vary as kNu^3, and the yields per gram of sample as ku^3. For Runs 34 and 19 the relative yields per gram at twenty-five-minute intervals from $t = 195$ to $t = 300$ min. were 300, 280, 290, 290, 260. Hence, in this 18.5° interval ku^3 increased by a factor of 290, so that k increased by a factor of $290/5 = 58$, equivalent to an activation energy E_k of 64,000 cal. for the nucleation process. The conclusion that the temperature coefficient of nucleation is much greater than that of growth of nuclei is confirmed by the qualitative experiments at 80°.

An E_k of 64,000 cal. is equivalent to an einstein of λ 445 mμ. With Oxalate I wave lengths > 520 mμ caused nucleation, but the much greater rates of decomposition of this material suggest that its E_k may have been less than 64,000.

Summary

In the decomposition of solid silver oxalate variations in rate due to long drying, preparation with excess of one or the other reagent, or fine grinding, were scarcely greater than the differences between two samples prepared and treated alike. Exposure to light, particularly to λλ < 520 mμ, greatly increased the rate of the subsequent thermal reaction. Contact with oxygen during exposure resulted in a marked initial poisoning as compared with exposure in nitrogen, carbon dioxide or vacuum. The increase in yield at any time over that for unexposed samples was roughly proportional, for the shorter exposures, to the number of quanta absorbed, but relatively much less for longer exposures. The effect of exposure was relatively less at higher decomposition temperatures. In the exposure itself λ 370 mμ produced about 0.1 molecule of carbon dioxide per quantum absorbed.

The earlier stages of decomposition have been found to be in fair agreement with a quantitative formulation of the kinetics (Eq. 3), based on simple assumptions regarding the formation of nuclei of product and their subsequent growth. In agreement with the theory, the extent of reaction at any time t, in the earlier stages, is approximately proportional to t^m, where m is found to be 3.5 for unexposed samples, but progressively less for increasing exposure.

For a particular sample of oxalate the activation energy of nucleation is about 64 kcal., while that for growth of nuclei is 8.5 kcal.

UNIVERSITY, VA. RECEIVED JUNE 3, 1935

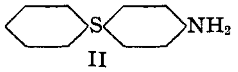
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

The Molecular Rearrangement of Sulfanilides. II

BY MAURICE L. MOORE[1] AND TREAT B. JOHNSON

In a previous paper[2] on this subject we have discussed the rearrangement of certain aromatic sulfanilide compounds of type I. We have shown

I



II

that on heating these alone or in the presence of an excess of the corresponding amine they undergo rearrangement to the corresponding aromatic para-amino sulfides II. In this paper we shall describe a second type of rearrangement characteristic of sulfanilides which is brought about by the action of alcoholic sodium hydroxide solution.

Smiles and his co-workers,[3] who have recently investigated the chemical behavior of *o*-amino sulfones and sulfides, have made the interesting observations that certain representatives of both series undergo molecular rearrangement in alkaline media to form the corresponding sulfinic acid and mercaptan derivatives of diphenylamine, respectively. The same type of rearrangement was also found to take place with the *o*-hydroxy sulfones.[4] The amino sulfide compound shows an irregularity in chemical behavior as is illustrated by the following observation. It was found that the acetyl and the 2-nitrobenzoyl derivatives of 2-nitro-2′-aminodiphenyl sulfide, for example, would undergo rearrangement to the corresponding diphenylamine structures, whereas under the same conditions the parent amine itself, the picryl and the benzenesulfonyl deriva-

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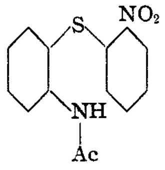
[1] A. Homer Smith Research Fellow in Organic Chemistry, 1934–1935.

[2] THIS JOURNAL, **57**, 1517 (1935); see also *Science*, **81**, 643 (1935).

[3] (a) Warren and Smiles, *J. Chem. Soc.*, 914 (1931); 2774 (1932); (b) Evans and Smiles, *ibid.*, 181 (1935); (c) Wight and Smiles, *ibid.*, 340 (1935).

[4] (a) Warren and Smiles, *ibid.*, 1040 (1932), (b) Levi and Smiles, *ibid.*, 1488 (1932); (c) Kent and Smiles, *ibid.*, 422 (1934).

tives were not altered. A theory coördinating the factors influencing this rearrangement was proposed by Smiles[3b] in which he postulated that the rearrangement of III to IV was favored in cases of substituted derivatives when the acyl groups were derived from relatively weak acids. It was later found that the formyl[3c] derivative of VI rearranged with deacylation to form the mercaptan derivative VII.



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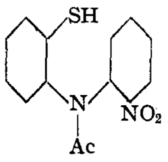

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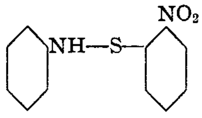
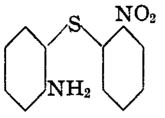
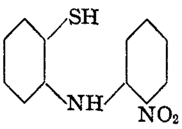


V



VI



VII

As our rearrangement of the sulfanilides of type I by application of heat appeared to be predominately of the para type, it was of especial interest to determine their behavior when warmed in alcoholic sodium hydroxide solution. We found that 2-nitrophenylsulfanilide, V, gave an excellent yield of the sodium salt of the aromatic mercaptan, VII, by heating it in sodium hydroxide solution for three hours. This rearranged product, VII, was isolated as a red crystalline compound, and was converted easily into the corresponding thiomethyl ether previously described by Smiles. This investigator prepared this thioether by methylation of the compound resulting by the rearrangement and deacylation of 2-nitrophenyl-2′-formamido-diphenyl sulfide.[3c] 2-Nitrophenylsulf-*o*-toluidide and the *p*-toluidide give the corresponding mercaptodiphenylamines by rearrangement when treated under similar conditions with sodium hydroxide. These results show conclusively that the 2-nitro-sulfanilides are capable of undergoing both ortho and para types of rearrangements. The first change is favored by the alkali treatment according to the technique of Smiles, leading to the formation of a mercaptodiphenylamine derivative, VII, while direct heating causes rearrangement to a stable para-substituted amino sulfide II. In the case of 2-nitrophenyl-5′-methyl-2′-aminophenyl sulfide, however, we obtained no rearrangement of the diphenylamine type after refluxing in alkaline solution for six hours. 2-Nitrophenyl-4′-aminophenyl sulfide and 2-nitrophenyl-3′-methyl-4′-aminophenyl sulfide obtained by rearrangement of the corresponding sulfanilides by heat underwent no further change by action of sodium hydroxide, as was to be expected. These observations are in accord with the results obtained by Smiles. In regard to the mechanism of the transformation of nitrosulfanilides V to diphenylamines VII it would appear that intermediates of the structure of ortho-amino sulfides VI are first formed which then undergo the second type of rearrangement in presence of alkali, giving the final product of reaction, VII. We have at present, however, insufficient evidence to substantiate such a conclusion and further research on the subject will be conducted in this Laboratory.

Experimental Part

Procedure for Rearrangement.—The necessary sulfanilide (5 g.) as previously prepared[3] was placed in alcohol (25 ml.) containing 20% sodium hydroxide (5 ml.) and refluxed until a given sample shows that all of the material has rearranged, usually after about three hours of heating. After allowing to cool, the solution was then diluted to twice its volume with water and upon chilling in an ice-bath the sodium salt of the mercaptan derivative was obtained as a red, glistening, crystalline mass. The mother liquor on concentration yielded a further quantity of the same material. The sodium salt was soluble in alcohol and

TABLE OF RESULTS

2-Nitrophenylsulfur-			Anilide	*o*-Toluidide	*p*-Toluidide
Sodium salt of mercaptan	Yield, %		87	80	90
	S, %	Calcd.	11.94	11.35	11.35
		Found	12.08	11.56 11.41	11.40 11.20
Thiomethyl ether	Yield, %		60	65	60
	M. p., °C.		97–98[a]	94	84–85
	S, %	Calcd.	12.31	11.68	11.68
		Found	12.39	11.76 11.84	11.61
	N, %	Calcd.	10.77	10.22	10.22
		Found	10.62 10.70	9.96 10.03	9.98 10.12

[a] Smiles reports m. p. 98° for the same compound prepared from the formamido derivatives of the residue.

water but insoluble in ether and benzene. Upon dissolving in water and neutralizing with dilute hydrochloric acid, the free mercaptan was obtained as an oily precipitate which was very difficult to purify.

Methylation of the Mercaptan.—The sodium salt from above operation (2 g.) was dissolved in alcohol (10 ml.) and refluxed for one hour with an excess of methyl iodide (2 ml.). The solution was then diluted with water, when the required thioether crystallized out upon cooling. The wall of the container was rubbed vigorously with a glass rod to facilitate crystallization. The methyl sulfides prepared were soluble in ether, alcohol and benzene but insoluble in water.

In the table are recorded the results of the different products obtained by rearrangement of different sulfanilides under the influence of alkali.

Summary

Certain sulfanilides have been rearranged by digestion in alcoholic sodium hydroxide solution to give the corresponding *o*-mercaptodiphenylamines, whereas, upon heating alone, the same compound gives *p*-amino sulfides. The free *o*-amino sulfides, so far as examined, do not suffer a rearrangement under the same conditions, hence, the question arises, do the sulfanilides pass through this intermediate stage before forming the *o*-mercaptan derivative. As yet this point has not been clarified.

NEW HAVEN, CONN. RECEIVED JULY 5, 1935

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Chloroform-d (Deuteriochloroform)[1]

BY F. W. BREUER

As part of the program on organic compounds of deuterium in progress in this Laboratory,[2] the reaction of chloral with sodium deutroxide has been studied. Chloroform-d, $CDCl_3$, is formed exclusively as shown by the Raman spectrum.[3] The boiling point and freezing point were about 0.5° higher and lower, respectively, than those of ordinary chloroform. No difference was found in the refractive index, $n^{20}\text{D}$ 1.4450. The most significant difference other than the Raman spectrum is in the density, d^{20}_4 1.5004 as compared with 1.4888 for ordinary chloroform determined in an identical manner. Assuming identical molecular volumes for $CHCl_3$ and $CDCl_3$, the calculated value is 1.5013.

Experimental

The various manipulations for making chloroform were first carefully worked out with ordinary water.

Chloral Deuterate, $Cl_3CCH(OD)_2$.—Chloral (E. K. Co.) was distilled through a still head (30 × 0.9 cm.) packed with glass helices[4] to give a middle fraction which was redistilled, the vapors being passed over anhydrous calcium sulfate (Drierite)[5] kept at 100°. After a third distillation, the middle cut ($n^{20}\text{D}$ 1.4568) was used. To 14.72 g. (0.1 mole) of the purified chloral was gradually added with cooling 5.47 g. (0.22 mole) of deuterium oxide (d^{20}_{20} 1.1079).

Reaction of Chloral Deuterate and Sodium Deutroxide.—In a container permitting the interaction of water vapors with metallic sodium a solution of sodium deutroxide in deuterium oxide was prepared from 2.2 g. (0.096 g. atom) of C. P. sodium metal and 5 g. (0.25 mole) of the deuterium oxide. The oxide was added slowly from a dropping funnel and the deuterium gas evolved collected under a pressure slightly below atmospheric. At first the reaction seemed to proceed at about the same rate as with ordinary water, as evidenced by the amount of gas formed. Soon, however, a coating of sodium deutroxide formed on the metal and the reaction rate decreased considerably. After five days the volume of gas remained constant during a period of twenty hours. A white crystalline precipitate had formed, whereas with ordinary water a clear solution was obtained. Apparently, sodium deutroxide or a deuterate of it is less soluble in deuterium oxide than the proto compounds in ordinary water. This is in accord with the decreased solubility of the chlorides of sodium and barium in heavy water.[6] In the present study chloral deuterate was found to be considerably less soluble in deuterium oxide than chloral hydrate in natural water.

In order to condense vaporized heavy water the reaction flask was cooled to −78° and the gas container heated for five hours with a stream of warm air.

After connection between the two vessels had been severed the reaction flask was equipped with a reflux condenser and the chloral deuterate solution was admitted from a dropping funnel over a period of five hours, the flask being kept below 5°. The first few drops caused a rather vigorous reaction; afterward the formation of chloroform-d continued smoothly. After standing overnight the reaction was completed by gentle warming of the flask for ten minutes. Complete separation into two layers, which occurs with the proto compounds, did not

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[1] Presented before the Division of Organic Chemistry at the New York Meeting, April, 1935.

[2] *Cf.* Whitmore and co-workers, THIS JOURNAL, **56**, 749 (1934).

[3] Wood and Rank, *Phys. Rev.*, [2], **48**, 63 (1935).

[4] Wilson and others, THIS JOURNAL, **55**, 2795 (1933).

[5] Hammond and Withrow, *Ind. Eng. Chem.*, **25**, 653, 1112 (1933).

[6] Taylor and others, THIS JOURNAL, **56**, 5334 (1934); Bingham and Stephens, *J. Chem. Phys.*, **2**, 107 (1934).