$$= \frac{N}{N_x} \sum_{i=1}^{n-1} x^i(1 - x)[2 + (n - i - 1)(1 - x)] + \frac{N}{N_x} x^n = 1 - x + \frac{x}{n} \quad (2c)$$

as found from the equations derived in the appendix of Ref. 5. The correction term for finite n and x is simply x/n.

By preparing different samples of the copolymer having different molecular weights, and different chlorine contents, it should be possible to test these considerations and the assumptions involved. It may be noted that (2b) was derived by assuming that the reaction rates for 1–2 and 1–3 pairs are equal, and reactions between 1–4 substituents do not occur. The condition that 1–2 reactions proceed much more rapidly or much more slowly than 1–3 reactions, does not alter the result. This was shown by Flory. Wall[8] proved this to be true for any value of the relative rate of reaction of 1–2 and 1–3 pairs.

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Preparation of S-Benzylmercaptoacetic Acid

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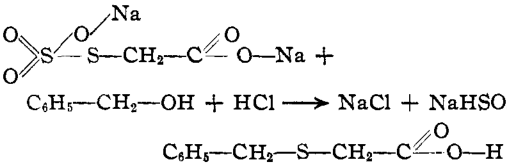
Certain alcohols can be condensed readily with mercaptans to yield sulfides. For example S-benzylmercaptoacetic acid was isolated in 72% yield after equimolar quantities of benzyl alcohol and mercaptoacetic acid had reacted in 2 *N* hydrochloric acid.[1] It has now been found that the same end can be achieved more directly and conveniently by using the Bunte salt, disodium S-carboxymethyl thiosulfate, prepared from chloroacetic acid and sodium thiosulfate.



$$O_2S(ONa)\text{—}S\text{—}CH_2\text{—}C(=O)\text{—}O\text{—}Na + C_6H_5\text{—}CH_2\text{—}OH + HCl \longrightarrow NaCl + NaHSO_4 + C_6H_5\text{—}CH_2\text{—}S\text{—}CH_2\text{—}C(=O)\text{—}O\text{—}H \quad (1)$$

Experimental Part

Solution of S-Carboxymethyl Thiosulfuric Acid.—Chloroacetic acid (9.5 g., 0.1 mole) was neutralized by sodium carbonate in 25 cc. of water, a solution of 25 g. (0.1 mole) of sodium thiosulfate in 40 cc. of water was added, and the resulting solution was kept at 100° for an hour. After cooling, 50 cc. (0.6 mole) of concentrated hydrochloric acid was added. No sulfur precipitated, but about 1 g. of sodium chloride was filtered off.

S-Benzylmercaptoacetic Acid.—The above solution was refluxed for twenty hours with 10.8 g. (0.1 mole) of benzyl alcohol. The oily layer was neutralized by sodium carbonate solution and washed with ether. Then 9.1 cc. (0.11 mole) of concentrated hydrochloric acid was added and after standing one day at 5° a yield of 10 g. (55%) was obtained, m. p. 60–61°,[2] equivalent weight calcd. 182.2, found 183.

Racemic Benzylsulfinylacetic Acid.—To a solution of 0.91 g. (0.005 mole) of S-benzylmercaptoacetic acid in 40 cc. of acetone, 0.55 cc. (0.0055 mole) of 30% hydrogen peroxide was added. The beaker was left uncovered for five days, by which time the solvent had evaporated, leaving a quantitative yield of sulfoxide, m. p. 126–127° after recrystallization from benzene.

Anal. Calcd. for $C_9H_{10}O_3S$: equiv. wt., 198.2; S, 16.17. Found: equiv. wt., 201; S, 16.5.

Benzylsulfonylacetic Acid.—A solution of 0.91 g. (0.005 mole) of S-benzylmercaptoacetic acid in 10 cc. of water was oxidized at room temperature for five days by 32 cc. (20% excess) of 4% potassium permanganate solution. The mixture was filtered and 0.05 mole of sulfuric acid was added. The solution was shaken with three 50 cc. portions of ether, 100 cc. of benzene was added to the extract, which then was concentrated to 40 cc. After one hour, 0.65 g. (60% yield) of fine crystals formed, m. p. 137°.[3]

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[1] Holmberg, *J. prakt. Chem.*, **141**, 93 (1934).

[2] Berg and Holmberg, *Svensk Kem. Tids.*, **47**, 257 (1935), reported 60°; Holmberg, *loc. cit.*, and *Arkiv Kemi, Mineral. Geol.*, **12A**, No. 11 (1936), reported 61–63°.

[3] Rothstein, *J. Chem. Soc.*, 309 (1937), reported 139–140°.

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The Use of Sulfuric Acid in Purifying Saturated Hydrocarbons: Its Action on 2,2,4-Trimethylpentane

BY FRANK C. WHITMORE AND H. H. JOHNSON, JR.

The use of sulfuric acid as a wash in the purification of saturated hydrocarbons is widespread. Observation has long led us in this Laboratory to the suspicion that such treatment is questionable. We have now studied the action of cold concentrated sulfuric acid on 2,2,4-trimethylpentane, isooctane. After treatment for ten days with cold 95% acid, we find that over half of the starting material has been changed to other products. Although the nature of these products has not been determined, there is no doubt that sulfuric acid has brought about profound changes.

The extent to which reaction took place makes imperative a most careful fractionation of a saturated hydrocarbon following a sulfuric acid wash. This fact and the possible loss of expensive material raise a real question as to the desirability of this method of purification.