TABLE II.

	Per cent. hydrolyzed by			
Time (hours).	Water.	1 per cent. KCl.	10 per cent. KCl.	20 per cent. KCl.
2.0	3.0	3.0	5.0	1.0
4.0	11.0	13.0	..	5.0
4.5	..	..	34.0	..
6.0	15.0	31.0	42.0	9.0
8.0	37.0	50.0	51.0	39.0
10.0	48.0	55.0	73.0	49.5
12.0	58.0	75.0	89.0	56.0
14.0	..	80.0	89.0	70.0
16.0	..	84.0	92.0	77.0
18.0	78.0	90.0	92.5	80.
20.0	86.0	..	93.0	94.0
22.0	..	..	96.0	..
24.0	89.0	92.5	..	95.0

rate of hydrolysis, even when no acid is present. They seem to warrant a more careful and extensive investigation of the subject, which is now in progress. I hope in the near future to be able to report on the relation between the rate of hydrolysis of ethyl acetate and (1) the concentration of the salt, (2) the nature of the salt, (3) the concentration of the ester itself, and (4) the temperature.

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SOME OXIDATION PRODUCTS OF 6-NITRO-1,3-DIMETHYLBENZENE-4-SULPHONIC ACID.

BY W. J. KARSLAKE AND P. A. BOND.

Received December 22, 1908.

According to Harmsen,[1] and Limpricht and Van Riesen,[2] 6-nitro-1,3-dimethylbenzene-4-sulphonic acid may be obtained either by the nitration of 1,3-dimethylbenzene-4-sulphonic acid or by the sulphonation of 4-nitro-1,3-dimethylbenzene. Claus and Schmidt[3] have also shown that while the nitration of 1,3-dimethylbenzene-4-sulphonic acid yields the 6-nitro-1,3-dimethylbenzene-4-sulphonic acid as the principal product, yet the 2-nitro and the 5-nitro acids are formed at the same time, the relative quantities of each depending upon the conditions under which nitration takes place. In the preparation of the 6-nitro acid we essentially followed the directions of Claus and Schmidt except that ordinary commercial concentrated nitric acid was used instead of fuming nitric acid. The method used was as follows: Commercial metaxylene was shaken with an equal volume of commercial concentrated sulphuric acid

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[1] *Ber.*, **13**, 1558.

[2] *Ibid.*, **18**, 2191.

[3] *Ibid.*, **19**, 1418.

until the heating action which took place had ceased and the mixture had cooled to room temperature. From sixty to seventy per cent. of the xylene went into solution and was drawn off from the undissolved hydrocarbon portion. The portion which had dissolved was nitrated by slowly adding two and one-half volumes of it to three volumes of ordinary concentrated nitric acid, sp. gr., 1.40, with constant stirring. The temperature was not allowed to rise above 16°. After standing two days the 6-nitro-1,3-dimethylbenzene-4-sulphonic acid which had separated out was filtered off by the aid of a suction pump. It was not washed, owing to its easy solubility in water. The total weight of the crude acid obtained in this way was about equal to the weight of the xylene dissolved by the sulphuric acid during sulphonation. To convert it into the potassium salt it was dissolved in hot water, neutralized with an excess of calcium carbonate, and filtered. The hot solution of the calcium salt so obtained was treated with an excess of a saturated solution of potassium carbonate and the precipitated calcium carbonate filtered off. The filtrate upon cooling deposited the potassium salt in long, narrow, thin plates or prisms of a slightly yellow color. It was filtered off and air-dried. It was identified through its acid chloride, which was found to melt at 98°, and its acid amide, which was found to melt at 187°.[1]

Oxidation of the Potassium Salt of 6-Nitro-1,3-Dimethylbenzene-4-Sulphonic Acid.—To 800 grams of the potassium salt dissolved in 36 liters of water were added 1200 grams potassium permanganate and 80 grams potassium hydroxide previously dissolved in 50 liters of water. The mixed solutions were placed in carboys and allowed to stand at room temperature for one month. At the end of that time a large amount of manganese dioxide had deposited, though the solution was still highly colored with permanganate. It was then heated to almost boiling temperature until complete decolorization had taken place, which required 15–20 hours. The manganese dioxide was filtered off by the aid of a press and the filtrate evaporated to crystallization. Several successive crops of crystals were obtained which, after many repeated crystallizations and fractionations, were finally obtained in three distinct sets. There first appeared a good yield of small, white glistening plates having a pearly or silky lustre. The filtrate from these upon evaporation gave, upon cooling, yellow plates or prisms mixed with a few of the white glistening plates first obtained. The remaining salts in the mother liquor were so soluble that it was difficult to get them to crystallize well. Upon acidifying with concentrated hydrochloric acid, however, a copious precipitate was obtained which was filtered off and recrystallized. In this way there was finally obtained 177 g. of the first salt, 60 g. of the second, and 120 g. of the third.

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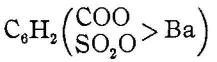
[1] Claus and Schmidt, *Loc. cit.*

4-Nitro-5-methyl-2-sulphobenzoic Acid: Neutral Potassium Salt, $C_6H_2(CO_2K)(SO_2OK)(NO_2)(CH_3)$.—This salt was the one which separated first from the solution of the oxidized mixture. It crystallized in small glistening plates possessing a pearly or silky lustre. In other preparations of this salt by one of us (K) it was also found to separate sometimes in small while nodules of radiating needles. These needles upon recrystallization usually separated as plates but in some cases the nodules themselves again reappeared. The analysis gave: N, 4.02; K, 20.96, 20.96, 20.94; calculated, N, 4.15; K, 23.21. The salt lost no appreciable weight upon heating to 210° for seven hours and hence is regarded as containing no water of crystallization. Limpricht[1] states that he obtained a small yield of a neutral potassium salt containing one-half a molecule of water of crystallization upon oxidizing 6-nitro-*m*-xylenesulphonic acid with potassium permanganate. He gives no analytical data, however, nor does he attempt to show which one of the two methyl groups was oxidized to a carboxyl group. The analyses of this salt disclose a decided tendency for the percentages of potassium to run below the theoretical values. The reason for this is not known, yet there can be no doubt that the salt is the one described.

Neutral Barium Salt,  $C_6H_2\left(\begin{matrix}COO\\SO_2O\end{matrix}>Ba\right)(NO_2)(CH_3)$.—This salt was prepared by adding a solution of barium chloride to a solution of the neutral potassium salt. It precipitates as a fine white crystalline powder, quite insoluble in water, but soluble in acids. From moderately dilute solutions the precipitation does not take place at once but slowly appears upon standing. Found: Ba, 33.78 and 33.83; Calculated, 34.60. The salt lost no weight upon heating to 210° for several hours.

Acid Barium Salt, $[C_6H_2(CH_3)(NO_2)(CO_2H)SO_2O]_2Ba + 2H_2O$.—This salt was made by precipitating the neutral barium salt from a hot solution of the neutral potassium salt and then adding just enough hydrochloric acid to dissolve it. Upon cooling, the acid barium salt separated in needles of a light yellow color, containing two molecules of water of crystallization. It crystallizes well from aqueous solutions made slightly acid with hydrochloric acid but when treated with water alone it gives an insoluble salt, probably the neutral barium salt. Found: Ba, 19.73, 19.67; $2H_2O$, 5.11, 5.21. Calculated: Ba: 19.76; $2H_2O$, 5.19.

Neutral Silver Salt, $C_6H_2(CO_2Ag)(SO_2OAg)(NO_2)(CH_3)$.—This salt was prepared by adding a hot solution of silver nitrate to a hot, concentrated solution of the neutral potassium salt. Upon cooling, needles separated out which were recrystallized from water. It contains no water of crystallization. Found: Ag, 45.53, 45.45. Calculated: Ag, 45.47. The *free acid* was obtained by adding just sufficient dilute hydrochloric acid

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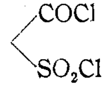
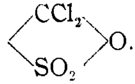
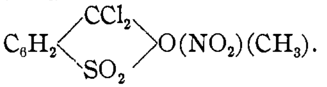
[1] *Loc. cit.*

to precipitate the silver from a dilute solution of the silver salt, filtering and evaporating the filtrate to crystallization. It crystallizes in colorless transparent needles.

Acid Chlorides.—To the neutral potassium salt placed in a flask connected with a reflux condenser was added a little phosphorus oxychloride together with slightly more than the calculated amount of phosphorus pentachloride. After heating to boiling for about half an hour the excess of phosphorus oxychloride was distilled off and the cooled residue in the flask treated with a large quantity of ice-cold water and thoroughly washed. The crude acid chloride so obtained was an oily, pasty mass which would only partially solidify even after a considerable time. There was always a considerable amount of an oily acid chloride present in the crude product. Upon crystallizing a portion of the crude product from benzene, plates were obtained which, upon recrystallization, melted at 133° (corr.). If crystallized from carbon tetrachloride small octahedral (?) crystals are obtained having the same melting point. From the mother liquors of the benzene and carbon tetrachloride solutions an oil separated which was difficult to crystallize. Finally, from ligroin solutions, crystals were obtained which melted at 59–60°. In the crystallization of another and different preparation of the crude acid chloride, howevèr, the oily residue gave crystals which melted sharply at 93°. That there are two distinct acid chlorides formed is certain, and that one of them melts at 133° is also certain, but the exact melting point of the second is perhaps somewhat doubtful and needs further confirmation. The work of Remsen,[1] List and Stein,[2] Blanchard,[3] Cobb,[4] and others has shown that orthosulphobenzoic acid, as well as some of its substitution products, yields *two* acid chlorides. Remsen calls that chloride having the higher melting point the *symmetrical* chloride since he thinks it contains the group  $<\begin{smallmatrix}COCl\\ SO_2Cl\end{smallmatrix}$ and the one having the lower melting point the *unsymmetrical* chloride because it contains the group  $<\begin{smallmatrix}CCl_2\\ SO_2\end{smallmatrix}>O$. Following the nomenclature of Remsen the acid chloride which melts at 133° is the *symmetrical* chloride, $C_6H_2(COCl)(SO_2Cl)(NO_2)(CH_3)$, while the one which melts at 93° is the *unsymmetrical* chloride,  $C_6H_2<\begin{smallmatrix}CCl_2\\ SO_2\end{smallmatrix}>O(NO_2)(CH_3)$. If this is so, then the acid chloride which melted at 59–60° is probably a mixture of the two.

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[1] *Am. Chem. Jour.*, **30**, 247.

[2] *Ber.*, **31**, 1648.

[3] *Am. Chem. Jour.*, **30**, 485.

[4] *Ibid.*, **35**, 486.

Upon treating the acid chloride which melted at 133° with concentrated ammonia in the cold and then after some time expelling the excess of ammonia by boiling, needles were obtained which melted at 302°. These were probably the ammonium salt of the corresponding sulphinide. On the other hand the acid chloride melting at 59–60° upon like treatment with ammonia gave a mixture of substances as might be expected if composed of a mixture of both the symmetrical and unsymmetrical chlorides. The substances obtained probably consisted of the ammonium salt of 4-nitro-5-methylbenzoic sulphinide and ammonium 2-cyan-4-methyl-5-nitrobenzenesulphonate.[1]

6-Nitro-3-methyl-4-sulphobenzoic Acid: Acid Potassium Salt, $C_6H_2(CH_3)(NO_2)(CO_2H)SO_2OK+H_2O$.—The second salt to separate in any amount from the solution of the original oxidized mixture was the neutral potassium salt of this acid. It separated in yellow prismatic plates. It was converted into the acid potassium salt by dissolving in water, adding hydrochloric acid in considerable excess, filtering off the precipitate formed and recrystallizing it from water. The acid salt separates in beautiful prisms of a light yellow color containing one molecule of water of crystallization. Found: K, 11.45, 11.98; H_2O, 5.58, 5.61; H (acid), 0.315, 0.327. Calculated: K, 12.33; H_2O, 5.67; H, 0.316.

The *silver* salt was made but not analyzed. It separated in needles. The *free* acid was made from the silver salt and it separated in prismatic plates.

Acid Chloride.—This was prepared by the action of phosphorus pentachloride, in the presence of a little phosphorus oxychloride, upon the acid potassium salt. After washing with cold water the crude chloride soon solidified. It was dissolved in carbon tetrachloride, decolorized with a little bone-black, filtered, and allowed to evaporate to crystallization. After one recrystallization it melted sharply at 90° (corr.). No signs whatever were found of a second chloride, the mother liquors in every case giving only additional amounts of the impure chloride. Upon treating the acid chloride with concentrated ammonia only one product was obtained. This melted at 274° and was probably the diamide, $C_6H_2(CONH_2)(CH_3)(SO_2NH_2)(NO_2)$.

6-Nitro-4-sulphoisophthalic Acid: Diacid Potassium Salt, $C_6H_2(COOH)_2(SO_2OK)(NO_2) + 2H_2O$.—This salt was the chief product obtained upon acidifying the final mother liquors of the original oxidized mixture. From aqueous solutions it separates in transparent prisms containing two molecules of water of crystallization. Found: K, 10.73, 10.79; H_2O, 10.06, 10.01; H (acid), 0.538, 0.536. Calculated: K, 10.72; H_2O, 9.86; H, 0.548. The acid hydrogen, or acidity, was determined by titration with standard caustic potash solution, using phenolphthalein as indicator.

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[1] Remsen, *Loc. cit.* List and Stein, *Loc. cit.* Blanchard, *Loc. cit.*

Acid Chlorides.—The diacid potassium salt was treated with phosphorus pentachloride, in the presence of a little phosphorus oxychloride, etc. The crude acid chloride obtained was an oily paste which would not solidify. It was dissolved in carbon tetrachloride, treated with a little dry calcium chloride in order to dry it more completely, decolorized with a little bone-black, filtered, and the filtrate allowed to evaporate slowly. Needles were obtained which upon recrystallization melted at 147°. The mother liquor gave an oily residue which could not be crystallized from ligroin, in which it was not very soluble, even when the solution was cooled to —20° for several hours. Distillation in a vacuum on a small scale was tried but not with much success. The acid chloride which melted at 147° was treated with strong ammonia and long thread-like needles were obtained which melted at 277°. The oily acid chloride with ammonia also gave needles but they were coarser in structure. It is quite possible that one of these compounds was the ammonium salt of 4-nitro-5-carbamylbenzoic sulphinide and the other the ammonium salt of 2-cyan-4-carbamyl-5-nitrobenzenesulphonic acid. Investigation is in process to clear up this and other obscure points brought out in this work.

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ON THE PREPARATION AND PHYSICAL PROPERTIES OF TETRACHLORETHER.

BY FRED NEHER AND WILLIAM FOSTER.

Received January 11, 1909.

1. *The Preparation of Tetrachlorether.*—The following methods for the preparation of 1,2,2,2-tetrachlorether, $CCl_3CHCl.OC_2H_5$, have been reported: 1. From monochlorether and chlorine in the presence of iodine[1] 2. From dichlorvinylethylether and chlorine.[2] 3. By treating chloral alcoholate with phosphorus pentachloride.[3] As is evident, the last named reaction is the one most suitable for the laboratory preparation of pure tetrachlorether. Chloral alcoholate is easily obtainable in any desired quantity and theoretically the only by-products of the reaction are the readily removable phosphorus oxychloride and hydrogen chloride. After the action of the phosphorus pentachloride on the alcoholate was complete, Henry treated the product with water to decompose phosphorus oxychloride, separated the heavy, oily tetrachlorether, washed it with a solution of sodium carbonate, dried over calcium chloride, and distilled. Almost the entire product distilled at 185°–190° and the boiling point was found to be 188° (uncor.).[4] In a later article[5] the limits of the main fraction

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[1] Wurtz and Vogt, *Z. Chem.*, 1871, 679.

[2] Godefroy, *Jsb. Chem.*, 1886, 1174.

[3] Henry, *Ber.*, 4, 101, 435. Paternò and Pisati, *Jsb. Chem.*, 1872, 303.

[4] *Ber.*, 4, 101.

[5] *Ibid.*, 4, 436.