembles that of the sodium salt of the 6-nitrosulfonic acid. Like this last named compound, it is precipitated when a concentrated solution of the acid is treated with saturated sodium chloride solution. It is dehydrated when heated six hours at 108°.

Calc.: H_2O, 12.8%; Na, 7.96%; found: H_2O, 12.68%; Na, 7.98%.

Potassium Salt, $C_6H_2(CH_3)_2NO_2SO_3K.H_2O$.—This forms tufts of colorless needle-like plates which are slightly less soluble than the crystals of the corresponding sodium salts. It retains its water of crystallization rather persistently, a temperature of 200° being required for complete dehydration.

Calc.: H_2O, 6.24%; K, 14.53%; found: H_2O, 6.02%; K, 14.18%, 14.36%.

Calcium Salt, $[C_6H_2(CH_3)_2NO_2SO_3]_2Ca.3H_2O$.—This salt crystallizes in slightly yellow translucent irregular crystals. It is more soluble than the calcium salts of either of the isomeric acids and than the barium salt of this same acid. It is only fairly soluble in alcohol. One of its three molecules of water of crystallization is given off when it is heated three hours at 108°. A temperature of 200° for eight hours is necessary for complete dehydration.

Calc.: H_2O, 9.74%; Ca, 7.24%; found: H_2O, 9.87%; Ca, 7.26%.

Barium Salt, $[C_6H_2(CH_3)_2NO_2SO_3]_2Ba.H_2O$.—It forms regular translucent crystals which resemble closely in appearance those of the calcium salt of the acid under consideration. It is more soluble than the barium salts of the isomeric acids. It is dehydrated when heated eight hours at 200°.

Calc.: H_2O, 2.92%; Ba, 22.32%; found: H_2O, 2.84%; Ba, 22.22%.

Silver Salt, $C_6H_2(CH_3)_2NO_2SO_3Ag.H_2O$.—This came down from the concentrated solution in readily soluble plates. It is slightly soluble in alcohol. When exposed to light it darkens more rapidly than either of the other silver salts. It is dehydrated at 108°.

Calc.: H_2O, 5.07%; Ag, 30.39%; found: H_2O, 5.05%, 5.12%; Ag, 30.44%.

Derivatives of 5-Nitro-1,4-dimethylbenzene-2-sulfonic Acid.

The Sulfonchloride, $C_6H_2(CH_3)_2NO_2SO_2Cl$.—The sulfonchloride crystallizes from the crude solution in small crystals which show a tendency to adhere to the sides of the beaker. On repeated recrystallization from ether or from a mixture of ether and petroleum ether the crystals take the form of colorless plates with slightly thickened centers. Its solubility in organic solvents is about the same as that of the 3-nitrosulfonchloride. It melts to an oil under hot water by which it is decomposed. When pure it melts at 74.5–75.5°.

Calc.: Cl, 14.2%; S, 12.82%; N, 5.61%; found: Cl, 14.29%; S, 12.8%, 13.03%; N, 5.64%, 5.68%.

The Acid, $C_6H_2(CH_3)_2NO_2SO_2OH.H_2O$.—This was prepared by hydrolyzing the corresponding sulfonchloride in the manner already described. The time necessary for the hydrolysis of 10 g. was two hours and ten minutes. The acid comes down in clusters of needle-like plates from the concentrated solution. It is slightly less soluble than its isomers in water and much less soluble in concentrated hydrochloric acid. When recrystallized from hydrochloric acid and dried over sodium hydroxide it melts with partial decomposition, between 138° and 140°. Like the other acids described it is extremely hygroscopic, has a bitter taste, and loses its water of crystallization at 108°.

Calc.: H_2O, 7.23%; acid hydrogen, 0.401%; N, 5.62%; found: H_2O, 7.22%; acid hydrogen, 0.394%; N, 5.49%, 5.56%.

The Amide, $C_6H_2(CH_3)_2NO_2SO_2NH_2$.—The sulfonchloride was readily decomposed by ammonium hydroxide. The amide comes down from 50% alcohol in fine prismatic plates which may or may not form clusters. When heated, the crystals become opaque at 170° and melt at 197–198°.

Calc.: S, 13.91%; N, 12.17%; found: S, 13.96%; N, 12.18%.

The Anilide, $C_6H_2(CH_3)_2NO_2SO_2HNC_6H_5$.—This compound was prepared in the same manner as the anilides already described. It crystallizes out of 50% alcohol, in which it is slightly less soluble than its isomers, in clusters of fine prismatic plates. It has a constant melting point of 130.5–131°.

Calc.: S, 10.46%; N, 9.07%; found: S, 10.36%, 10.42%; N, 9.02%.

The Phenyl Ester, $C_6H_2(CH_3)_2NO_2SO_3C_6H_5$.—This was prepared by the Reverdin method. The sulfonchloride passed into solution immediately with evolution of heat. The ester comes down from alcoholic solution in clusters of light yellow, needle-like plates having a constant melting point of 120°–120.5°.

Calc.: S, 10.4%; N, 4.56%; found: S, 10.47%; N, 4.49%, 4.61%.

Sodium Salt, $C_6H_2(CH_3)_2NO_2SO_3Na.H_2O$.—This forms clusters of flat colorless needles. It is less soluble in water than either of the other sodium salts and rather sparingly soluble in alcohol. It gives up its water of crystallization readily at 108°.

Calc.: H_2O, 6.64%; Na, 8.48%; found: H_2O, 6.75%; Na, 8.33%.

Potassium Salt, $C_6H_2(CH_3)_2NO_2SO_3K.H_2O$.—Prepared in the usual manner, this salt comes down in clusters of shining colorless needle-like plates. It is the least soluble in water and alcohol of any of the sodium or potassium salts studied. It is completely dehydrated when heated six hours at 108°

Calc.: H_2O, 6.24%; K, 14.53%; found: H_2O, 6.36%, 6.21%; K, 14.12% (puffed), 14.45%.

Calcium Salt, $[C_6H_2(CH_3)_2NO_2SO_3]_2Ca.3H_2O$.—This salt was prepared in the usual manner from calcium carbonate and a solution of the acid. It is the least soluble of the calcium salts studied. It comes down in tufts of long, flat, colorless needles which are very sparingly soluble in alcohol. It loses one of its three molecules of water of crystallization when heated four hours at 108°. A temperature of 200° for ten hours is required for complete dehydration.

Calc.: H_2O, 9.74%; Ca, 7.24%; found: H_2O, 9.57%; Ca, 7.16%.

Barium Salt, $[C_6H_2(CH_3)_2NO_2SO_3]_2Ba.2H_2O$.—This is the least soluble of the barium salts of the nitrosulfonic acids of *p*-xylene. It comes down in tufts of very fine, colorless needles which show a tendency to adhere to the sides of the beaker. Its solubility in alcohol is about the same as that of the calcium salt of the same acid. It is dehydrated when heated six hours at 200°.

Calc.: H_2O, 5.68%; Ba, 21.69%; found: H_2O, 5.56%; Ba, 21.73%.

Silver Salt, $C_6H_2(CH_3)_2NO_2SO_3Ag.H_2O$.—It forms clusters of long, shining needles. It is considerably less soluble than either of the other silver salts studied and darkens when exposed to the light more slowly than these.

Calc.: H_2O, 5.07%; Ag, 30.39%; found: H_2O, 4.95%; Ag, 30.29%.

5-Amino-1,4-dimethylbenzene-2-sulfonic Acid, $C_6H_2(CH_3)_2NH_2SO_2OH$.—The barium and sodium salts of this acid have been studied but there is very little in the literature concerning the properties of the acid itself. As prepared by the reduction of the corresponding nitrosulfonic acid or by the sulfonation of *p*-xylidine and subsequent purification by means of the barium salt, the acid comes down in clusters of fine, prismatic plates or needles. It is somewhat less soluble in water and dilute acids than the 6-aminosulfonic acid. It is quite readily soluble in fairly concentrated sulfuric acid. When heated above 230° it begins to char and does not melt even when heated as high as 300°.

Calc.: S, 15.91%; found: S, 15.62%, 15.74%.

The Barium Salt of 6-Amino-1,4-dimethylbenzene-2-sulfonic Acid, $[C_6H_2(CH_3)_2NH_2SO_3]_2Ba.7H_2O$.—This salt comes down in plates which resemble closely in appearance the barium salt of the 5-amino sulfonic acid. They are, however, slightly more soluble. It contains seven molecules of water of crystallization which it loses when heated to 108°.

Calc.: H_2O, 19%; Ba, 20.7%; found: H_2O, 19.28%, 19.18%; Ba, 20.52%, 20.61%.

3. Summary.

1. Nitric acid acts upon the sulfonic acid of *p*-xylene to produce three nitrosulfonic acids. The 6-nitro- and the 3-nitro-1,4-dimethylbenzene-2-sulfonic acid are produced in fairly good yields and in about equal amounts while the 5-nitro-1,4-dimethylbenzene-2-sulfonic acid is produced in very small amounts. It has been shown by Nolting and Geissmann,[1] Lellman,[2] and others that concentrated nitric acid when warmed with *p*-xylene produces, in the main, the 2,6- and the 2,3-dinitro-*p*-xylenes with a very small amount of 2,5-dinitro-*p*-xylene. It would seem, therefore, that the entering nitro group tends to take the meta or ortho position to the sulfonic acid group just as the second nitro group tends to take the meta or ortho position to the first nitro group.

2. The nitrosulfonic acids of *p*-xylene, produced by the nitration of *p*-xylene-sulfonic acid, are best separated by converting them into the sulfonchlorides and crystallizing the latter from a mixture of ether and petroleum ether.[3]

---

[1] *Ber.*, **19**, 144 (1886).

[2] *Ann.*, **228**, 250 (1885).

[3] One separation was made by fractional crystallization of the barium salts. This method gave a somewhat larger yield of the 6-nitro-1,4-dimethylbenzene-2-sulfonic acid than was obtained by the separation of the sulfonchlorides.

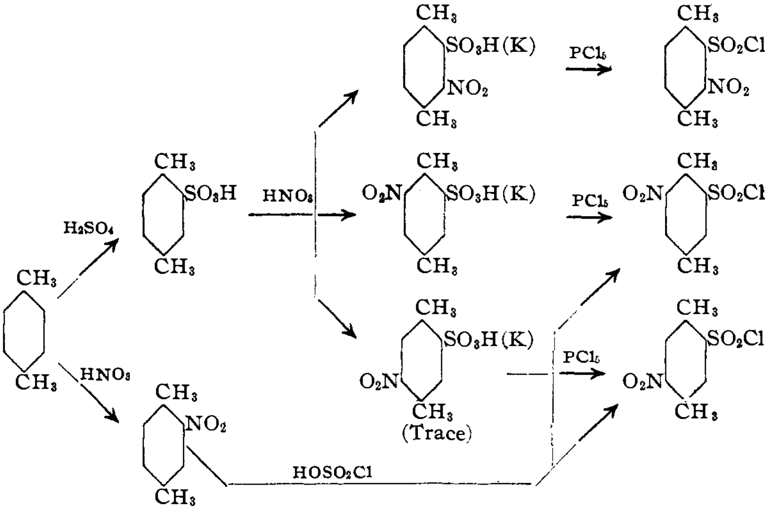
3. Attempts to nitrate the sulfonchloride of *p*-xylene by means of various reagents met with only limited success. In all trials, but one, only one sulfonchloride, and that in small quantities, was produced, *i. e.*, 3-nitro-1,4-dimethylbenzene-2-sulfonchloride. In one case a very small yield of 6-nitro-1-4-dimethylbenzene-2-sulfonchloride was isolated. A rather large excess of nitrosulfuric acid gave the largest yield.

4. Nitro-*p*-xylene is not easily sulfonated. Attempts to sulfonate this compound with sulfuric acid, either at room temperature or on the water bath were not successful.

5. Chlorosulfonic acid acts upon nitro-*p*-xylene at the temperature of boiling water to produce, in about equal amounts, two nitrosulfonchlorides, *i. e.*, 6-nitro- and 5-nitro-1,4-dimethylbenzene-2-sulfonchloride. A considerable amount of tarry matter is also formed. Of these two sulfonchlorides, the last named is the less soluble and may be separated from the other by fractional crystallization from ether and petroleum ether.

6. The configuration of the acids under consideration was determined by reducing them to the corresponding aminosulfonic acids and comparing the properties of these with the properties of the aminosulfonic acids described by Nolting and Kohn.[1] Attempts to reduce 3-nitro-1,4-dimethylbenzene-2-sulfonic acid to the amino acid with hydrogen sulfide in alcoholic solution were not successful. When stannous chloride and hydrochloric acid were used the amino acid formed was at once hydrolyzed.

7. The production of the sulfonchlorides of the three nitrosulfonic acids of *p*-xylene may be briefly represented by the following scheme:



Iowa City, Ia.

---

[1] *Ber.*, **19**, 141 (1886).