the Minnesota Mining and Manufacturing Company.

Summary

Five new fluorocarbon bromides have been prepared by the thermal reaction of the corresponding hydrogen containing fluorocarbon with bromine.

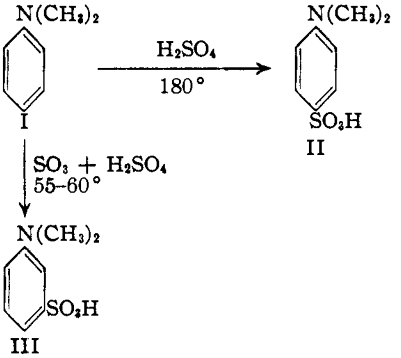
STATE COLLEGE, PA. RECEIVED JANUARY 28, 1946

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

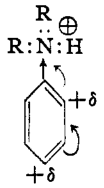
Mechanism of the Sulfonation of Aromatic Amines. I. Sulfonation with Fuming Sulfuric Acid

BY ELLIOT R. ALEXANDER[1]

It is well known that the sulfonation of aromatic amines produces different isomers depending upon the experimental conditions employed. Thus when the acid sulfate of dimethylaniline is heated to 180° it is transformed into dimethylsulfanilic acid (II),[2] while sulfonation with fuming sulfuric acid at 55–60° produces dimethylmetanilic acid (III).[3] Under these conditions the reactions are clean cut and the isomers are obtained in pure form.

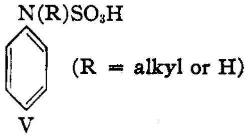


Theoretically the formation of *para* substitution products is somewhat surprising in view of the fact that a positively charged nitrogen atom would be expected to deactivate the aromatic nucleus and to cause *meta* orientation by the electronic mechanism (IV).



IV

For aniline and secondary aromatic amines a mechanism for *para* sulfonation has been advanced which is based upon the rearrangement of arylsulfamic acids (V), which were postulated as intermediates.[4]



V

This mechanism, however, is not completely satisfactory because it cannot be applied to the *para* sulfonation of tertiary aromatic amines where such intermediates are impossible, and it has been pointed out that there is evidence that the formation of arylsulfamic acids does not occur at low temperatures when the amine is present as a salt.[5]

Accordingly as a preliminary step in the investigation of the mechanism of the "baking process," a study of the effect of temperature upon the position of the entering group in the sulfonation of aniline was undertaken since there was available a quantitative method for distinguishing between *ortho–para* and *meta* sulfonation[6] and since it was reported possible to convert aniline into either *ortho*, *meta* or *para*-aminobenzenesulfonic acid.[7]

In Table I is shown a summary of sulfonation experiments carried out with aniline at temperatures ranging from 10 to 95°. It is quite surprising that in all cases the ratio of *meta* to *ortho–para* derivatives is less than one. This clearly indicates either that the anilinium ion is not the only reacting species or that there is a difference between the mechanism of the sulfonation of aniline and dimethylaniline.

It appeared at first that possibly the minute amount of undissociated aniline in solution might be responsible for this anomalous behavior. Undissociated aniline by virtue of its unshared electron pair would be expected to facilitate the attack of electrophilic reagents by mechanism VI, and even though if only present in very small amounts, the greater reactivity of this molecule with respect to the anilinium ion might be sufficient to overbalance the ratio of isomers formed in favor of *ortho–para* substitution. Experiments

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[1] Frank B. Jewett Fellow. Present address: Department of Chemistry, University of California, Berkeley, California. Presented before the Division of Organic Chemistry at the 109th Meeting of the American Chemical Society, April, 1946, Atlantic City, New Jersey.

[2] Evans, *Chem. News*, **73**, 54 (1896).

[3] German Patent 44,792; *Friedländer*, **2**, 11 (1887–1890).

[4] Bamberger and Hinderman, *Ber.*, **30**, 655 (1897).

[5] C. M. Suter, "Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 247.

[6] Amiantov and Titkov, *Anilinokrasochnaya Prom.*, **2**, No. 8–9, 24–26 (1932); *C. A.*, **27**, 5315 (1933).

[7] Armstrong and Berry, *Chem. News*, **82**, 46 (1900).

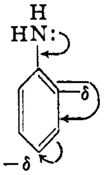
TABLE I

SULFONATION OF ANILINE[a]

No.	Moles H_2SO_4 per mole $C_6H_5NH_2$	Moles SO_3 per mole $C_6H_5NH_2$	Temp., °C.	Time, hr.	Reaction products, %: Aniline	Reaction products, %: Metanilic acid	Reaction products, %: Orthanilic, sulfanilic acid	Reaction products, %: Residue from cryst.[b]	Ratio $m/o + p$	% Material accounted for
1	3.5[c]		90	24.0	99.2					99.2
2	2.8	2.4	0–10	2.0	17.4	23.7	37.7	9.1	0.63	87.9
3	2.8	2.4	0–10	6.0	15.7	22.8	35.5	13.8	.64	87.8
4	2.8	2.4	40–45	1.0	0	28.5	46.1	14.7	.62	89.3
5	2.8	2.4	40–45	1.8	0	26.8	41.6	17.9	.65	86.3
6	11.1	2.1	40–45	0.2	48.4	14.4	21.4	11.5	.67	95.7
7	5.4	1.4	40–45	3.0	46.3	7.4	29.6	13.9	.25	98.2
8	4.6	0.5	40–45	6.0	81.1	1.7	9.8	5.5	.17	98.1
9	3.5	2.6	90–95	0.2	0	12.7	48.6	23.9	.26	85.2
10	3.5	2.6	90–95	0.8	0	13.9[d]	37.0[d]	39.6	.38	90.5

[a] Carried out with 0.1 mole aniline. [b] Obtained by evaporating the mother liquor to dryness and calculated arbitrarily as disulfonation product $C_6H_7O_6NS_2$. [c] As concentrated sulfuric acid containing 4% water. [d] The mixture of these acids was found to be 94% pure by titration with nitrite. Judging from the amount of residue obtained from this run it would seem that the disulfonation product was probably the impurity.

6, 7 and 8, however, do not support this hypothesis.



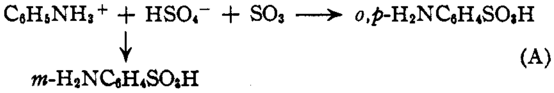
VI

Increasing the amount of sulfuric acid in the reaction mixture four-fold (which should decrease the amount of free aniline in solution by the law of mass action) does not significantly increase the proportion of *meta* isomer in the mixture, as is shown in experiment 6. Furthermore, the conclusion that there is not a sufficient amount of free aniline in sulfuric acid solution to be responsible for the *para*-sulfonation is supported, qualitatively at least, by the observation that the color of bromine was not discharged when a mixture of bromine, concentrated sulfuric acid and aniline sulfate was allowed to stand overnight at room temperature.

In experiments 7 and 8 it will be observed that decreasing the amount of sulfur trioxide in the reaction mixture sharply decreases the ratio of *meta* to *ortho–para* isomers. This suggests that there are two mechanisms in operation which are proceeding more or less independently, and since the yield of the *ortho–para* isomers is *not decreased* when the quality of sulfur trioxide is reduced (experiments 6 and 7) the formation of a complex between aniline and sulfur trioxide was suspected as an intermediate in *ortho–para* substitution.

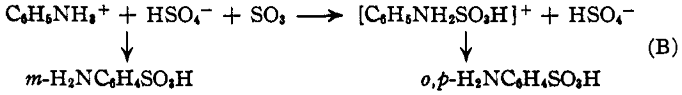
Regardless of the mechanism by which sulfonation occurs there are at least three possible courses the reaction between aniline sulfate and sulfur trioxide might take:

First, sulfur trioxide could react directly with the anilinium ion to produce *ortho–para* and *meta* substitution products by separate, but unknown, mechanisms. Such reaction could be represented by scheme A.



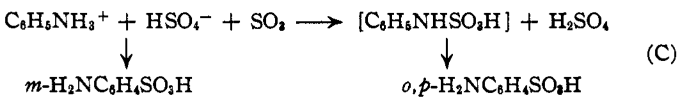
$$\begin{array}{l} C_6H_5NH_3^+ + HSO_4^- + SO_3 \longrightarrow o,p\text{-}H_2NC_6H_4SO_3H \\ \qquad\quad\downarrow \\ m\text{-}H_2NC_6H_4SO_3H \end{array} \qquad (A)$$

Another possibility is that sulfur trioxide might react with the anilinium ion to form a complex cation (such as $[C_6H_5NH_2SO_3H]^+$) which might then rearrange intramolecularly to produce *ortho–para* substitution while direct sulfonation would account for the presence of a meta isomer. Such a reaction scheme would be represented by B.



$$\begin{array}{lcl} C_6H_5NH_3^+ + HSO_4^- + SO_3 & \longrightarrow & [C_6H_5NH_2SO_3H]^+ + HSO_4^- \\ \qquad\downarrow & & \qquad\downarrow \\ m\text{-}H_2NC_6H_4SO_3H & & o,p\text{-}H_2NC_6H_4SO_3H \end{array} \qquad (B)$$

Finally, sulfur trioxide and anilinium ion could react to form a molecular addition complex of aniline and sulfur trioxide (probably phenylsulfamic acid) by the displacement of a proton from the anilinium ion. That is scheme C.



$$\begin{array}{lcl} C_6H_5NH_3^+ + HSO_4^- + SO_3 & \longrightarrow & [C_6H_5NHSO_3H] + H_2SO_4 \\ \qquad\downarrow & & \qquad\downarrow \\ m\text{-}H_2NC_6H_4SO_3H & & o,p\text{-}H_2NC_6H_4SO_3H \end{array} \qquad (C)$$

From an electronic point of view scheme C is to be preferred. With an unshared electron pair on the nitrogen atom the complex shown in C would be expected to orient *ortho–para* either to further electrophilic attack by sulfur trioxide or by intramolecular rearrangement.

An examination of the total number of molecular and ionic species to be expected from each of these possibilities shows that it should be possible to decide among them by means of a freezing point determination. Thus if the reaction proceeds slowly enough so that a correction may be made for the sulfonated products which are formed, the solution just before *ortho–para* substitution occurs according to scheme A would be expected to have a molar depression of three, (*i. e.*, $[C_6H_5NH_3]^+$, $[HSO_4]^-$ and SO_3). Scheme B would have a molar depression of two, ($[C_6H_5NH_2SO_3H]^+$ and $[HSO_4]^-$), and scheme C would have a molar depression of one ($C_6H_5NHSO_3H$). That is, the freezing point of a solution of aniline sulfate dissolved in 100% sulfuric acid would *rise* upon the addition of sulfur trioxide if scheme C obtains. It would remain unchanged for B and drop still further if scheme A represents the total number of particles in solution. In the event of measurable equilibrium between the reactants and the respective complexes, intermediate freezing points would be expected.

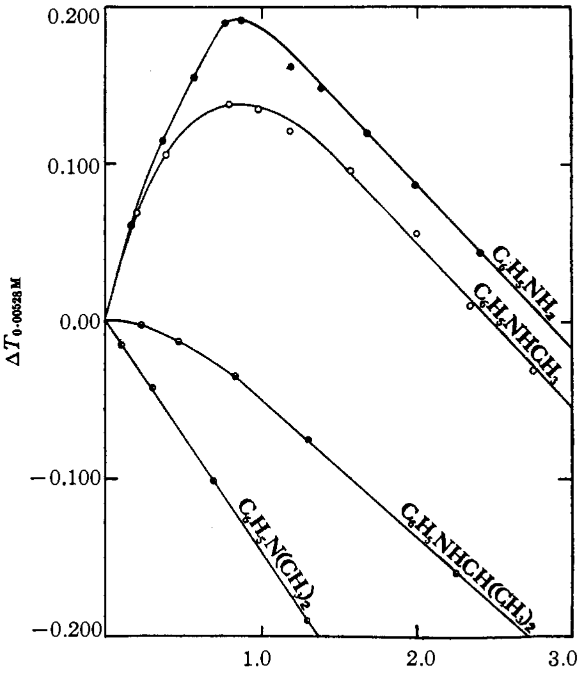
TABLE II

INFLUENCE OF SULFUR TRIOXIDE ON FREEZING POINT OF SOLUTIONS OF AROMATIC AMINES IN 100% SULFURIC ACID

G. $H_2SO_4 \cdot SO_3$ sol. added[a]	Δf.p., °C.	ΔT_{SO_3}, °C.	$\Delta T_{0.00528\ M.}$, °C.	Moles SO_3 per mole amine
Aniline sulfate,[b,c] (0.7504 g. in 80.5 g. H_2SO_4)				
0.735	0.061	0.061		0.163
1.655	.117	.115		.366
2.575	.160	.155		.571
3.490	.198	.190		.772
3.951	.200	.192		.873
5.350	.172	.162		1.185
6.252	.160	.148		1.383
7.631	.131	.120		1.689
9.002	.097	.087		1.990
10.841	.050	.044		2.400
Methylaniline sulfate,[d,c] (0.4291 g. in 83.0 g. H_2SO_4)				
0.459	0.036	0.036	0.069	0.196
0.918	.045	.045	.106	.392
1.841	.074	.072	.138	.785
2.302	.072	.070	.135	.981
2.759	.065	.063	.121	1.178
3.678	.052	.050	.096	1.570
4.591	.031	.029	.056	1.961
5.511	.005	.005	.010	2.346
6.429	− .017	− .016	− .031	2.745
Dimethylaniline hydrogen sulfate,[e,c] (0.5944 g. in 85.5 g. H_2SO_4)				
0.459	−0.015	−0.015	−0.015	0.099
1.381	− .044	− .043	− .042	.298
3.219	− .109	− .105	− .102	.694
5.980	− .209	− .195	− .190	1.292
9.651	− .345	− .310	− .302	2.080
11.501	− .422	− .372	− .362	2.482
Isopropylaniline sulfate,[f,c] (0.8419 g. in 103.6 g. H_2SO_4)				
0.918	−0.002	−0.002	−0.002	0.232
1.838	− .011	− .011	− .013	.473
3.215	− .031	− .030	− .035	.828
5.051	− .068	− .065	− .075	1.300
8.732	− .150	− .138	− .160	2.245
12.600	− .252	− .224	− .260	3.243

[a] 0.001172 moles SO_3 per gram. [b] The freezing point depression (ΔT) produced by the addition of amine salt to the sulfuric acid solution was 0.733° (van't Hoff factor, $i = 3.78$). [c] That i for these salts is somewhat less than the theoretical value is an effect to be expected of any salt which dissociates to form $[HSO_4]^-$ (Hammett, "Physical Organic Chemistry," McGraw Hill, Inc., New York, N. Y., 1940, p. 280). [d] $\Delta T = 0.367$ ($i = 3.75$). [e] $\Delta T = 0.323$ ($i = 1.72$). [f] $\Delta T = 0.478$ ($i = 3.66$).

In Table II are presented data showing the behavior of the freezing point of solutions of aniline, methylaniline, dimethylaniline and isopropylaniline in 100% sulfuric acid when they are treated with fuming sulfuric acid. Δf.p. represents the change in freezing point of the solution upon the addition of sulfur trioxide solution. ΔT_{SO_3} represents the change in freezing point caused by the sulfur trioxide added (*i. e.*, corrected for the amount of solvent sulfuric acid added with the sulfur trioxide), and $\Delta T_{0.00528\ M}$ represents the value of ΔT_{SO_3} which would have been obtained if 0.00528 mole of amine had been used.[8] In Fig. 1 is shown a plot for $\Delta T_{0.00528\ M}$ against the ratio of moles sulfur trioxide/moles amine.



Moles SO_3/moles amine.

Fig. 1.—Curves showing the effect of sulfur trioxide on the freezing point of solutions of aromatic amines in 100% sulfuric acid.

From the curves it can be seen readily that both aniline and methylaniline form addition complexes with sulfur trioxide at the expense of the anilinium ion in accordance with scheme C.[9] Thus it would be expected that considerable amounts of *ortho* and *para* substitution products should be obtained either by direct substitution or by intramolecular rearrangement. On the

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[8] The amines were all corrected by direct proportion to the number of moles of aniline used so that they could be compared graphically.

[9] Equilibrium, however, appears to favor the anilinium ion, since a rise of 0.627° would be expected if each molecule of sulfur trioxide added reacted to form a complex.

other hand, dimethylanilinium ion which is not converted to a complex would be expected to sulfonate exclusively in the meta position under these conditions. The recorded sulfonation experiments of methylaniline[10] and dimethylaniline[3] are in accord with these observations.

At first glance it is tempting to explain the failure of dimethylaniline to form a complex with sulfur trioxide in terms of the fact that there are no hydrogen atoms on the nitrogen atom with which sulfur trioxide could combine. Closer examination, however, shows that in sulfuric acid solution there is a proton attached to the dimethylanilinium ion which is no different from the one displaced by sulfur trioxide from the anilinium ion. Thus a complex *could* form between dimethylanilinium ion and sulfur trioxide although it would probably carry a positive charge.[11]

$$[C_6H_5NR_2H]^+ + SO_3 \longrightarrow [C_6H_5NR_2SO_3H]^+$$

The lack of complex formation of dimethylanilinium ion with sulfur trioxide appears to be due to steric hindrance or "F-Strain."[12] In accordance with this view it is interesting to observe that the freezing point curve of isopropylaniline (which has a replaceable hydrogen but also a large alkyl group attached to the nitrogen atom) resembles the curve of dimethylaniline more closely than the curve of methylaniline.

Acknowledgment.—The author wishes to express his appreciation to Professor P. D. Bartlett for the helpful interest shown in this work and for the hospitality of his laboratory where it was carried out. He is further indebted to the trustees of the Frank B. Jewett Fellowships for a fellowship which made this investigation possible.

Experimental

Sulfonation Experiments.—The sulfonation experiments summarized in Table I were carried out as follows:

Aniline sulfate (14.2 g., 0.05 mole) and the desired amount of concentrated sulfuric acid were placed in a 200-cc., pear-shaped, three-necked flask equipped with a thermometer, mechanical stirrer and dropping funnel. The apparatus, previously dried in an oven, was assembled hot and protected from moisture with a calcium chloride tube. Stirring was commenced and the suspension or solution was warmed or cooled to the desired temperature. The flask was then immersed in a water-bath about 20° cooler than the contents of the flask and the calculated amount of commercial 60% fuming sulfuric acid[13] was added dropwise at such a rate that the temperature remained almost constant. The reaction mixture, which was always homogeneous after addition of the fuming acid, was then stirred for the periods shown in Table I and poured over 100 g. of ice.

To determine the unreacted aniline, the solution was made just basic with solid barium hydroxide and the thick paste steam distilled in a Kjeldahl apparatus. The tip of the condenser was led into 100 cc. of 6 *M* hydrochloric acid in a 1-liter volumetric flask and when slightly less than 1 liter had been collected the tip was rinsed with distilled water, the volume made up to 1 liter, and an aliquot portion titrated with standard sodium nitrite solution.[14]

The steam distilled paste was then centrifuged to remove the precipitated barium sulfate and the sulfate washed with three 100-cc. portions of distilled water by slurrying and recentrifuging. The washings and mother liquor were then combined, heated to boiling, acidified with sulfuric acid to *p*H 1, and filtered hot with the aid of kieselguhr. The clear, faintly pink solution, was evaporated to dryness on the steam-bath and the mixture of aminobenzenesulfonic acids was recrystallized from hot water.

The proportion of isomers in the mixture was determined by the method of Amiantov and Titkov[6] using bromine dissolved in acetic acid as the brominating mixture.[15]

Preparation of Amine Sulfates.—The amine sulfates (Table III) were prepared by treating a solution of 2.0 g. of the appropriate purified amine in 5 cc. of absolute ethanol with 5 cc. of absolute ethanol containing the calculated amount of concentrated sulfuric acid. The homogeneous solution which was formed was warmed to boiling and dry ether added to the point of turbidity. By cooling the solution slowly to room temperature, followed by cooling overnight in the ice box, compact crystals were obtained in almost the theoretical yield. A second recrystallization from absolute alcohol and dry ether did not improve the melting point but removed a slight amine odor from the crystals.

TABLE III

AMINE SULFATES

Amine	Yield, %	M. p., °C.[a]	Formula	Sulfate, % Calcd.	Sulfate, % Found
Aniline	[b]	>250[c]	$C_{12}H_{16}O_4N_2S$[d]	33.79	33.84
Methylaniline[e]	89	149–150	$C_{14}H_{20}O_4N_2S$	30.75	30.82
Dimethylaniline[f]	92	88–89	$C_8H_{13}O_4NS$[g]		
Isopropylaniline[h]	94	158–159	$C_{18}H_{28}O_4N_2S$	26.07	26.02

[a] Uncorrected. [b] J. T. Baker analyzed; recrystallized from 95% ethanol. [c] The salt shrinks noticeably from the sides of the capillary at 165–170° but does not melt. [d] Schröder, *Ber.*, **12**, 1613 (1879). [e] Eastman Kodak Co., #353. [f] Eastman Kodak Co., #97; redistilled from acetic anhydride. [g] Prepared as the acid sulfate; Sugden and Wilkins, *J. Chem. Soc.*, 1296 (1929). [h] Prepared and purified according to Hickinbottom, *ibid.*, 994 (1930).

Freezing Point Determinations.—The freezing point determinations were carried out in the usual Beckmann apparatus using the technique described by Hammett and Deyrup.[16] The solution of sulfur trioxide in sulfuric acid was introduced from an automatic filling buret[17] through a hole in the stopper drilled to fit the tip snugly so as not to permit the admission of moisture. It was standardized by determining the rise in freezing point a measured volume of this solution produced upon a given amount of 100% sulfuric acid containing a trace of water. Before starting each run, enough of this sulfur trioxide solution was added

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(10) Uppal and Venkataraman, *J. Soc. Chem. Ind.*, **57**, 410 (1938).

(11) It is possible for this complex to have no net electrical charge by losing a proton to form a dipolar ion: $[C_6H_5NR_2SO_3H]^+ \rightarrow C_6H_5N^+R_2SO_3^- + H^+$. Although there are no conductivity data available for these substituted sulfamic acids (including phenylsulfamic acid), Baumgarten has pointed out that sulfamic acid itself behaves as a true strong acid, and that in solution its structure is better represented by the formula H_2NSO_3H rather than $H_3N^+SO_3^-$ [*Ber.*, **62B**, 823 (1929)].

(12) H. C. Brown, THIS JOURNAL, **66**, 441 (1944).

(13) The sulfur trioxide content was determined by titration with standard base.

(14) Kolthoff and Stenger, "Volumetric Analysis," Interscience Publishers, Inc., New York, N. Y., 1942, p. 240.

(15) This method of analysis is based upon the fact that sulfo groups in the *ortho* and *para* positions are removed quantitatively from aminobenzenesulfonic acids by treatment with bromine to form tribromoaniline, which is insoluble in water. The 3-amino-2,4,6,-tribromobenzenesulfonic acid which is formed by the bromination of metanilic acid remains in solution after filtration and may be titrated with standard nitrite.

(16) Hammett and Deyrup, THIS JOURNAL, **55**, 1900 (1933).

(17) Made by the Scientific Glass Apparatus Co., Bloomfield, New Jersey.

to stock 100% sulfuric acid to obtain the maximum freezing point.

In the run with aniline the reaction mixture was neutralized, steam distilled, and titrated with nitrite to determine the combined sulfonation products. No detectable amount of aminobenzenesulfonic acid could be found, but the fact that the curves of aniline, methylaniline, and isopropylaniline have lower limiting slopes than the curve of dimethylaniline suggests that some sulfonation took place.

Summary

In contrast to dimethylaniline, which may be sulfonated selectively in the *meta* position at low temperature with fuming sulfuric acid, aniline yields a mixture of products in which the *ortho-para* isomers predominate. Evidence is presented that the difference in behavior is due to the formation of a molecular addition complex between aniline and sulfur trioxide which carries no electrical charge.

CAMBRIDGE, MASS. RECEIVED JANUARY 30, 1946

[CONTRIBUTION FROM THE DEPARTAMENTO DE QUIMICA, FACULDADE DE FILOSOFIA, UNIVERSIDADE DE SÃO PAULO, BRAZIL]

The Configuration of Sulfoxides. Mixed Crystals of Sulfoxides with Sulfones

BY HEINRICH RHEINBOLDT AND ERNESTO GIESBRECHT

In 1926 Strecker and Spitaler[1] showed that dimethyl sulfoxide and sulfone, diethyl sulfoxide and sulfone, as well as di-*n*-propyl sulfoxide and sulfone, have, in pairs, practically the same value of molecular refraction with the result of an identical refraction equivalent for the groups $SO^{=}$ and $SO_2^{=}$ in such sulfoxides and sulfones.

On the basis of the relation existing between the molecular refraction and the real volume of the molecules arose the idea that perhaps corresponding sulfoxides and sulfones, in general, could be isomorphous if the valency angle in the sulfur atom would not be too divergent because of the different nature of the two organic substituents.

We investigated, therefore, by the thermal analysis method, the binary systems of a series of symmetrically substituted sulfoxides and sulfones of the general formulas R_2SO and R_2SO_2 comprising the following very different types where the substituted group R was as follows

1. $CH_2(CH_2)_2CH_3$
2. $CH_2(CH_2)_{14}CH_3$
3. CH_2CH_2OH
4. $CH_2C_6H_5$
5. $CH_2C_6H_4NO_2$-*p*
6. $CH_2CH_2C_6H_5$
7. C_6H_5
8. $C_6H_4CH_3$-*p*
9. C_6H_4Br-*p*
10. $C_6H_4OCH_3$-*p*

In every case we found the formation of continuous series of mixed crystals. The systems of the compounds 1, 3, 4, 5 (Fig. 1) show a mixed crystal series of the type I, and the ones of the compounds 2, 6, 7, 8, 9, 10 (Fig. 2) a series of the type III of Bakhuis-Roozeboom's classification.[2]

On the contrary, sulfides do not give mixed crystals either with the pertaining sulfoxides or with the sulfones. This was proved by the binary systems of dibenzyl sulfide and bis-*p*-bromophenyl sulfide with the corresponding sulfoxides and sulfones.

This finding indicates that these pairs of sulfoxides and sulfones must have the same steric configuration.

In the **sulfones** the tetrahedral configuration seems sufficiently established. Electron diffraction measurements on dimethyl sulfone gave results that were best explained by the tetrahedral configuration of the molecule.[3]

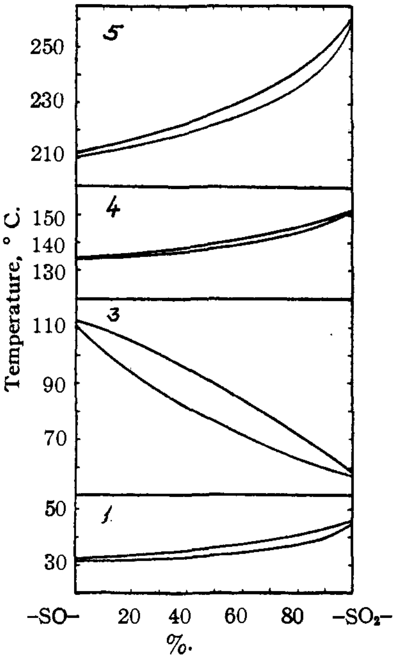

Fig. 1.—Binary systems of sulfoxides and sulfones with mixed crystals series of type I.

Determinations of the dipole moments for dimethyl sulfone in the vapor-phase,[4] and for diethyl sulfone,[5] diphenyl sulfone[6,7] and derivatives[7] in solution demonstrated a tetrahedral arrangement of the four valence bonds.

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[1] W. Strecker and R. Spitaler, *Ber.*, **59**, 1754 (1926).

[2] H. W. Bakhuis-Roozeboom, *Z. physik. Chem.*, **30**, 385 (1899).

[3] M. W. Lister and L. E. Sutton, *Trans. Faraday Soc.*, **35**, 495 (1939).

[4] I. E. Coop and L. E. Sutton, *ibid.*, **35**, 505 (1939).

[5] L. E. Sutton, R. G. A. New and J. B. Bentley, *J. Chem. Soc.*, 652 (1933).

[6] J. de Vries and W. H. Rodebush, THIS JOURNAL, **53**, 2888 (1931).

[7] E. Bergmann and M. Tschudnowsky, *Ber.*, **65**, 457 (1932).