definite conclusions as to its nature. While the low-temperature diffuse glow appears perfectly homogeneous, there is no doubt whatever that the moving "flames" at the lower ignition point are largely surface phenomena; their distinctly ring-shaped appearance is in marked contrast to that of the true flames observed at the inflammation point.

Although light emission is observed at all temperatures from the beginning of oxidation up to the inflammation point, it is not at all certain that each one of the sequence of reactions occurring at a given temperature is luminescent. Hence, the experiments with the falling fuel drops and the vapor jet give only strong indication, and not definite proof, of the possibility of oxidation occurring without the aid of a surface as a starting point. The failure to observe any effect of various surfaces introduced into the center of the furnace may have been due to their small area.

In general, the observations over the entire temperature range of the slow oxidation of *n*-heptane are in complete accord with our knowledge of the amount, velocity and temperature coefficient of that reaction,[7] and are similar to the results of Prettre, Dumanois and Laffitte[5] for the oxidation of pentane.

Summary

The autoxidation of a theoretically equivalent (2%) mixture of *n*-heptane in air from the temperature of initial reaction (250°) to the point of inflammation (525°) emits a visible chemiluminescence, which appears as a steady, diffuse glow except at the "lower ignition point" (270–300°) where moving "cold flames" sweep along the furnace walls. By directing the fuel charge into the center of the furnace, the glow may be observed there, entirely removed from the walls.

The autoxidation of 3-heptene emits a luminescence differing from that of *n*-heptane in a manner corresponding to the relative rates of reaction of the two fuels.

DETROIT, MICH. RECEIVED JULY 6, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Hydrolysis of Substituted Benzenesulfonanilides

BY R. S. SCHREIBER AND R. L. SHRINER

Since Hinsberg first pointed out the value of benzene sulfonchloride as a reagent for distinguishing between primary, secondary and tertiary amines, many substituted aromatic sulfonyl chlorides[1] and aliphatic sulfonyl chlorides[2] have been used for this purpose. Although many of these yield solid derivatives suitable for identification all have one disadvantage in that the original amine cannot be readily recovered.

The usual hydrolysis according to the equation

$$RSO_2NHR' + H_2O \longrightarrow RSO_3H + R'NH_2$$

requires the use of strong acid and drastic conditions.[3] Since sodium benzene sulfonate is cleaved by alkalies a similar splitting of sulfonamides should be accomplished according to the equation

$$RSO_2NHR' + 3NaOH \longrightarrow RONa + R'NH_2 + Na_2SO_3 + H_2O$$

However, benzenesulfonanilide was unaffected by fusion with 80% sodium hydroxide at 250°. Hence, in order to make this reaction useful, a means of weakening the carbon–sulfur linkage is necessary. One promising way of accomplishing this would be the introduction of ortho and para nitro groups which are known to accelerate the alkaline hydrolysis of *o*- and *p*-nitrochlorobenzenes[4] and *o*- and *p*-nitranilines.[5] This prediction has been fulfilled in the present investigation.

Ortho and para nitrobenzene sulfonchlorides were prepared according to the method of Fierz, Schlittler and Waldmann.[6] The 2,4-dinitrobenzene sulfonchloride was prepared by the action of phosphorus pentachloride on 2,4-dinitrobenzene sodium sulfonate. The latter compound was obtained by the nitric acid oxidation of 2,4,2′,4′-tetranitrodiphenyl disulfide. The substituted

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(1) Witt and Uerményi, *Ber.*, **46**, 296 (1913); Marvel and Smith, THIS JOURNAL, **45**, 2696 (1923); Marvel, Kingsbury and Smith, *ibid.*, **47**, 166 (1925); Johnson and Ambler, *ibid.*, **36**, 372 (1914).

(2) Marvel, Helfrick and Belsley, *ibid.*, **51**, 1272 (1929); Marvel and Gillespie, *ibid.*, **48**, 2943 (1926).

(3) The use of concentrated sulfuric acid or chlorosulfonic acid as hydrolytic agents is prohibited in the case of sulfonamides of aromatic amines since the latter are readily sulfonated. Rearrangement may also occur. Halberkann, *Ber.*, **55**, 3074 (1922).

(4) Kenner, *J. Chem. Soc.*, **105**, 2717 (1914); Sprung, THIS JOURNAL, **52**, 1650 (1930).

(5) Merz and Ris, *Ber.*, **19**, 1749 (1886).

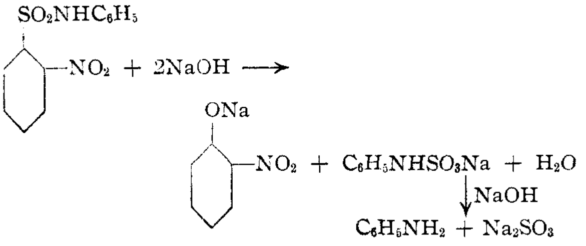
(6) Fierz, Schlittler and Waldmann, *Helv. Chim. Acta*, **12**, 667 (1929).

sulfonamides were prepared by the reaction between these nitrobenzene sulfonchlorides with aniline and methylaniline, which were chosen as typical examples of primary and secondary amines, respectively.

A study of the hydrolysis of these nitrobenzene sulfonamides was made. It was found that various concentrations of sulfuric and phosphoric acids could not hydrolyze them appreciably whereas alkalies did split the sulfonamides. Eighty per cent. sodium hydroxide was found to be the optimum concentration. In order to obtain good yields of the amine it was found that the temperature range of the decomposition must also be controlled.

An examination of the products formed by the action of the hot concentrated alkali showed that the chief products at lower temperatures were the amine, *o*-nitrophenol and sodium sulfite.

No *o*-nitro sodium benzene sulfonate could be detected. This clearly indicates that the initial reaction is probably a cleavage between carbon and sulfur, as follows



At higher temperatures the *o*-nitrophenol reacted further with the alkali and produced azobenzene, 2,2′-dihydroxyazobenzene and tarry products.

The results of the study of the alkaline cleavage of the nitrosulfonamides are summarized in Table I.

TABLE I

PERCENTAGE YIELDS OF AMINE

Compounds	Dilute alkali Strength of alkali 20%	30%	40%	80% Sodium hydroxide Maximum temp., °C.	Yield, %
2-$NO_2C_6H_4SO_2NHC_6H_5$	10	22	25	210	61
2-$NO_2C_6H_4SO_2NCH_3C_6H_5$	8	21	24	195	60
4-$NO_2C_6H_4SO_2NHC_6H_6$	5	9	12	220	38
4-$NO_2C_6H_4SO_2NCH_3C_6H_5$	3.5	7	10	210	39
2,4-$(NO_2)_2C_6H_3SO_2NHC_6H_5$	17	32	35	155	79
2,4-$(NO_2)_2C_6H_3SO_2NCH_3C_6H_5$	16	32	34	125	71
3-$NO_2C_6H_4SO_2NHC_6H_5$	..	..	5	240	14
$C_6H_5SO_2NHC_6H_5$	..	0	0	250	0

The data in Table I show that an ortho-nitro group is about twice as effective as a para-nitro group in rendering the carbon-sulfur linkage susceptible to alkaline hydrolysis. The 2,4-dinitro derivative was still more effective and hence the 2,4,6-trinitro compound should be expected to exert the greatest activating effect on this carbon-sulfur linkage. However, all attempts to prepare picryl sulfonchloride have failed up to the present. It is to be noted that the nitro group in the meta position had little or no activating effect, which behavior parallels that of *m*-nitrochlorobenzene and *m*-nitraniline toward alkalies.

If the loosening of the sulfur-carbon linkage is connected with alternating polarities induced by the nitro group the ortho-nitro group should have the greatest effect since it is only two carbons removed from the sulfonamide group. The para-nitro group, on the other hand, must transmit its effect through four carbon atoms. A meta-nitro group would of course exert just the opposite polarity effect. The data in Table I are in agreement with these theories.

Since *o*-nitrobenzene sulfonchloride is more easily prepared than the 2,4-dinitrobenzene sulfonchloride it appears to be the most practical one to use for the separation of amines by the Hinsberg method. A mixture of aniline, methylaniline and dimethylaniline was satisfactorily separated by this reagent and the amines recovered in good yields.

Experimental

2,2′-Dinitrodiphenyldisulfide.—The reaction between sodium disulfide and *o*-nitrochlorobenzene was carried out according to the directions of Elgersma[7] and 2,2′-dinitrodiphenyldisulfide obtained in 75% yields, m. p. 195°.

4,4′-Dinitrodiphenyldisulfide.—Using the same procedure as above sodium disulfide and *p*-nitrochlorobenzene gave 68% yields of the disulfide, m. p. 180°.

2,4,2′,5′-Tetranitrodiphenyldisulfide.—This disulfide was produced in practically quantitative yields by the reaction between sodium disulfide and 2,4-dinitrochlorobenzene, m. p. 280° (dec.).

2-Nitrobenzenesulfonchloride.—One hundred grams of 2,2′-dinitrodiphenyldisulfide was mixed with 600 cc. of concentrated hydrochloric acid (sp. gr. 1.19) and 100 cc. of concentrated nitric acid (sp. gr. 1.42). Chlorine was passed into the mixture rapidly for two hours after which the solution was warmed to 70°. The sulfonchloride settled out at the bottom of the flask and the supernatant liquid was decanted. The sulfonchloride was washed well with water and recrystallized from glacial acetic acid. The yield was 80% and m. p. 67–69°.

4-Nitrobenzenesulfonchloride.—This compound was obtained in 70% yields by the above procedure, using 4,4′-dinitrodiphenyldisulfide. The product melted at 77°.

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[7] Elgersma, *Rec. trav. chim.*, **48**, 752 (1929).

2,4-Dinitrobenzenesulfonchloride.—(A) The direct conversion of the 2,4,2',4'-tetranitrodiphenyldisulfide to the dinitrobenzenesulfonchloride required more vigorous oxidizing conditions. A mixture of 100 cc. of concentrated hydrochloric acid and 300 cc. of fuming nitric acid (sp. gr. 1.59) was used for each 100 g. of the sulfide. The yields varied from 10 to 50%, m. p. 100–101°. Because of the wide variation in yields this sulfonchloride was more satisfactorily prepared by the following method.

(B) One hundred grams of 2,2',4,4'-tetranitrodiphenyldisulfide was treated with 250 cc. of fuming nitric acid (sp. gr 1.50). After the first violent reaction had subsided the mixture was heated on a water-bath. The small precipitate produced by dilution with 400 cc. of water was filtered and the filtrate evaporated to 200 cc. Water was again added and the evaporation repeated to remove the excess nitric acid. Sodium carbonate was added to neutralize the sulfonic acid and the precipitated sodium salt was filtered and dried at 120° for twelve hours. The yield was 80 g. or 60% of the theoretical value.

Fifty grams of the above well-dried sodium 2,4-dinitrobenzene sulfonate was treated with 100 g. of phosphorus pentachloride and the mixture heated in an oil-bath at 160° for ten hours. The pasty mass was extracted several times with benzene and this benzene solution was evaporated to a dark oil from which the sulfonyl chloride was extracted by ether. The yield was 36 g. or 72%, m. p. 100–101°.

Preparation of Anilides and N-Methylanilides.—The following general procedure was used to prepare the anilides and N-methylanilides of the above sulfonchlorides. Approximately 25-g. samples of the sulfonchlorides were added directly to twice the calculated amounts of the amine very slowly and with vigorous stirring. The mixture was kept cool in an ice-bath to prevent decomposition due to the heat of reaction, and after stirring for fifteen minutes, about 25 cc. of dilute hydrochloric acid and an equal amount of water was added. The mixture was then filtered and the crude anilides and N-methylanilides were recrystallized from alcohol. The yields, melting points and analyses are given in Table II.

TABLE II

Compound	M. p., °C.	Yield, %	S analyses, % Calcd.	S analyses, % Found
2-$NO_2C_6H_4SO_2NHC_6H_5$	114–115	74	11.51	11.68
2-$NO_2C_6H_4SO_2NCH_3C_6H_5$	71–72	73	10.92	10.94
4-$NO_2C_6H_4SO_2NHC_6H_5$	135–136	74	11.51	11.65
4-$NO_2C_6H_4SO_2NCH_3C_6H_5$	117–118	65	10.92	11.10
2,4-$(NO_2)_2C_6H_3SO_2NHC_6H_5$	112–113	83	9.91	9.90
2,4-$(NO_2)_2C_6H_3SO_2NCH_3C_6H_5$	148–149	92	9.49	9.56
3-$NO_2C_6H_4SO_2NHC_6H_5$	122–123	81	...	...

Hydrolysis of Nitrosulfonanilides.—The above nitrosulfonanilides were subjected to various hydrolytic procedures with acids and alkalies. The optimum procedure was the following.

A 5-g. sample of each compound was placed in a copper flask which contained a large excess of an 80% mixture of sodium hydroxide with water (10 g. of water with 40 g. of sodium hydroxide). To the copper flask was then attached a condenser and a dropping funnel which was filled with water. The flask was then heated carefully until distillation was noted. At this point for each drop of distillate that came over, a drop or two of water was run in from the dropping funnel. The temperature was slowly raised to the critical temperature to continue the distillation. This temperature varied for each individual compound (see Table I). The distillation must be carried out cautiously; otherwise if the temperature is raised too swiftly or too high, some reddish-black tar will distil and it was difficult to separate the aniline or methylaniline from this. The yields and temperatures are given in Table I.

By-products of the Alkaline Hydrolysis.—After 25 g. of 2-nitrobenzenesulfonanilide had been subjected to the concentrated alkaline hydrolysis as mentioned above, the residue remaining in the copper flask was investigated. This black, tarry residue was carefully neutralized with dilute sulfuric acid and the mixture steam distilled. During the neutralization considerable sulfur dioxide was evolved. By steam distillation, a small amount of an orange colored solid was obtained (about 3 g.), and by fractional crystallization with alcohol two substances were separated. One, a low melting, reddish orange solid after recrystallization from ether melted at 66–67°. A mixed melting point with pure azobenzene produced no depression. Also the dibromide of this solid was prepared by treatment with bromine in glacial acetic acid and recrystallization from alcohol, and found to melt at 188° (lit. 187°).

The other golden yellow solid which separated from the above azobenzene during recrystallization from acetone and water mixture melted at 170°. Further investigation and mixed melting point with 2,2'-dihydroxyazobenzene proved that this compound was identical with the latter. The conditions under which the hydrolyses took place were nearly identical to those used in preparing 2,2'-dihydroxyazobenzene from 2-nitrophenol by the method of Weselsky and Benedikt.[8]

No other compound could be isolated from the residue, but since all indications, especially the formation of the above 2,2'-dihydroxyazobenzene, pointed to the formation of 2-nitrophenol as an intermediate, the hydrolysis was run at 100° instead of 200° in hopes of isolating some of this compound. The distillate contained an oil which was recrystallized from ether but due to its extremely low melting point, it was impossible to get a good melting point. However, conversion to the dibromide by treatment with bromine in glacial acetic acid and making a mixed melting point with the known dibromide of *o*-nitrophenol identified this compound as 2-nitrophenol; melting point of dibromide 117°.

Separation of Primary, Secondary and Tertiary Amines with *o*-Nitrobenzenesulfonchloride and Recovery of the Amines.—The procedure was as follows. Twenty-five grams of aniline, methylaniline, and dimethylaniline were mixed together and suspended in a 5% solution of sodium hydroxide (40 g. in 800 cc. of water). To this mixture, 125 g. of *o*-nitrobenzene sulfone chloride (10% in excess of the theoretical) was added very slowly with constant agitation and cooling in an ice-bath. The reaction was allowed to run for one hour after the sulfone chloride had been added. The mixture was then extracted three times with ether to remove the neutral *o*-nitrobenzene sulfone methyl anilide and the basic dimethylaniline. The aque-

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(8) Weselsky and Benedikt, *Ann.*, **196**, 344 (1874).

ous solution was acidified with hydrochloric acid and the *o*-nitrobenzene sulfone anilide precipitate was recrystallized twice from alcohol. The yield was 64 g. (85%). The dimethylaniline was removed from the ether layer by washing it three times with dilute hydrochloric acid, neutralizing this solution with sodium hydroxide, and extracting the free amine with ether. The ether solution was dried and distilled. The yield of dimethylaniline was 21.4 g. (85%). The ether solution containing the *o*-nitrobenzene sulfone methyl anilide was concentrated and a dark, dirty red-brown product was obtained which was then treated with alcoholic sodium hydroxide to hydrolyze any disulfone derivative that might have been formed from the aniline. This solution was then diluted with water and extracted three times with ether, the ether evaporated and the resulting red-brown solid was recrystallized three times from alcohol. The yield of the pure *o*-nitrobenzene sulfone methyl anilide was 52 g. (74%).

The two purified yields of the above *o*-nitrobenzene sulfonanilide and methyl anilide were then subjected to the concentrated alkali hydrolysis procedure as described previously (80 g. of sodium hydroxide and 20 cc. of water). The distillates of aniline and methylaniline were extracted with ether, dried and distilled. The yield of aniline was 15.3 g. and of methylaniline 13.1 g. The percentage yield of aniline for this reaction was 71% and for methylaniline, 70%. The over-all yield of aniline was 61.2% while that of methylaniline was 52.4%.

Summary

Substituted benzenesulfonanilides containing nitro groups ortho or para to the sulfone group may be decomposed by concentrated alkali to the amine, nitrophenol and sodium sulfite. This cleavage between the carbon of the ring and the sulfur atom offers a different mode of decomposition from previous hydrolyses which attempted cleavage between the sulfur and nitrogen. It was found that an ortho-nitro group is more effective than a para-nitro group and that a meta-nitro group has little effect. The 2,4-dinitrobenzenesulfonanilides were very readily cleaved by alkali.

A mixture of primary, secondary and tertiary amines may be separated satisfactorily by means of *o*-nitrobenzenesulfonchloride and the amines recovered from the sulfonamides in good yields.

URBANA, ILL.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KANSAS]

Iodo Derivatives of Diphenyl Ether. I. The Mono- and Certain Diiodo-Derivatives of Diphenyl Ether, and of 2- and 4-Carboxy Diphenyl Ethers[1]

BY R. Q. BREWSTER AND FRANKLIN STRAIN

The properties of the iodo derivatives of diphenyl ether, of which only a few have been prepared in connection with other researches, merit investigation not only from the standpoint of pure chemistry, but also from that of physiology, since Harington and Barger[2] have shown that the molecular structure of thyroxine is built upon a diphenyl ether nucleus containing four iodine atoms. Accordingly a systematic study of iodo derivatives of diphenyl ether, including those containing amino, hydroxyl and carboxyl groups, has been begun in this Laboratory. The present paper describes the three mono-iodo substitution products, five of the diiodo derivatives of diphenyl ether, and five of the iodo compounds of 2- and 4-carboxydiphenyl ethers, together with the intermediate nitro and amino compounds used in the syntheses.

Incidentally in the preparation of these substances the orienting influences of the carboxyl group and of the iodine atom, upon further substitution in the diphenyl ether nuclei, were found to conform to the general results obtained by other investigators[3] in their studies upon the orienting influences of other substituents in the diphenyl ether series.

The substances here reported, except possibly some of the iodo-carboxy compounds upon which tests are not yet complete, do not possess any marked physiological activity.

Experimental Part

The substances described here were for the most part prepared by well-known methods, any description of which is therefore omitted, and the process is recorded in the tabulated results only by letter, as follows: A, diazotization plus potassium iodide (Sandmeyer); B, same as A plus acetic acid as a solvent; C, iodination with iodine

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[1] From the thesis of Franklin Strain, presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1933.

[2] Harington and Barger, *Biochem. J.*, **21**, 169 (1927).

[3] Lea and Robinson, *J. Chem. Soc.*, **129**, 376 and 411 (1926); Scarborough and collaborators, *ibid.*, **132**, 2361 (1929); **133**, 1202 (1930); **134**, 529 (1931); Henley and Turner, *ibid.*, **133**, 928 and 1115 (1930).