formed by the action of the oxygen on the triphenylmethyl, was collected on a filter and washed with a small amount of benzene: 2.38 g. of dry product was obtained, melting point, 183°. One recrystallization from carbon disulfide gave a product melting at 185°. The recorded melting point of pure triphenylmethyl peroxide is 185–186°; yield of peroxide, 78%. The filtrate was analyzed for any isocyanates that might be present. Dry ammonia gas was passed through the solution and in a few minutes a white precipitate of the urea was obtained. This was collected on a filter, after 25 cc. of ligroin had been added to decrease its solubility in the benzene solution; 1.00 g. of dry product was obtained, melting point 146°. One recrystallization from alcohol and water gave a solid melting at 149°; yield assuming but the one isocyanate to have been formed, 97%.

The filtrate from the urea was concentrated and some oily products were obtained. Attempts to isolate any compounds of known constitution that might be expected to be formed failed. In all probability these oily products are produced by the decomposition of the triphenylmethyl peroxide. As has been already stated in the literature, although the absorption of oxygen by triphenylmethyl is nearly quantitative, the amount of triphenylmethyl peroxide obtained from a known weight of triphenylmethyl is not quantitative; other substances of unknown constitution are produced.

Summary

The Beckmann rearrangement of an acylazide in the presence of a free radical has been studied, and the products of the rearrangement have been determined. Benzylmethylacetazide was allowed to rearrange in the absence of air in a benzene solution of triphenylmethyl. Evidence is submitted in this paper to show that only one isocyanate, benzylmethylisocyanate, is formed. A discussion of this fact with reference to certain theories on the Beckmann rearrangement is given.

ANNAPOLIS, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE PENNSYLVANIA STATE COLLEGE]

A CLEAVAGE OF AZO DYES BY MEANS OF SULFITES*

BY KARL H. ENGEL

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Cleavage of azo dyes through the action of sulfurous acid or of acid sulfites has frequently been observed heretofore but, apparently, has not been investigated in detail. A few experiments of the writer, the interaction of 4-hydroxyazobenzene and sodium bisulfite, for example, indicated that a cleavage of the dye was apt to be complicated by various secondary changes, the rearrangement of primary reaction products sometimes, the formation of resinous by-products and a reduction of some of the azo nitrogen to ammonia. In short, such a reaction looked rather unpromising.

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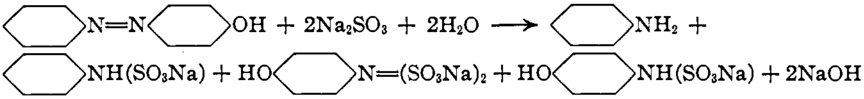
* The material here presented has been submitted as a thesis in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the Pennsylvania State College.

A number of years ago, however, the author made the observation that neutral alkali or ammonium sulfites react with azo dyes, in an exact ratio of two moles of sulfite to one mole of dye, resulting in a clear-cut fission of the dye between the two nitrogen atoms of the azo group. The reaction does not parallel the reduction by means of hydrosulfite, which, as is well known, leads to the formation of two primary amines. The sulfite cleavage, it is true, also yields a certain amount of primary amine. It differs in that the reacting sulfite tends to combine with the nitrogen atom attached to the secondary dye component, to a smaller extent with the nitrogen of the primary component. 4-Hydroxyazobenzene, for example, yields the following primary cleavage products



The formation of N-sulfonic acids points to certain similarities with the sulfite reduction of aromatic nitro and nitroso compounds. As expected, the resulting N-sulfonic acids, according to their specific nature, may either hydrolyze or rearrange, in the presence of mineral acids.

Some forty monoazo dyes were treated with ammonium, sodium or potassium sulfite, the dyes comprising hydroxy- and amino-azobenzene derivatives as well as dyes which contained hydroxy- or aminonaphthalene derivatives as secondary components. Most of these were found to react according to the scheme above. In a few cases, 2,4-dihydroxyazobenzene, for example, only two cleavage products were obtained: the original primary amine (aniline) and the N-disulfonic acid of the secondary component, of aminoresorcinol. A totally unsulfonated nitrogen of the secondary component was not observed, except in one instance: dimethylaminoazobenzene yielded a trace of dimethyldiaminobenzene.

A detailed investigation of the cleavage of 4-hydroxyazobenzene and of 4′-hydroxyazobenzene-4-sulfonic acid is the subject of the following pages.

Earlier References.—An interesting cleavage of an azo compound was observed by Schmitt and Bennewitz,[1] who found that aqueous suspensions of 2,2′-dichloro-azobenzene reacted readily with sulfurous acid or sodium bisulfite, yielding a difficultly soluble 1-amino-4-phenol-6-sulfonic acid. A. Spiegel,[2] on heating azobenzene in an alcoholic solution of ammonium bisulfite, obtained a white crystalline reaction product which corresponded to the composition $C_{12}H_{11}N_2SO_3H$. It yielded benzidine sulfate in dilute mineral acid, and was therefore taken to be a monosulfaminic acid of benzidine, $H_2NC_6H_4C_6H_4NHSO_3H$. Bucherer and Sonnenberg[3] heated azobenzene in an aqueous solution of ammonium

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[1] Schmitt and Bennewitz, *J. prakt. Chem.*, [2] **8**, 7 (1874).

[2] A. Spiegel, *Ber.*, **18**, 148 (1885).

[3] H. Th. Bucherer and Sonnenberg, *J. prakt. Chem.*, **81**, 33 (1910).

sulfite at 110° and obtained a nearly quantitative yield of the ammonium salt of an N-sulfonic acid of hydrazobenzene, which, like Spiegel's reduction product, yielded benzidine sulfate on addition of mineral acid.

The Cleavage Reaction.—The experimental procedure, briefly, consisted of heating accurately weighed samples of pure dye and measured volumes of sulfite solution in closed containers, generally at 90 to 95°, until the dye was dissolved and decolorized. Primary amines such as aniline could then be separated by extraction or distillation. The N-sulfonic acids, on account of their extreme solubility and their sensitive character, could not be isolated. They rearranged with great ease, as free acids, forming primary amines or sulfonic acids of primary aromatic amines. To supplement the information that might be gained from such secondary products, the reaction course of the inorganic reagent, the sulfite, was quantitatively traced. The cleavage of the unsulfonated dye may be considered representative.

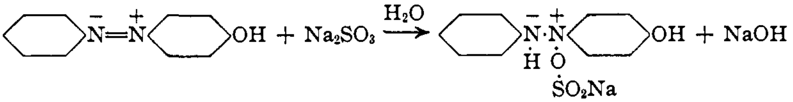
It was found that one mole of 4-hydroxyazobenzene yielded 0.78 mole of free aniline and 0.22 mole of an N-sulfonic acid of aniline, whereas the secondary dye component yielded 0.78 mole of N-disulfonic acid of 1-amino-4-phenol and 0.22 mole of N-monosulfonic acid of 1-amino-4-phenol. On addition of mineral acid to the cleavage products, the N-sulfonic acid of aniline hydrolyzed to give aniline. All of the primary dye component could therefore be recovered in its original form. The secondary dye component, upon rearrangement, yielded 0.54 mole of the insoluble 1-amino-4-phenol-5-sulfonic acid, and 0.46 mole of 1-amino-4-phenol-sulfonic ester, $H_2NC_6H_4OSO_3H$, a compound surprisingly resistant to hydrolytic action of mineral acids and so extremely soluble that it could not be isolated as such, in pure form. In all, two moles of diazotizable amines were ultimately obtained, through cleavage and rearrangements, from one mole of azo dye.

It appeared most likely that a cleavage of an azo group should proceed in two distinct steps, *i. e.*, that formation of N-sulfonic acids of hydrazo bodies should precede a final cleavage. Such intermediate stages, however, have not been observed, so far.

The most interesting feature of the reaction, from a theoretical viewpoint, appeared to be the distribution of the two sulfite molecules between two nitrogen atoms of the azo group. It was observed, in every dye examined, that the two sulfite molecules showed a pronounced tendency to combine with the nitrogen atom attached to the secondary dye component. The nitrogen of the primary component tended to combine with hydrogen. A conclusion that the two nitrogen atoms were marked by rather definitely fixed functional differences suggested itself. Plainly the nitrogen of the secondary component must have functioned very much like the nitrogen of a nitro or nitroso group toward the sulfite, as a positive atom; the nitrogen of the primary dye component, presumably, as a negative atom.[4]

Observation of a number of N-sulfonic acids showed differences, frequently very pronounced, in the character of N-mono- and N-disulfonic acid derivatives of the same amine, particularly in regard to orientation of sulfonic acid groups during rearrangement. Observations of this kind suggested that deeper-lying constitutional differences existed between the N-mono- and N-disulfonic acids in question and it was concluded that only the former were amine derivatives, or "sulfaminic" acids, of a type formula $RNHSO_3Na$; that the N-disulfonic acids, on the other hand, were derivatives of a positive nitrogen, presumably conforming to the type $RN(OSO_2Na)_2$. These various considerations led to the following view regarding the mechanism of the cleavage reaction.

It appeared most likely that an addition product of sulfite molecule and azo group should first be formed, the negative nitrogen joining a sodium atom (or its equivalent hydrogen), the positive nitrogen joining an oxygen of the sulfite molecule and that a reshifting of valency forces should result in a hydrazo derivative



If such a compound suffered no further intramolecular rearrangement, the second sulfite molecule might add and combine in the same manner as the first, forming the final cleavage products, aniline and the N-disulfonic acid, $HOC_6H_4N(OSO_2Na)_2$. Yield figures indicated that 78% of the dye could have reacted in this way. The remaining 22% formed N-monosulfonic acids of aniline and of aminophenol. Possibly such products might have been formed following an intramolecular shift of the hydrazo-N-sulfonic acid. The N-disulfonic acid of the experiment might be considered as a sulfurous ester of an hypothetical ortho-nitrous acid derivative, $HOC_6H_4N(OH)_2$. The N-monosulfonic acids, presumably, were true sulfaminic acids, $C_6H_5NHSO_3Na$ and $HOC_6H_4NHSO_3Na$.

The tentatively suggested explanation of the cleavage reaction will be substantiated, it is believed, by further experiments in this field. The reaction may have a practical value as a convenient tool in the synthesis of dye intermediates.

Experimental

Preparation of Materials.—The dyes required were prepared by coupling diazobenzene, or 1-diazobenzene-4-sulfonic acid, respectively, with pure phenol in solutions

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[4] It might be of interest in this connection to recount the origin of the two atoms, the negative one being derived from an aromatic amine, *i. e.*, a substituted ammonia· the positive one from nitrous acid.

containing sodium acetate and acetic acid.[5] 4-Hydroxyazobenzene was repeatedly recrystallized from ethyl alcohol. The pure dye melted at 156.5°, corr.

Anal. Calcd. for $C_{12}H_{10}ON_2$: N, 14.14. Found: N, 14.06.

The sodium salt of the sulfonated dye was recrystallized from water until free from the chlorides originally present.

Anal. Calcd. for $C_{12}H_9O_4N_2SNa$: N, 9.32; S, 10.67; Na, 7.67. Found: N, 9.29; S, 10.62; Na, 7.63.

A stock solution of ammonium sulfite, approximately 5 *N*, was prepared from pure ammonia solution and liquid sulfur dioxide. The solution was guarded against air oxidation by keeping the storage bottle filled to capacity with benzene. Slight traces of sulfate were determined and properly discounted later on.

Cleavage of 4-Hydroxyazobenzene.—19.8200 g. of dye (1/10 mole), and 320 cc. of ammonium sulfite solution, equivalent to 490.3 cc. of a normal solution of sulfurous acid and to 496.7 cc. of a normal solution of ammonia, were placed in nitrogen-filled pressure bottles (to prevent oxidation and loss of volatile substances). Experiments were made in triplicate. The bottles, tightly closed in a reclining position, were heated in a constant-temperature oven at 90 to 93°. The suspended dye, slightly soluble, gradually disappeared. After seventy-two hours, the solution assumed a pale yellowish coloration which did not change on further heating. After seventy-eight hours of continuous heating, the bottle contents were diluted to 500 cc., accurately. Portions of these solutions were used in subsequent analytical determinations.

Removal of Aniline.—Aniline formed during cleavage was quantitatively removed from solution by six extractions with 50-cc. portions of benzene. It required 78.8, 78.2 and 77.4 cc. of 1 *N* nitrite solution for diazotization, corresponding to an average yield of 0.78 mole per mole of dye. No trace of 1-amino-4-phenol could be detected in the benzene extract, nor upon complete evaporation of the original solution and extraction of the residue with organic solvents.

After removal of the aniline, a small part of the primary and all of the secondary component of the dye remained in solution. It showed a pronounced bluish fluorescence. A few drops diluted to about 10 cc. showed a beautiful sky blue coloration with ferric chloride in the presence of a little acetic acid. The coloration changed to claret after about thirty minutes.

Attempts were made to isolate the N-sulfonic acids as barium salts. Crystallization, however, did not begin until the solution had been evaporated to a very small volume. The addition of alcohol to more dilute solutions caused a precipitate that was not of uniform composition. These products, dry or in solution, were extraordinarily sensitive to air oxidation, in the absence of protecting traces of sulfite, short exposure causing immediate darkening and an overpowering odor suggestive of isocyanides.

Ammonia, determined in 25-cc. portions, corresponded to 496.4 cc. of 1 *N* solution, against 496.7 cc. present before cleavage. No ammonia, therefore, could have been generated through reduction of the azo nitrogen.

Aromatic Amines.—One hundred-cc. portions, freed from sulfite by addition of barium chloride, required, after addition of concd. hydrochloric acid, 24.2 and 24.4 cc. of 1 *N* nitrite solution for diazotization, potassium iodide–starch indicator giving sharp end-points. One tenth mole of dye, therefore, yielded amines corresponding to 121.5 cc. of 1 *N* nitrite solution, or 0.121 mole, in addition to the previously isolated 0.078 mole of aniline; one mole of dye yielded a total of 1.99 mole of diazotizable amines

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[5] The reaction was slower under these conditions but yielded cleaner products than the customary coupling in the presence of alkali.

through cleavage and upon addition of acid, cleavage of the azo group had been complete and quantitative. The diazotized solution contained diazobenzene hydrochloride (which could be separated by preferential coupling with 2-naphthol) and sulfonic acids of 1-amino-4-diazobenzene.

Sulfite Consumed.—Excess of hydrochloric acid was added to 50-cc. portions of original solution and the liberated sulfur dioxide distilled into standardized iodine solution: 9.00, 9.10 and 9.17 cc. of a normal solution being reduced, an average of 9.07 cc., corresponding to 90.7 cc. of normal sulfite solution in the original. Since 490.3 cc. was present before cleavage, the difference, 399.6 cc. of a normal solution (0.5 *M*) was consumed in reacting with one-tenth mole of dye. Quite accurately, two moles of sulfite reacted with one mole of dye.

Sulfate Formed During Cleavage.—Addition of mineral acids to the solution of cleavage products would have caused formation of sulfuric acid through hydrolysis of N-sulfonic acids. The sulfate formed during cleavage was therefore isolated from the ammoniacal solution as barium sulfate: 0.0280 g. of barium sulfate was found in 25-cc. portions of solution, which corresponded to 0.56 g. for the original solution, or to 4.8 cc. of normal sulfite solution that had been oxidized to sulfate during cleavage. Of the 399.6 cc. of sulfite solution, all but 1.2% remained in combination with cleavage products of the dye.

Distribution of Combined Sulfite between the Two Dye Components.—Conclusions could now be drawn regarding the probable composition of the reaction products; 0.78 equivalents of the primary component had been isolated, as free aniline. Two molar equivalents of sulfite (minus 1.2%), therefore, remained in combination with one full equivalent of 1-amino-4-phenol, and 0.22 equivalent of aniline. The solution contained N-mono- as well as N-disulfonic acids. Free 1-amino-4-phenol could not be detected. All of the secondary component was combined with at least one molecule of sulfite. If a single dye molecule combined with two molecules of sulfite, free aniline being formed as a result, both sulfite molecules must have attached themselves to the nitrogen atom of the secondary component. Conversely, since no free aminophenol had been formed, no N-*di*sulfonic acid of the primary component could have been formed either. Disregarding the small amount of sulfate formation, one mole of dye should have yielded, approximately, 0.22 mole of an N-sulfonic acid of aniline, 0.22 mole (or slightly more) of N-monosulfonic acid of 1-amino-4-phenol and 0.78 mole (or slightly less) of an N-disulfonic acid of 1-amino-4-phenol.

Intramolecular Rearrangement and Hydrolysis of the N-Sulfonic Acids.—Two 50-cc. portions, boiled with an excess of hydrochloric acid to expel sulfur dioxide (residues from determinations of excess sulfite), were combined; an insoluble precipitate formed on cooling was isolated and dried over concd. sulfuric acid; a 100-cc. portion yielded 2.055 and 2.029 g., 0.1 mole of dye gave an average of 10.21 g. of substance. It showed the same characteristics, crystal habit, solubility, etc., as the 1-amino-4-phenol-5-sulfonic acid.[6]

Anal. Calcd. for $C_6H_7O_4NS$: N, 7.40; S, 16.93; acidity, 1.0000 g. equiv. to 5.29 cc. of 1 *N* NaOH. Found: N, 7.39; S, 16.86; acidity, 1.0000 g. equiv. to 5.30 cc. of 1 *N* NaOH (phenolphthalein). The yield, 10.21 g., corresponded to 0.54 mole of 1-amino-4-phenol-5-sulfonic acid per mole of dye.

Aniline, Originating through Hydrolysis of Its N-Sulfonic Acid.—The filtrate and wash liquor of the insoluble aminophenolsulfonic acid contained aniline, originating through decomposition of its free N-sulfonic acid. Two residual filtrates from the last-mentioned determination were combined, representing thus a 200-cc. portion of the original. The solution, after neutralization with sodium hydroxide, was evaporated

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[6] Post, *Ann.*, **205**, 46 (1880).

to a smaller volume in a distilling flask. The aniline entrained was absorbed in dilute sulfuric acid and diazotized, 7.2 cc. of 1 *N* nitrite solution being required, corresponding to 18.0 cc., or to 0.018 mole of aniline per tenth mole of dye. 0.078 mole of aniline had been accounted for as a primary cleavage product; 0.096 mole, or 96%, of the primary dye component, therefore, was ultimately recovered as unchanged aniline.

Soluble 1-Amino-4-phenol-sulfonic Acid.—The distillation residue, free from traces of aniline or of aniline sulfonic acids, contained an aminophenol derivative of extraordinary solubility. By determining the amount of sulfuric acid formed through hydrolysis of N-sulfonic acids, it could be shown that the soluble product was a monosulfonated derivative of 1-amino-4-phenol. Its solution, again acidified with an excess of hydrochloric acid, required 17.8 cc. of 1 *N* nitrite solution for diazotization, corresponding to a total yield of 0.45 mole per mole of dye. The yield of this product, together with a yield of 0.54 mole of 1-amino-4-phenol-5-sulfonic acid, accounted for practically all of the secondary component of the dye. The diazonium compound of the soluble product showed similar characteristics as the 1-diazo-4-hydroxybenzene-5-sulfonic acid. It coupled with active azo components such as 1-naphthylamine, *m*-phenylenediamine, resorcinol, etc. Dyed upon untreated wool these dyes yielded shades which differed from those of corresponding azo derivatives of 1-amino-4-phenol-5-sulfonic acids by a noticeably greater tendency toward absorption in regions of longer wave lengths. Thus the dye containing 1-amino-8-hydroxynaphthalene-3,6-disulfonic ("H") acid as secondary component, gave clear bluish violet shades; the corresponding aminophenol-5-sulfonic acid derivative carmine red shades.

The dye containing 1-naphthylamine as secondary component was insoluble in the form of its free acid. It could be quantitatively isolated and was freed from impurities such as salts by thorough washing.

Anal. Calcd. for $C_{16}H_{13}O_4N_3S$: N, 12.25; S, 9.32. Found: N, 12.18; S, 9.34.

Identification of the Soluble Aminophenol Sulfonic Acid.—Since the product differed decidedly from the 1-amino-4-phenol-5-sulfonic acid, it was at first surmised that it was identical with the only other isomeric, nuclear, sulfonic acid, the 6-sulfonic acid. For comparison, the latter compound was prepared by two different methods.[7] The products thus obtained, identical with each other, were decidedly soluble in hot water but very little so at room temperature. They yielded azo dyes which were more soluble than corresponding dyes of the 5-sulfonic acid. The isomeric dyes did not differ visibly in color reactions or dyeing shades. The two sets differed perceptibly, however, from corresponding azo derivatives of the unknown substance. The possibility that the sulfonic acid group occupied the 2-, 3-, 5- or 6-position of the 1-amino-4-phenol nucleus was therefore excluded; it could exist only in combination with either the amino or the hydroxyl group. The formation of sulfonated, and distinctive azo derivatives excluded the first of these possibilities, leaving as the only remaining alternative conclusion that the product in question was a sulfonic ester of 1-amino-4-phenol, $H_2NC_6H_4OSO_3H$, a compound which apparently has not been observed previously, and which should also occur among the end-products of the sulfite reduction of nitro and nitrosophenol. The stability of this product in the presence of mineral acids seemed surprising in view of the comparative instability of the unsubstituted phenolsulfonic acid.[8] The compound hydrolyzed, apparently completely, when heated with about 5 *N* hydrochloric acid, at 90 to 93°, for eighty hours. The nuclear sulfonic acids of 1-amino-4-phenol proved perfectly stable under parallel conditions. Attempts to isolate the soluble compound as a potassium, barium or lead salt proved fruitless.

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[7] German Patents 150,982 and 160,170.

[8] Baumann, *Ber.*, 9, 1715 (1876); **11**, 1907 (1878).

Boiling of its solution with alkalies, even with lead monoxide, caused destruction or displacement of the aromatic amino group.

The conditions under which hydrolysis and rearrangement of N-sulfonic acids proceeded were so chosen as to produce stable end-products in the most rapid manner (at 100° and a few minutes of boiling). Under slightly milder conditions hydrolysis proceeded more slowly. Portions of the original solution were heated to 90° and hydrochloric acid was added. On cooling the difficultly soluble 1-amino-4-phenol-5-sulfonic acid crystallized out and was isolated. Determination of sulfuric acid in solution yielded notably smaller amounts than were found previously, indicating the presence of disulfonic acids of aminophenol. On diazotization at 0° and subsequent coupling with azo components, derivatives of the aminophenol-sulfonic ester were obtained. Presumably, then, the disulfonic acid present before diazotization still possessed a sulfonic acid group attached to the nitrogen atom. The reaction (as well as yield figures) indicated that part of the N-disulfonic acid rearranged to form 1-amino-4-phenol-5-sulfonic acid, part of it to form the aminophenol-sulfonic ester described above.

Cleavage of 4-Hydroxyazobenzene at Higher Temperatures.—Cleavage of the dye proceeded more rapidly at higher temperatures. The reagents, in the same proportions as before, were heated at 130 to 135°, in a small steel autoclave. Cleavage was complete after fifteen hours. Determination of molar ratio of reagents of primarily formed aniline gave practically the same results as were found in preceding experiments. A greater amount of sulfate, from 12 to 15% of the sulfite consumed, was formed. Since no trace of free aminophenol could be found, the formation of sulfate did not coincide with formation of greater amounts of totally unsulfonated products, but must have occurred at the expense of the N-*di*sulfonic acid yield. Hydrolysis and rearrangement, under the influence of acids, gave the same final reaction products as before. The yield of 1-amino-4-phenol-5-sulfonic acid was smaller; that of the aminophenol-sulfonic ester, however, correspondingly larger.

Sodium and Potassium Sulfite as Reagents.—Interaction between sodium or potassium sulfite and 4-hydroxyazobenzene was exceedingly slow below 100°, but went to completion in reasonable time at higher temperatures, requiring, for example, fifty hours of heating at 145 to 150°. The reaction proceeded as with ammonium sulfite. As before, higher temperatures caused an increase in sulfate formation.

Cleavage of 4-Hydroxyazobenzene-4-sulfonic Acid, Na-Salt.—30.1270 g. of dye, exactly 0.1 mole, and 320 cc. of ammonium sulfite solution, equivalent to 490.3 cc. of 1 *N* solution, were heated under the same condition as described before, at 90 to 93°. Cleavage in this case was complete after eighteen hours. The decolorized solution was made up to volume and analyzed as previously described: 401.4 cc. of 0.5 *M* ammonium sulfite was consumed; 2.007 moles of sulfite reacted with one mole of dye. Ammonium sulfate formed during cleavage was equivalent to 0.6843 g. of barium sulfate, or to 5.6 cc. of normal sulfite solution, 1.4% of the sulfite consumed. An aliquot portion was freed of sulfite, acidified and diazotized with 1 *N* nitrite solution. A total of aromatic amines corresponding to 199.7 cc. of nitrite solution was found present, or practically the theoretically possible limit.

The addition of sodium chloride to the solution of cleavage products caused precipitation of sodium sulfanilate, which was identified by its crystal form. An exact quantitative estimation of primarily formed sulfanilate could not be made. Undoubtedly by far the greater part of the primary dye component was regenerated in its original form, as a result of cleavage.

An excess of hydrochloric acid was added to a portion of the original solution at 90 to 95°. The final useful products were sulfanilic acid (quantitative regeneration of the primary dye component), 1-amino-4-phenol-5-sulfonic acid (0.54 mole per mole of dye) and the extremely soluble 1-amino-4-phenol-sulfonic ester (0.46 mole per mole of dye). The yield ratio of the latter two products was identically the same as obtained in the cleavage of the unsulfonated dye.

Cleavage of 4-Hydroxyazobenzene-4-sulfonic Acid at 140 to 145°.—The sodium salt of the dye and sodium sulfite solution of approximately 0.75 *M* concentration were heated in a steel autoclave at 140 to 145°. At the end of twenty hours cleavage was found complete. Analytical determinations yielded very nearly the same results: 3.6% of the consumed sulfite was changed to sulfate, a little more than was formed at the lower temperature.

Summary

1. A new type reaction of monoazo dyes has been observed. They combine with two moles of a neutral sulfite, in solution, suffering cleavage into a primary amine and the salts of N-sulfonic and N-disulfonic acids.

2. 4-Hydroxyazobenzene yielded approximately 0.78 mole of aniline, 0.22 mole of an N-sulfonic acid of aniline, 0.78 mole of an N-disulfonic and 0.22 mole of an N-monosulfonic acid of 1-amino-4-phenol and no trace of unsulfonated aminophenol.

3. 4′-Hydroxyazobenzene-4-sulfonic acid reacted similarly, sulfanilate being formed as a result of cleavage.

4. Hydrolysis and rearrangement of free N-sulfonic acids resulted in complete recovery of the primary dye component in its original form; the secondary component yielded 1-amino-4-phenol-5-sulfonic acid and an extremely soluble, stable 1-amino-4-phenol-sulfonic ester, a compound not previously reported.

5. An explanation of the cleavage reaction has been suggested, founded on an assumption of functional differences between the two nitrogen atoms of the azo group.

STATE COLLEGE, PENNSYLVANIA

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

STUDIES ON THE POLYMETHYLBENZENES. I. A STUDY OF THE JACOBSEN REACTION WITH PENTAMETHYLBENZENE, AND THE PREPARATION OF PREHNITENE[1]

BY LEE IRVIN SMITH AND ALBERT R. LUX

RECEIVED MARCH 2, 1929 PUBLISHED OCTOBER 5, 1929

I. Introduction and Historical

In 1887 Oscar Jacobsen[2] discovered that pentamethylbenzene when treated with concd. sulfuric acid undergoes a rather curious reaction in which a methyl group migrates from one molecule to another, leading to hexamethylbenzene and a tetramethylbenzene, prehnitene (1,2,3,4-),

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[1] Abstracted from a thesis by Albert R. Lux, presented to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the degree of Master of Science.

[2] Jacobsen, *Ber.*, 20, 896 (1887).