After adding 60 cc. of 37% formalin the mixture was heated for four hours at 100°. Another 70 cc. of 98% formic acid and 50 cc. of 37% formalin were added and heating was continued for six hours. The reaction mixture was acidified with 60 cc. of concentrated hydrochloric acid and evaporated to dryness *in vacuo*. The residue was purified by several recrystallizations from isopropyl alcohol and gave 50–52 g. (90–95%) of II dihydrochloride, m.p. 239–240°.

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Steric Factors in the Hydrolysis of Potassium Dinitrochlorobenzenesulfonates

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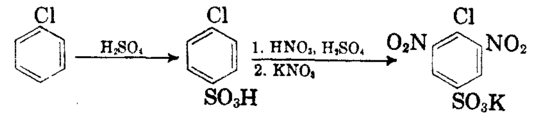
The sulfonate group in potassium 2-chloro-3,5-dinitrobenzenesulfonate, in contrast to its isomer potassium 4-chloro-3,5-dinitrobenzenesulfonate, hydrolyzes readily under nonequilibrium conditions. This was deduced from an examination of the mixture of these isomers obtained by the monosulfonation of chlorobenzene followed by subsequent dinitration. It is suggested that steric factors play an important role in the differential reactivity of these compounds.

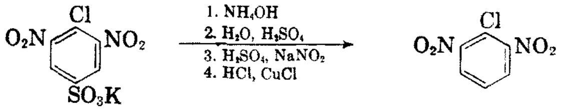
DISCUSSION

An attempt to prepare 2,6-dinitrochlorobenzene (IV) directly from potassium 4-chloro-3,5-dinitrobenzenesulfonate (III)[1] showed that the 4-chloro compound III contained significant amounts of the isomer, potassium 2-chloro-3,5-dinitrobenzenesulfonate (V). Upon refluxing with aqueous sulfuric acid, V but not III could be hydrolyzed under nonequilibrium conditions. However, refluxing under equilibrium conditions resulted in no detectable quantity of either dinitrochlorobenzene isomer.

In the recommended procedure[1,2] for the preparation of potassium 4-chloro-3,5-dinitrobenzenesulfonate (III), the first step involves the sulfonation of chlorobenzene, followed by dinitration and isolation of the potassium salt (III). 2,6-Dinitrochlorobenzene (IV) may be prepared[1,2] from III by the circuitous route involving conversion of the chlorine atom to an amino group, then hydrolysis of the sulfonate function followed by diazotization of the amino group and replacement with a chlorine atom.



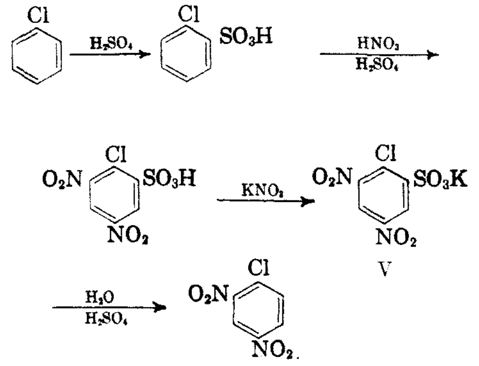
II III



III IV

Since hydrolysis of the sulfonate group in III would lead directly to the desired product, IV, this approach was undertaken. No information is reported on this hydrolysis in the literature.

From the refluxing aqueous sulfuric acid solution of potassium dinitrochlorobenzenesulfonates (I) was steam-distilled a light yellow water-insoluble solid, under nonequilibrium conditions, which was identified as 2,4-dinitrochlorobenzene. Most of the starting material (69.3%) could be accounted for by the recovery of pure III. These results indicate the sulfonation of chlorobenzene resulted in the formation of 2-chlorobenzenesulfonic acid as well as the 4-chlorobenzenesulfonic acid. The reactions converting 4-chlorobenzenesulfonic acid to III, which failed to hydrolyze, have been described above. The 2-chlorobenzenesulfonic acid that formed underwent a similar series of reactions. The latter was nitrated to 2-chloro-3,5-dinitrobenzenesulfonic acid which was isolated as a potassium salt (V). Compound V upon hydrolysis formed 2,4-dinitrochlorobenzene (VI).



V

VI

The attempt to hydrolyze the same material (I) by simple refluxing with aqueous sulfuric acid failed. This indicated that the equilibrium is far on the side of the sulfonic acid and unfavorable for the hydrolysis of 2-chloro-3,5-dinitrobenzenesulfonate (V). However, under nonequilibrium conditions where the product is removed by steam-distillation as soon as it is formed, complete hydrolysis of V is accomplished. Although the equilibrium is not very favorable it must be established rather readily since the hydrolysis was complete in two hours.

No 2,6-dinitrochlorobenzene (IV) steam-distilled during the 26 hours the aqueous sulfuric acid solution was refluxed, nor could any be isolated from

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(1) H. P. Schultz, *Org. Syntheses*, **31**, 45 (1951).

(2) F. D. Gunstone and S. H. Tucker, *Org. Syntheses*, **32**, 23 (1952).

the benzene used to extract the reaction mixture. The failure of compound III to hydrolyze to IV under equilibrium or nonequilibrium conditions must be due to the fact that either the hydrolysis product (IV) is not steam-distillable or the equilibrium in this hydrolysis is both very slow and the position of the equilibrium is very unfavorable in forming IV.

Recrystallization of I from water gave a single pure component which had an x-ray powder diffraction pattern identical with that of unreacted III recovered from the hydrolysis. This indicates that the two samples having the same x-ray powder diffraction patterns are pure III. The latter can be obtained by the hydrolysis or recrystallization of I. This information can be utilized to make a complete separation of a mixture of isomers III and V by exhaustively hydrolyzing isomer V and steam distilling the product, VI.

It appears that electronic considerations cannot be important in explaining the observed behavior. The nitro groups in molecules III and V should exert the same electronic (inductive and resonance) effects on the respective carbon atoms bearing sulfonate substituents. This is true because these groups are in the 3,5-positions in both molecules. The resonance contribution of the chlorine in both molecules might be expected to be the same because of the well-known equivalent $+T$ effect in the *ortho* and *para* positions. However, the chlorine atom in V, because of its proximity, exerts a more pronounced $-I$ effect on the position to which the sulfonate group is attached than does the chlorine atom in III. Experimental evidence[3] indicates that electron-attracting substituents in an aromatic sulfonate retard the hydrolysis of the sulfonate group. Hence, it would be expected that the sulfonate group in III would be hydrolyzed more readily than in V. However, III was recovered unchanged and V was completely hydrolyzed.

The Stuart-Briegleb atomic models show that there is free rotation around the C—S bond of III and restricted rotation around the C—S bond in V. This steric interaction must have weakened the C—S bond in the latter and facilitated the hydrolysis of the sulfonate group. This effect becomes more significant when we realize that the ease of hydrolysis of the sulfonate group in these two isomers is the reverse of what would have been expected from a consideration of inductive effects alone.

EXPERIMENTAL[4]

Potassium dinitrochlorobenzenesulfonates. This mixture was obtained by the procedure in *Organic Syntheses.*[1,2] The unrecrystallized material was isolated after pouring the sulfonation reaction mixture on ice. The mixture of dinitrochlorobenzenesulfonic acids, isolated by filtration after most of the ice had melted, was slowly added to 1.5 l. of water containing 105 g. of anhydrous potassium carbonate. The filtered and air-dried (48 hours) solid (I) weighted 160 g. and was water-soluble.

Equilibrium hydrolysis of potassium dinitrochlorobenzenesulfonates. A solution of 20 g. of I in 525 g. of 75% aqueous sulfuric acid was refluxed for 22 hours at 144°. The refluxed solution after cooling, was continuously extracted with benzene for 24 hours. No detectable solid was isolated from the evaporated benzene extract. When the same procedure was repeated with 85% sulfuric acid, the solution turned black after refluxing at 165° for 23 hours. The black reaction mixture was extracted in the same manner. Evaporation of the benzene extract to dryness left only traces of solid insufficient for characterization.

Nonequilibrium hydrolysis of potassium dinitrochlorobenzenesulfonates. To a flask fitted with a 25-ml. Dean and Stark distilling receiver filled with water was added 20 g. of I, 81 g. of water, 240 g. of concentrated sulfuric acid (*sp. gr.* 1.84), and some carborundum boiling chips. During the first 2 hours there steam-distilled from the refluxing solution a yellow solid. No more water-insoluble material collected after an additional 24 hours of refluxing. The yellow solid was filtered and washed with 5 × 20-ml. portions of water on a sintered glass funnel. The last wash was still yellow but neutral to litmus paper. The yield of dinitrochlorobenzene was 1.6 g. (12.7%),[5] m.p. 46.5–47.5°. This material was recrystallized by dissolving in 15 ml. of benzene, with heat, and adding 5 ml. of isopropyl alcohol to the filtered, cooled, and concentrated (to 8 ml.) benzene solution. The crystallized solid was filtered at 0–5° and washed with 5 × 2-ml. portions of low-boiling petroleum ether cooled to 0°. The light yellow solid gave a negative ferric chloride test for phenol, a positive Beilstein test for halogen, and a positive soda lime test for nitrogen. After 18 hours at 25° and 1 mm. over phosphorus pentoxide in an Abderhalden drier, the yellow solid weighed 1.2 g. This was, evidently, the 2,4-isomer since it had an undepressed melting point and an infrared absorption spectrum identical with that of an authentic sample of 2,4-dinitrochlorobenzene.

Anal. Calc'd for $C_6H_3ClN_2O_4$: C, 35.57; H, 1.49; N, 13.83. Found: C, 35.84; H, 1.53; N, 14.02.

The combined aqueous solution of mother liquor and washes was continuously extracted with benzene for 72 hours. No residue was obtained after the benzene was evaporated to dryness. During the extraction a solid formed in the extraction chamber. After filtration and drying it weighed 12.1 g. (69.3%).[5] This material had an x-ray powder diffraction pattern different from I but the same as the product obtained from the recrystallization of I from hot water.

Infrared absorption data. Spectra were obtained on a Perkin-Elmer Model 21 double beam infrared spectrophotometer. Solutions (30 mg. of sample in 1 ml. of $CHCl_3$) in 0.1-mm. cells were examined between 2–15 microns using a sodium chloride prism.

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[3] C. M. Suter, *The Organic Chemistry of Sulfur*, John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 387–393.

[4] All melting points are uncorrected. Analyses were performed by Oakwold Laboratories, Alexandria, Virginia.

[5] These yields are calculated on the assumption that I contains no inorganic salts.