with the findings of Hurd and Schmerling,[7] who rearranged a mixture of allyl ethers without finding mixed products. The ring closure mechanism would be expected to involve a considerably larger entropy decrease than is observed here, while in the absence of strong solvation effects the second mechanism should involve an entropy *increase* on the formation of the activated complex. Since it seems impossible to prove the exact mechanism from the data available at present, further discussion will be deferred until later papers of this series.

## Summary

1. The rate of the rearrangement of allyl *p*-tolyl ether in diphenyl ether solution has been measured at 214.7, 200.6, and 185.8°, the reaction being followed by determination of the phenol formed by quantitative acetylation with pyridine and acetic anhydride.

2. Over this temperature range and for a five-fold change in concentration the reaction is unimolecular, and the initial rate of the rearrangement in the pure liquid is the same as in solution.

3. The rate is not appreciably affected by the addition of 10% of dimethylaniline, 1% of acetic acid, or by the presence of air or oxygen.

4. The energy of activation is 33.1 kcal./mole, the data for the one normal solutions being represented by the expression $k = 1.60 \times 10^{11} \exp(-33.1/RT)$.

5. The rearrangement has been shown to be at least 95% quantitative at 200° in solution.

ROCHESTER, N. Y. RECEIVED AUGUST 14, 1939

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, THE UNIVERSITY OF CHICAGO]

# Sulfonation Reactions with Sulfuryl Chloride

BY M. S. KHARASCH AND ALICE TANNER READ[1]

## Introduction

In a recent paper[2] chlorination reactions with sulfuryl chloride were discussed, and it was shown that many types of organic molecules can be chlorinated with this reagent by the use of a peroxide catalyst. If the mechanism which was postulated for that reaction is correct, namely, a chain reaction involving the formation of chlorine atoms and $SO_2Cl$ free radicals, then sulfonation as well as chlorination should take place, by the direct action of the $SO_2Cl$ radical on the hydrocarbon, *i. e.*, sulfuryl chloride should, under the proper conditions, be a sulfonating as well as a chlorinating agent. Although no sulfonation products are isolated from the peroxide-catalyzed reaction, even when the sulfuryl chloride is added slowly (a procedure which minimizes any inhibitory effect of sulfuryl chloride itself), other catalysts have been found which, in the light, give both sulfonated and chlorinated products, the proportion of each being dependent upon the type of catalyst and the conditions used. With the exception of peroxides, which yield only the chlorinated hydrocarbons both in the dark and in the light, none of the catalysts investigated were very active in complete darkness. If the reaction were allowed to continue for some time, a small yield of chlorinated product could be obtained, but in no case did we obtain in the absence of light more than a trace of sulfonated product.

## Discussion

Since a free-radical mechanism has been demonstrated in the addition of mercaptans to unsaturated molecules in the presence of oxygen,[3] the mercaptan type of compound seemed a likely catalyst for reactions with sulfuryl chloride. A number of such compounds were tried in preliminary test-tube experiments and found to be effective in starting the reaction. The most promising of these were studied on a larger scale with cyclohexane, which was selected as a suitable hydrocarbon because all the hydrogen atoms in this molecule are equivalent, and the products, cyclohexyl chloride and cyclohexylsulfonyl chloride, are easily separated and identified. In all the reactions in which the mercaptan type of catalyst was used, sulfonation as well as chlorination took place. In order to ascertain the op-

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[1] When the experimental part of this work was almost complete, but before it was written up, Mrs. Read died suddenly. Her cheerful coöperation in many problems in this Laboratory, her delightful sense of humor, her enthusiasm and devotion to duty, will long be cherished by her associates.—(M. S. K.)

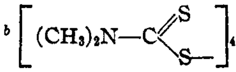
[2] Kharasch and Brown, THIS JOURNAL, **61**, 2142 (1939).

[3] Kharasch, Read and Mayo, *Chemistry and Industry*, **57**, 752 (1938).

TABLE I

CATALYZED REACTION BETWEEN SULFURYL CHLORIDE AND CYCLOHEXANE

| Expt. | Catalyst | Conditions | % Yield[a] Chlorination | Sulfonation | Ratio $RSO_2Cl/RCl$ |
|---|---|---|---|---|---|
| 1–3 | 2-Mercaptothiazoline | Dark, in absence and presence of $O_2$ and $SO_2$ | 6.7–15.8 | 0.0–6.8 | 0.0–0.43 |
| 4–12 | 2-Mercaptothiazoline | Irradiated, in absence and presence of $O_2$, $SO_2$, and $H_2O$ | 45.1–58.9 | 11.0–20.1 | 0.19–0.35 |
| 13 | 2-Mercaptothiazoline | Irradiated, $C_6H_6$ as solvent | 28.6 | 34.0 | 1.2 |
| 14–17 | Selenide[b] | In diff. light, and irradiated | 5.1–51.8 | 0.0–7.7 | 0.0–0.15 |
| 18–20 | Thiourea, thiosinamine, thiourea, resp. | Irradiated | 20.2–52.2 | 0.0–14.9 | 0.0–0.29 |
| 21–24 | Tuads[c] | In diff. light, and irradiated | 24.6–51.2 | 8.8–18.2 | 0.21–0.41 |
| 25–26 | Thionex[d] | In diff. light, and irradiated | 20.2–44.4 | 5.9–17.8 | 0.29–0.40 |
| 27–36 | 2.6-Diaminopyridine | Irradiated, with and without filters in presence and absence of $O_2$ and $SO_2$ | 26.9–54.9 | 3.5–28.5 | 0.12–0.67 |
| 37 | 2,6-Diaminopyridine | Irradiated; $C_6H_6$ as solvent[e] | 20.9 | 46.3 | 2.2 |
| 38–41 | Pyridine | Irradiated | 23.6–44.8 | 11.0–51.5 | 0.3–2.2 |
| 42 | Pyridine | Irradiated; $C_6H_6$ as solvent[e] | 9.4 | 54.8 | 5.3 |
| 43–50 | Nicotinamide, pyridinum acetohydrazide, phenanthroline, aniline, ethanolamine, metal, *p*-phenylenediamine, dimethylstearylamine oxide, resp. | Irradiated[e] | 10.8–70.7 | 0.0–33.8 | 0.0–0.87 |
| 51–56 | Quinoline, quinaldine, piperidine, morpholine, cyclohexyldimethylamine stearylamine, resp. | Irradiated[e] | 25.3–36.7 | 37.7–47.1 | 1.1–1.6 |
| 57–58 | Diphenylamine, Triphenylamine, resp. | Irradiated[e] | No reaction | | ... |
| 59–60 | Triphenylamine + pyridine | Irradiated[e] | 24.6–29.0 | 42.5–46.3 | 1.5–1.9 |
| 61 | None | Irradiated[e] | 42.1 | ... | ... |

[a] Yields recorded do not represent the maximum, obtainable for no attempt was made to trap material carried off by escaping gases. Yields are calculated on basis of sulfuryl chloride used. [b] 
$[(CH_3)_2N-C(=S)-S-]_4Se$. [c] Tetramethylthiuram disulfide. [d] Tetramethylthiuram monosulfide. [e] Sulfuryl chloride added dropwise.

timum conditions for sulfonation, the effects of light, oxygen, sulfur dioxide, water, and concentration of sulfuryl chloride were investigated. The results are given in Table I.

Since even under the optimum conditions the mercaptan-catalyzed reaction gave low yields of cyclohexylsulfonyl chloride, other catalysts for the reaction were sought. In preliminary experiments, a number of anthroquinonesulfonic acids were found to initiate the reaction in the light, but were without effect in the dark. Of these, the potassium salt of anthraquinone-1-sulfonic acid was tried on a larger scale with cyclohexane and gave a 64% yield of the chloride and 4% of the sulfonyl chloride.

Many types of organic nitrogen compounds were tried as catalysts, and in all cases sulfonation as well as chlorination was obtained, except in the presence of those compounds which are bromination and oxidation inhibitors (diphenylamine, *p*-phenylenediamine, etc.) in which case either no reaction at all, or a small amount of chlorination, took place (Table I). Of all the catalysts studied, by far the most effective for sulfonation are the aromatic nitrogen ring compounds, the pyridines and quinolines. With these catalysts, under the proper conditions, the extent of chlorination is greatly reduced and good yields of cyclohexylsulfonyl chloride are obtained.

In Table II are given the results of experiments with hydrocarbons other than cyclohexane. In all aliphatic or aromatic compounds with an aliphatic side-chain, sulfonation in the aliphatic part of the molecule took place. A notable exception is toluene. Attempts to prepare benzylsulfonyl chloride from toluene and sulfuryl chloride, using optimum conditions for sulfonation, and operating at a low temperature (55–60°), were unsuccessful. However, that sulfonation of aliphatic side-chains is possible by this method, is demonstrated by the formation of phenethylsulfonyl chloride in small yields from ethylbenzene,

TABLE II

REACTIONS BETWEEN SULFURYL CHLORIDE AND HYDROCARBONS

| Expt. | Hydrocarbon | Catalyst | % Yield[a] Chlorination | % Yield[a] Sulfonation | Ratio $RSO_2Cl/RCl$ |
|---|---|---|---|---|---|
| 62–65 | Toluene | 2-Mercaptothiazoline, mercaptobenzothiazole, anthraquinone-1-sulfonic acid,[b] resp. | 26.5–65.6 | ... | ... |
| 66–67 | Ethylbenzene | Selenide, 2-mercaptothiazoline, resp. | 33.9–48.6 | ... | ... |
| 68 | Ethylbenzene | Quinoline | 74.6 | 12.4 | 0.17 |
| 69–71 | *n*-Heptane | Pyridine[c,e] quinoline,[d] resp. | 28.0–56.0 | 17.3–31.0 | .31–1.1 |
| 72 | Benzene | Pyridine[f] | 12.0 | ... | ... |
| 73 | *t*-Butylbenzene | Pyridine[e] | 22.0 | 39.0 | 1.8 |
| 74 | Methylcyclohexane | Pyridine[e] | 21.0 | 44.0 | 2.1 |

[a] Yields are based on the sulfuryl chloride added. [b] The potassium salt was used. The reaction was carried out in strong light. [c] The reaction was carried out in strong light at the boiling point of the hydrocarbon, 99°. [d] The reaction was carried out in strong light; the temperature was kept between 60 and 70°. [e] Benzene was used as a solvent; the reaction was carried out in strong light and the sulfuryl chloride was added dropwise. [f] The reaction mixture was refluxed in strong light.

and of fair yields of 2-phenyl-2-methyl propylsulfonyl chloride from *t*-butylbenzene.

It is fairly well established that in the peroxide-catalyzed chlorinations with sulfuryl chloride the aliphatic side-chain of the aromatic hydrocarbon is always the point of attack. We now find the same is true of sulfonation reactions with this reagent. Heretofore, sulfuryl chloride has been used in conjunction with halogen carriers, as an agent for chlorination, and with the aid of aluminum chloride for sulfonation of aromatic nuclei. The above experiments indicate that when the reaction takes place through a free radical mechanism, the aliphatic type of molecule is attacked much more readily than the aromatic. This brings out the striking difference between reagents which can share an electron pair, and act exclusively upon the aromatic nucleus, and reagents, such as atoms and free-radicals, which preferentially attack aliphatic molecules. In this connection it should be noted that benzene, itself, is attacked by sulfuryl chloride in strong light when a catalyst is used, but the only product obtained is hexachlorobenzene. However, when an equimolecular mixture of benzene and cyclohexane is allowed to react with sulfuryl chloride under the same conditions, the benzene is not attacked and good yields of cyclohexylsulfonyl chloride are obtained.[4]

An examination of the foregoing tables discloses the fact that the catalyst, more than any other one factor, determines the course of the reaction. Under similar conditions of light and low sulfuryl chloride concentration, peroxides, as already has been stated, give chlorination exclusively; anthraquinonesulfonic acids give almost entirely chlorination; mercaptans and organic nitrogen compounds give chlorination and sulfonation in varying amounts, the best yields of sulfonation product being obtained with the aromatic nitrogen ring compounds. With any one catalyst, the most favorable conditions for sulfonation are strong light and a low concentration of sulfuryl chloride in the reaction mixture at any one time. Oxygen, which might be expected to inhibit chlorination, inhibits both reactions in diffused light, and has no appreciable effect in strong light, except in the case of the pyridine type of catalyst, where chlorination is somewhat inhibited, but the yield of cyclohexylsulfonyl chloride is not increased. Sulfur dioxide, which, in excess, favors sulfonation when a mixture of sulfur dioxide and chlorine is used as the sulfonating agent,[5] has no effect with sulfuryl chloride in strong light, and inhibits both chlorination and sulfonation in diffused light. The effect of temperature can be seen in the experiments with *n*-heptane (Table II); when the reaction is carried out at the boiling point of the hydrocarbon the proportion of heptylsulfonyl chloride is considerably less than when the temperature is kept at 70°. This is accounted for readily by the fact that sulfuryl chloride is largely dissociated at temperatures above its boiling point, into sulfur dioxide and chlorine[6] and, consequently, some of the reaction takes place through the action of molecular chlorine, rather than through a free-radical mechanism.

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(4) With 2-mercaptothiazoline as a catalyst, the yield of sulfonation product was greatly increased by the use of benzene as a solvent, instead of excess cyclohexane, but the effect of benzene as a diluent was not appreciable when the reaction was catalyzed by pyridine.

(5) Reed, U. S. Patent 2,046,090; Kharasch and Alsop, unpublished work.

(6) Trautz, *Z. Elektrochem.*, **14**, 534 (1908).

Although the number of compounds sulfonated by this method is not large, there is little doubt that the reaction is quite general for aliphatic hydrocarbons, and has been extended to alkyl halides and many other types of molecules. Since sulfuryl chloride can now be used either as a sulfonating or a chlorinating agent with aliphatic compounds, it should prove a useful reagent in organic chemistry. The primary purpose of the present investigation, however, was to demonstrate that sulfonation should and does take place when sulfuryl chloride reacts with aliphatic hydrocarbons through a free-radical mechanism.

## Experimental Part

The cyclohexane (0.5 mole) and sulfuryl chloride (0.25 mole) were introduced into a 125-cc. round-bottomed flask connected by a ground-glass joint to a Hopkins-type condenser, and brought to a gentle reflux. A small amount of catalyst (0.02–0.12 g.) was added, and the reaction mixture was heated over a low flame until no more gas was evolved. The progress of the reaction was followed by means of a bubble counter attached by a rubber tube to the top of the condenser. No attempt was made to trap any of the reactants swept over with the gases, and in cases where oxygen or sulfur dioxide was bubbled through the mixture during the reaction, the losses were appreciable. After the reaction was complete, the mixture was filtered through a glass-wool plug, and the excess cyclohexane was removed by distillation through an indented column 45 cm. long. The solution was then transferred to a 50-cc. Claisen flask, and the rest of the distillation was carried out at reduced pressure. Cyclohexyl chloride was identified by its boiling point, and cyclohexylsulfonyl chloride by its boiling point and anilide.

The experiments in which the sulfuryl chloride was added slowly, or in which gases were passed through the solution, were carried out in a 125-cc. round-bottomed flask into which was sealed a capillary delivery tube reaching to the bottom of the flask and sealed to a wide neck which held a dropping funnel and gas delivery tube. The flask was connected to the condenser by a ground-glass joint.

The source of illumination was a 2000-watt lamp placed about twelve inches (31 cm.) from the reaction flask. The cyclohexane used was Eastman Kodak Co. practical grade, dried over sodium. The sulfuryl chloride was obtained from the Hooker Electrochemical Company and was not purified further.

The identification of *n*-heptylsulfonyl chloride, and phenethylsulfonyl chloride was made by conversion to the amides.

## Summary

1. Simultaneous chlorination and sulfonation of aliphatic hydrocarbons with the aid of sulfuryl chloride, a catalyst, and light is recorded.

2. It is shown that aromatic nitrogen ring compounds when used as catalysts in this reaction, favor the formation of the aliphatic sulfonyl chlorides.

3. The mechanism of the reaction is discussed.

CHICAGO, ILLINOIS RECEIVED AUGUST 10, 1939

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, THE UNIVERSITY OF CHICAGO]

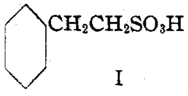
# The Peroxide Effect in the Addition of Reagents to Unsaturated Compounds. XXIII. The Reaction of Styrene with Bisulfite

BY M. S. KHARASCH, REMSEN TEN EYCK SCHENCK AND F. R. MAYO

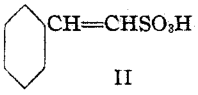
A recent paper from this Laboratory discussed the addition of bisulfite to various olefins.[1] The unique behavior of styrene suggested further study of this reaction.

### The Interaction of Styrene and Bisulfite

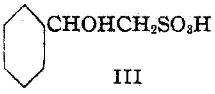
The formation, by the oxygen-catalyzed reaction between ammonium bisulfite and styrene, of benzoic acid, 2-phenylethanesulfonic acid (I), and 2-phenylethylenesulfonic acid (II) has been confirmed qualitatively. The material isolated in greatest amount, however (about 65% of the total yield in most instances), was found to be not II, as observed by the workers cited, but a new compound, 2-hydroxy-2-phenylethanesulfonic acid (III). This substance, on treatment with phosphorus pentachloride and then with ammonia, loses the elements of water to form the same amide as II, and can be identified in a mixture of the two only by fractional crystallization of the sodium or potassium salt from dilute alcohol. It is not surprising that the previous workers in the field did not suspect its presence since they for the most part converted the crude salts directly into amides without previous puri-



I



II



III

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[1] Kharasch, May and Mayo, *J. Org. Chem.*, **3**, 175 (1938); a summary of the earlier literature is given in this article.