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ANNOUNCEMENT

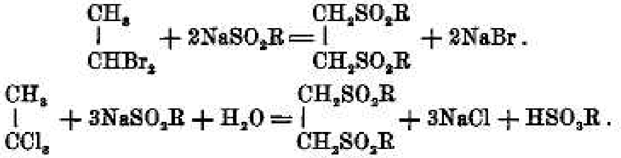
The Bryn Mawr College Monographs are issued in two series ; the first, the **Monograph Series,** containing articles that appear here for the first time; the second, the **Reprint Series,** containing reprints of articles that have appeared in other journals.

It is proposed to publish these monographs in separate numbers at irregular intervals as material is accumulated. The numbers will be combined into volumes of about 500 pages.

The monographs are edited by a committee of the Faculty of Bryn Mawr College, consisting at present of President M. Carey Thomas, ex-officio, Professor Thomas Hunt Morgan (chairman), Professor Charlotte Angas Scott, and Professor Charles McClean Andrews.

THE ADDITION REACTIONS OF SULPHINIC ACIDS.

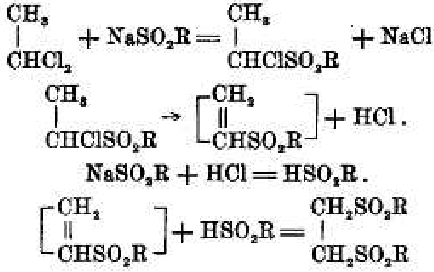
The study of the sulphinic acids and their salts has led to the discovery of certain peculiar reactions for which no satisfactory explanation has been offered. Otto[1] found, for example, that unsymmetrical di- or tri-halogen substituted aliphatic hydrocarbons yield symmetrical di-sulphones when treated with a sodium sulphinate:



$$\begin{array}{l} CH_3 \\ | \\ CHBr_2 \end{array} + 2NaSO_2R = \begin{array}{l} CH_2SO_2R \\ | \\ CH_2SO_2R \end{array} + 2NaBr\,.$$

$$\begin{array}{l} CH_3 \\ | \\ CCl_3 \end{array} + 3NaSO_2R + H_2O = \begin{array}{l} CH_2SO_2R \\ | \\ CH_2SO_2R \end{array} + 3NaCl + HSO_3R\,.$$

These reactions Otto explained by assuming molecular rearrangement, an assumption for which there is no experimental evidence and which is improbable. An interpretation not involving molecular rearrangement is possible by assuming the formation of an intermediate unsaturated compound, which subsequently combines with the sulphinic acid to form the final product:



$$\begin{array}{l} CH_3 \\ | \\ CHCl_2 \end{array} + NaSO_2R = \begin{array}{l} CH_3 \\ | \\ CHClSO_2R \end{array} + NaCl\,^{2}.$$

$$\begin{array}{l} CH_3 \\ | \\ CHClSO_2R \end{array} \rightarrow \left[\begin{array}{l} CH_2 \\ \| \\ CHSO_2R \end{array}\right] + HCl\,.$$

$$NaSO_2R + HCl = HSO_2R\,.$$

$$\left[\begin{array}{l} CH_2 \\ \| \\ CHSO_2R \end{array}\right] + HSO_2R = \begin{array}{l} CH_2SO_2R \\ | \\ CH_2SO_2R \end{array}$$

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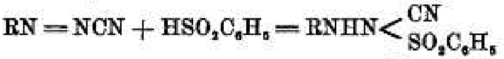
[1] J. prakt. Chem., [2] **40**, 505.

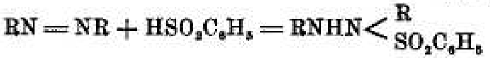
[2] Otto: J. prakt. Chem. [2] **40**, 505.

This mechanism is based on the assumption that sulphinic acids are capable of combining directly with unsaturated compounds and that this combination takes place in a definite way.

But few cases of addition reactions of sulphinic acids are known. Hantzsch and Glogauer[3] found that benzene sulphinic acid combines with azo and diazo compounds to form sulphone hydrazo compounds and hydrazones:



$$RN = NCN + HSO_2C_6H_5 = RNHN<\begin{matrix}CN\\SO_2C_6H_5\end{matrix}$$



$$RN = NR + HSO_2C_6H_5 = RNHN<\begin{matrix}R\\SO_2C_6H_5\end{matrix}$$

Hinsberg[4] found that sulphinic acids add to quinone and to substances having a quinoid structure:

$$C_6H_4O_2 + HSO_2C_6H_5 = C_6H_3(OH)_2SO_2C_6H_5 .$$

No case of direct addition of a sulphinic acid to a double linkage between carbon atoms has been described. In view of the analogy between sulphinic acids and acid sulphites, it seemed probable, however, that these acids would combine, as do the sulphites, with a number of unsaturated compounds. The object of this investigation was to determine with what classes of unsaturated compounds sulphinic acids combine, the conditions under which such combination takes place, the structure of the resulting compounds and the extent to which these addition reactions account for the abnormal reactions before mentioned.

The reactions of sulphinic acids with unsaturated acids were studied first, because it seemed improbable that sulphinic acids would combine with the carbonyl group in view of the fact that reactions which would be expected to give α, oxysulphones give only products of decomposition of these substances.[5] In the course of the work, the reactions with cinnamic aldehyde were investigated and it was found that, in this case, the sulphinic acid adds to the aldehyde group. The work was, therefore, extended to other aldehydes.

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[3] Ber. d. chem. Ges., **30**, 2548.

[4] Ber. d. chem. Ges., **27**, 3259.

[5] Fromm: Ann. Chem., (Liebig) **258**, 135,

The experiments described include the addition reactions of sulphinic acids with saturated and unsaturated aldehydes, unsaturated acids, and saturated and unsaturated ketones.

I. ADDITION OF PARA-TOLUENE SULPHINIC ACID TO SATURATED ALDEHYDES.

While this work was in progress, a paper by Meyer[*] on the reactions of para-toluene sulphinic acid appeared. Meyer found that para-toluene sulphinic acid combined with formaldehyde but not with acetaldehyde nor benzaldehyde. The following experiments show, however, that the combination of toluene sulphinic acid with aldehydes is a general reaction. In many cases it is extremely difficult to isolate the addition-products. This is explained by the fact that the reaction is a reversible one, taking place according to the equation:

$$\mathrm{RCHO} + \mathrm{HSO_2R'} \rightleftarrows \mathrm{RCH}<\begin{smallmatrix}\mathrm{OH}\\ \mathrm{SO_2R'}\end{smallmatrix}.$$

The products can be isolated only under particular conditions.

1. *Addition to acetaldehyde:*

1-para-tolylsulphonethanol (1), $\mathrm{CH_3CH}<\begin{smallmatrix}\mathrm{OH}\\ \mathrm{SO_2C_7H_7}\end{smallmatrix}$.

When p-toluene sulphinic acid is treated with acetaldehyde there is an evolution of heat showing that a reaction takes place. In order to isolate the product it was found necessary to carry on the reaction in ethereal solution. A considerable excess of the aldehyde was added to an ethereal solution of the sulphinic acid and the mixture boiled for half an hour. The solution was then cooled with ice-water and ligroin added slowly. The addition-product separated in thick white plates. It was dissolved several times in ether to which a few drops of acetaldehyde were added and reprecipitated with ligroin. The substance was then filtered, dried rapidly in a current of air and analyzed at once.

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[*] J. prakt. Chem., [2] 68; 167.

I. 0.2291 gr. subs. gave 0.4531 gr. CO_2 and 0.1261 gr. H_2O.
II. 0.2254 gr. subs. gave 0.4442 gr. CO_2.
III. 0.2089 gr. subs. gave 0.2692 gr. $BaSO_4$.

	Calculated for $C_9H_{12}SO_3$	Found.		
		I.	II.	III.
C	54.00	53.94	53.73	
H	6.00	6.11		
S	16.00			16.5

The compound separates in thick plates which may be kept for some time in solution in ether and ligroin containing a little acetaldehyde. It is extremely unstable in the air, giving up the aldehyde. For this reason it does not melt sharply. It begins to soften at 52° and is liquid at 72°.

2. *Addition of para-toluene sulphinic acid to isobutyl aldehyde:*

1-para-tolylsulphon-3-methylpropanol (1),

$$\begin{matrix}CH_3\\CH_3\end{matrix}>CHCH<\begin{matrix}OH\\SO_2C_7H_7\end{matrix}.$$

Five grams of sulphinic acid were dissolved in ether and added to an ethereal solution of three grams of isobutyl aldehyde. The solution was boiled and cooled. The product of the reaction separated out on addition of ligroin. It was dissolved again in ether, reprecipitated with ligroin, washed with ether and dried on a porcelain plate.

0.2020 gr. subs. gave 0.4277 gr. CO_2 and 0.1290 gr. H_2O.

	Calculated for $C_{11}H_{16}SO_3$.	Found.
C	57.90	57.67
H	7.02	7.09

The substance crystallizes from ether in colorless needles, from ether and ligroin in thick plates. It melts at 72°-73°. It is unstable in the air.

3. *Addition of para-toluene sulphinic acid to heptoic aldehyde:*

1-para-tolylsulphon heptanol (1),

$$CH_3(CH_2)_5CH<\begin{matrix}OH\\SO_2C_7H_7\end{matrix}.$$

Ethereal solutions of the two substances in molecular proportions were brought together, boiled and cooled. The product separated on addition of ligroin. It is less soluble in ether than the substances previously described, hence it was possible to purify it by dissolving it in boiling absolute ether and cooling the solution in ice-water.

I. 0.1932 gr. subs. gave 0.4361 gr. CO_2 and 0.1386 gr H_2O .

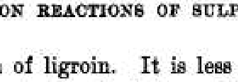
II. 0.2224 gr. subs. gave 0.5020 gr. CO_2 and 0.1608 gr. H_2O .

	Calculated for $C_{14}H_{22}SO_3$.	Found. I.	II.
C	62.22	61.56	61.55
H	8.15	7.97	8.03

The substance crystallizes in fine white needles, melting at 72°. It is insoluble in water and ligroin, readily soluble in ether, alcohol, acetone, benzene and chloroform. It is unstable, losing aldehyde on exposure to the air.

4. *Addition of para-toluene sulphinic acid to chloral:*

2, 2, 2-trichlor-1-para-tolylsulphonethanol (1),



$$CCl_3CH < {OH \atop SO_2C_7H_7} .$$

Ethereal solutions of the two substances in molecular proportions were brought together and heated as in the other cases. A dense white crystalline precipitate was formed on the addition of ligroin. The compound was extremely difficult to purify and was not further investigated.

5. *Addition of para-toluene sulphinic acid to benzaldehyde:*

When the sulphinic acid was treated with benzaldehyde there was no evidence of a reaction. If ethereal solutions of the two substances were brought together and allowed to stand at room temperature no product separated. If this ethereal solution was heated as in the other cases and ligroin added an addition-product separated out. This product was exceedingly unstable and could not be obtained in condition pure enough for analysis.

6. *Addition of para-toluene sulphinic acid to meta-nitro-benzaldehyde:*

1-para-tolylsulphon-1-meta-nitro-phenylmethanol (1),

$$NO_2C_6H_4CH < {OH \atop SO_2C_7H_7} .$$