

CHLOROSULFATES

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I. Introduction

A. SCOPE OF THE REVIEW

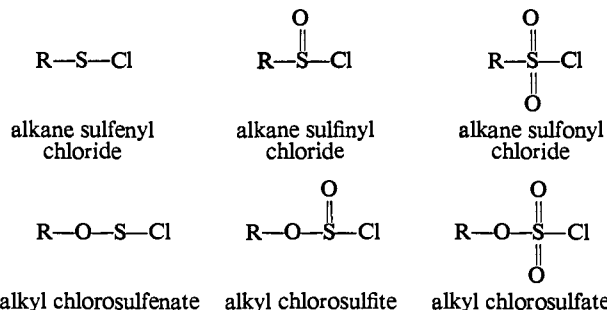
Although alkyl chlorosulfates have been known for over 100 years,¹ their systematic study began only recently. A comprehensive review is here presented with emphasis placed on correlation and interpretation of the varied chemistry of the chlorosulfates.

The classes of compounds discussed are the alkyl (including perhaloalkyl) chlorosulfates, aryl chlorosulfates, carbohydrate chlorosulfates, and the chlorosulfates of a number of metals and nonmetals. Comparison is drawn with other classes of organosulfur compounds containing chlorine and oxygen. The industrial importance of chlorosulfates is pointed out.

A considerable portion of the review is concerned with clarification of nucleophilic substitution processes in this series. Aspects of nucleophilic reactivity at other sulfur centers are contained in several reviews.²⁻⁵

B. STRUCTURAL RELATIONSHIPS

The alkyl chlorosulfates, ROSO_2Cl , are structurally related to other chlorine- and oxygen-containing organic sulfur derivatives, such as chlorosulfites, ROSOCl , and sulfonyl chlorides, RSO_2Cl . This relationship may be illustrated through the following series, beginning with alkane sulfonyl chloride.



With the exception of the alkyl chlorosulfenates (or alkoxy sulfonyl chlorides), which are apparently unknown, the various members of the series have been extensively studied. Relationships between structure and reactivity, or at least some trends therein, might well be expected in such a series.

Of considerable interest is the possibility of reaction at the various atomic centers: sulfur, carbon, and chlorine. Reaction at sulfur is common to all the classes of the series. Since most reactions under consideration are of the nucleophilic substitution type, and may therefore occur in principle by a bimolecular or a unimolecular ionization process, the following series of cationic organosulfur intermediates is conceivable: RS^+ , RSO^+ , RSO_2^+ , ROSO^+ , and ROSO_2^+ . Evidence for the formation of sulfenium ions, RS^+ , as intermediates in certain reactions of alkane or arene sulfonyl halides has been presented.⁶ Hydrolysis of a number of sulfonyl derivatives, however, has been shown to proceed by bimolecular^{7,8} (or termolecular)⁹ mechanisms. There has been little directly relevant

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(2) A. J. Parker and N. Kharasch, *Chem. Rev.*, 59, 583 (1959).

(3) J. F. Bunnett, *Ann. Rev. Phys. Chem.*, 14, 271 (1963).

(4) J. L. Kice, *Accounts Chem. Res.*, 1, 58 (1968).

(5) E. Ciuffarin and A. Fava, *Progr. Phys. Org. Chem.*, 6, 81 (1968).

(6) N. Kharasch, "Organic Sulfur Compounds," Vol. 1, N. Kharasch, Ed., Pergamon Press, New York, N. Y., 1961, Chapter 32.

(7) J. L. Kice and J. M. Anderson, *J. Org. Chem.*, 33, 3331 (1968).

(8) C. Brown and D. R. Hogg, *Chem. Commun.*, 38 (1967).

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study of alkane sulfinyl chlorides,¹⁰ but a solvolytic study of aryl sulfinyl derivatives¹¹ indicates that bimolecular displacement at sulfur predominates. Sulfonylium cations, RSO_2^+ , are formed from sulfonyl chlorides or sulfonyl fluorides by the action of strong Lewis acids such as antimony pentafluoride,¹² but not under solvolytic conditions.¹³ Displacement reactions at the carbon center have not been observed for the first three members of the series, RSCl , RSOCl , and RSO_2Cl .

The alkyl chlorosulfites (or alkyl chlorosulfinates) react by a multiplicity of mechanisms:^{14, 15} ionization at the sulfur-chlorine bond to give the cation ROSO^+ , ionization at the carbon-oxygen bond to give a carbonium ion, and reaction by the intramolecular S_{Ni} mechanism. Studies with alkyl chlorosulfites led to some of the original postulates on the intermediacy of ion pairs in carbonium ion reactions.¹⁵

The alkyl chlorosulfates resemble the alkyl chlorosulfites in that the corresponding processes have all been postulated (though not always definitively established) in order to explain certain observations. However, in addition, the alkyl chlorosulfates can apparently also take part in displacement reactions at the chlorine atom. The alkane sulfonyl chlorides are the only other members of the above series to undergo displacement at chlorine.¹⁶ Thus the alkyl chlorosulfates are unique to this series to exhibit substitution at carbon, sulfur, and chlorine.

The predominant process in reactions of alkyl chlorosulfates is bimolecular displacement at carbon, since the OSO_2Cl moiety is shown to be one of the best of leaving groups. Quite unusual is the finding that, with certain chlorosulfates, in the displacement process at sulfur, alkoxy is the leaving group in preference to chlorine. The evident possibility of competing mechanisms in the reaction of chlorosulfates often provides a challenging requirement for the application of definitive criteria.

C. GENERAL COMMENTS

The alkyl chlorosulfates, in addition to being of interest from the mechanistic viewpoint, have potential in organic synthesis. First, they have been employed as intermediates in the synthesis of alkyl hydrogen sulfates, particularly of the long-chain alcohols: the reaction products are of use as detergents. Owing to the ease of conversion of alcohols to chlorosulfates, by reaction with the readily available sulfuryl chloride, this may provide an attractive method for the preparation of detergents. Secondly, alkyl chlorosulfates can serve as alkylating agents, which is a reflection of the ability of the OSO_2Cl moiety to act as a good leaving group. Thirdly, and by the same token, the alkyl chlorosulfates may find use as intermediates in the conversion of alcohols to some less accessible derivatives such as alkyl fluorides, etc., which is in fact the basis of some in-

dustrial processes, particularly in the case of perhaloalkyl fluorides. There is extensive patent literature on these aspects.

Before proceeding to the section on synthetic methods, it is of interest to note that almost all the common alkyl chlorosulfates are primary derivatives. Simple secondary chlorosulfates, e.g., isopropyl, etc., are not known, though some hindered secondary alkyl chlorosulfates, e.g., 2-octyl chlorosulfate, have been prepared, as have chlorosulfates in the cyclohexane and pyranose series. A stable tertiary alkyl chlorosulfate has not been reported. Therefore in the following sections on the synthesis and reactions of chlorosulfates, unless stated otherwise, the discussion will be assumed to be applicable only to the primary alkyl chlorosulfates. Many of the reactions discussed in this article were originally reported before the development of current theories of structure and mechanism; the rationalization of these reactions in terms of current theories is one of the main objectives of the present article. A summary of the early literature is available.¹⁷

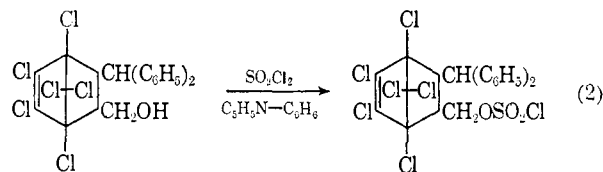
II. Synthesis of Alkyl and Aryl Chlorosulfates

A. BY NUCLEOPHILIC DISPLACEMENT ON SULFURYL CHLORIDE

The reaction of alcohols with sulfuryl chloride represents the most general synthetic method and clearly proceeds by nucleophilic displacement on sulfur with chlorine as leaving group.



Methyl chlorosulfate was prepared by this method in 1876.¹⁸ With slight variants, such as use of dry nitrogen or a tertiary amine to remove the hydrogen halide, low reaction temperatures (0 to -80°), and an inert solvent (ether, pentane, benzene etc.), this method has since been applied to the synthesis of many simple primary alkyl chlorosulfates: methyl,^{19, 20} ethyl,^{19, 21} *n*-propyl,^{19, 20} *n*-butyl,^{19, 20, 22} isobutyl,^{22, 23} *n*-amyl,²⁰ neopentyl,^{22, 23} *n*-hexyl,²⁰ *n*-heptyl,²⁰ and lauryl chlorosulfate.²⁴ Halogen- and nitro-substituted alkyl chlorosulfates have been prepared similarly: 2-chloroethyl,²⁵ 2,2,2-trichloro-



ethyl,²² 2,2,2-trifluoroethyl,²² and 2,2,2-trinitroethyl²⁶ chlorosulfate, as well as the secondary chlorosulfates derived from

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(18) P. Behrend, *Chem. Ber.*, **9**, 1334 (1876); *J. Prakt. Chem.*, [2] **15**, 23 (1877).

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(20) R. Levaillant, *Ann. Chim.*, **6**, 459 (1936).

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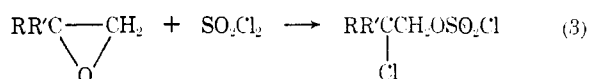
(25) D. R. Martin, J. F. Suttle, and H. S. Booth, *Inorg. Syn.*, **4**, 85 (1953).

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1,3-dichloropropan-2-ol²² and ethyl α -hydroxypropionate.²² A rather unusual chlorosulfate has been described (eq 2).²⁷ 8-Hydroxymethylcaffeine has similarly been converted to the chlorosulfate.²⁸ Polyfluoroalkyl chlorosulfates, $\text{YCF}_2(\text{CF}_2)_n\text{CH}_2\text{OSO}_2\text{Cl}$ (Y = H or F, $n = 0-12$), were prepared²⁹ by reaction of the respective alkoxides with SO_2Cl_2 .

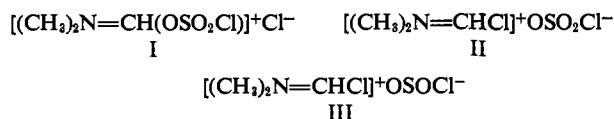
Phenyl chlorosulfate, PhOSO_2Cl , was prepared from phenol and sulfonyl chloride in presence of pyridine.³⁰ This compound had previously been prepared,^{31,32} but in lower yield, from sodium phenoxide and sulfonyl chloride. Methoxy-,³¹ chloro-,^{33,34} and nitrosubstituted³³ phenyl chlorosulfates have been prepared from the corresponding phenoxides, while methyl- and fluoro-substituted phenyl chlorosulfates were obtained by the pyridine method.²²

Sulfonyl chloride reacts with epoxides to give β -chloroalkyl chlorosulfates³⁵



In each case (R = R' = H; R = CH₃, R' = H; R = R' = CH₃; R = (CH₃)₂CH, R' = H; R = CH₂Cl, R' = H) the product obtained was the primary alkyl chlorosulfate. Cyclohexene epoxide did, however, give the secondary 2-chloro-cyclohexyl chlorosulfate (cf. ref 36).

Dimethylformamide reacts with sulfonyl chloride to give a complex which has been of use in synthesis.^{37,38} The structure of this complex has been formulated as I³⁸ and II.³⁹ The adduct of dimethylformamide with thionyl chloride is assigned⁴⁰ structure III.

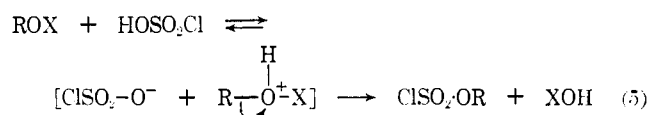
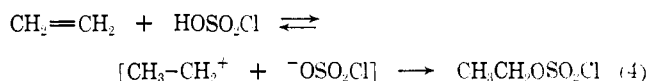


B. BY ALKYLATION OF CHLOROSULFONIC ACID

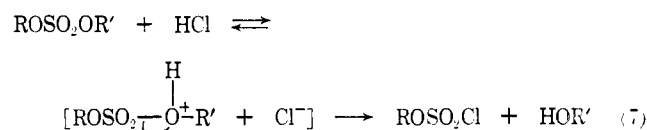
The following compounds are reported to form chlorosulfate derivatives on reaction with chlorosulfonic acid: ethanol,⁴¹

ethylene,⁴² di(chloromethyl) ether,⁴³ paraformaldehyde,⁴³ dimethyl sulfate,⁴⁴ methyl hydrogen sulfate,⁴⁴ methyl chloroformate,⁴⁵ polyfluoroalkyl halides,⁴⁶⁻⁴⁸ tetrafluoroethylene,⁴⁹ and azoxybenzene.^{32,50}

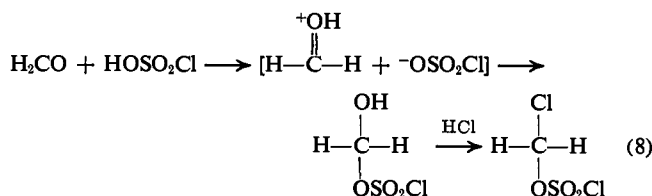
It is proposed that, with the possible exception of one or two cases, there is a common mechanism to these reactions. The probable mechanism is a normal carbonium ion type: reaction of substrate with HOSO_2Cl with formation of a carbonium or oxonium ion, followed by its combination with $^-\text{OSO}_2\text{Cl}$. The reaction of ethylene is then represented by eq 4, and the conversion of alcohol (X = H), ether (X = R), dialkyl sulfate (X = SO₂OR), and hydrogen sulfate (X = SO₂OH) by eq 5.



An alternative mechanism can, however, be written for the cases X = SO₂OR, SO₂OH, if it is considered⁵¹ that chlorosulfonic acid can act as a source of hydrogen chloride (eq 6); the HCl would react with the substrates through oxygen-protonation and displacement at sulfur (eq 7). Similarly, the



reaction of paraformaldehyde may be represented by



The formation of alkyl chlorosulfates by reaction of polyfluoroalkyl halides with chlorosulfonic acid is noteworthy in several ways: (i) this is one of the very few instances of sub-

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(39) H. A. Lehmann, C. Ringel, and V. Koeltsch, *ibid.*, **5**, 313 (1965).

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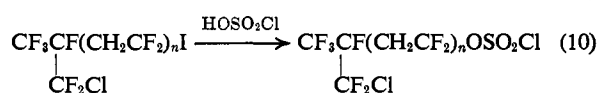
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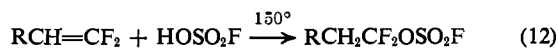
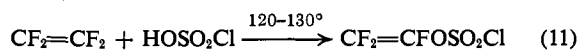
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stitution of halogen by OSO_2Cl ; (ii) a halogen other than fluorine is displaced; (iii) iodine is displaced in preference to chlorine, as exemplified⁴⁶ in eq 9 and 10. Secondary fluoroalkyl

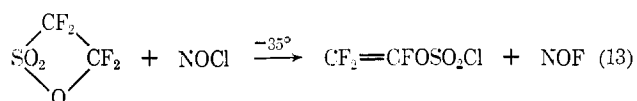


chlorosulfates⁴⁷ and fluoroalkyl terminal dichlorosulfates⁴⁸ have been prepared similarly. The observed order of reactivity with respect to the leaving group, $\text{I} > \text{Cl} \gg \text{F}$, is in accord with a carbonium ion mechanism. Although such a mechanism is not usually considered to occur with primary alkyl halides, under the vigor of the reaction conditions (temperatures of the order of 100° and prolonged reaction times), it might well be feasible. Recent reports⁵² of the stabilization of carbonium ions by fluoro substituents are germane in this connection.

The reaction of tetrafluoroethylene with chlorosulfonic acid is unusual in that the product is reported⁴⁹ to be trifluorovinyl chlorosulfate; that is, instead of addition to the double bond as in the case of ethylene (eq 4), substitution apparently occurs (eq 11). In the reaction of fluoroolefins with fluorosulfonic acid the reported⁵³ product is that of addition to the double bond (eq 12). Tetrafluoroethylene also reacts with fluorosulfonic acid by addition.⁵⁴ The reaction of tetrafluoroethane β -



sultone with nitrosyl chloride gives rise to trifluorovinyl chlorosulfate.⁵⁵



The formation of azobenzene-4-chlorosulfate from azoxybenzene and chlorosulfonic acid⁵² is connected with the Wallach rearrangement,⁵⁶ that is, the conversion of azoxybenzene to 4-hydroxyazobenzene in aqueous sulfuric acid. Since in sulfuric acid the process is known to be intermolecular, the formation of the 4-chlorosulfate in chlorosulfonic acid medium is unlikely to occur by reaction of an intermediate 4-hydroxyazobenzene with chlorosulfonic acid. Evidence has been given^{57,58} for the intermediacy of a dicationic intermediate (IV)^{59,60} in the Wallach rearrangement. In chlorosulfonic acid this intermediate would give rise to the observed product by the processes shown in eq 15. Azoxybenzene is converted by means of fluorosulfonic acid into azobenzene-4-fluorosulfate,⁶¹ presumably by a similar mechanism.

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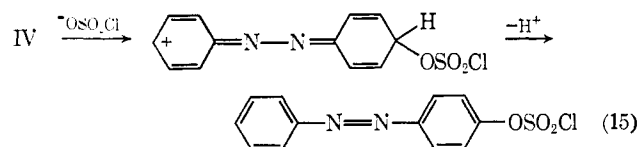
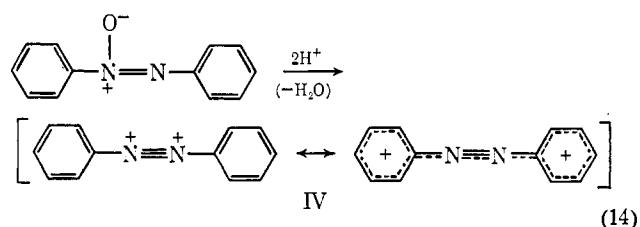
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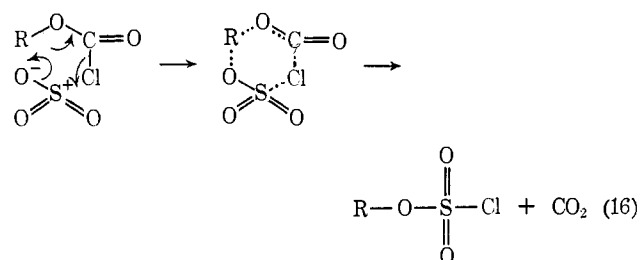
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C. SYNTHESSES USING SULFUR TRIOXIDE AND SULFUR DIOXIDE

Ethyl chloride⁶² and ethyl chloroformate⁶² were reported to react with sulfur trioxide to form ethyl chlorosulfate in fair yield. More recently,⁶³ 1,2-dichloroethane was similarly shown to yield the chlorosulfate $\text{ClCH}_2\text{CH}_2\text{OSO}_2\text{Cl}$ on reaction with SO_3 . These reactions presumably proceed by cyclic transition states and might be initiated by a Lewis acid type interaction of sulfur trioxide and halogen, as depicted in eq 16. The reac-



tion of ethyl chloride or of 1,2-dichloroethane with sulfur trioxide can be formulated similarly but *via* a four-centered transition state. Methyl and ethyl hypochlorite also yielded the corresponding chlorosulfates on reaction with sulfur dioxide.⁶⁴ Recently the preparation of some perfluoroalkyl chlorosulfates (primary and secondary) has been described,⁶⁵ from sulfur dioxide and the perfluoroalkyl hypochlorites. If this type of reaction also proceeds by a cyclic mechanism, one would have an instance of a three-center transition state.

D. BY REACTION OF ALKYL SULFITES WITH CHLORINE OR SULFURYL CHLORIDE

Excellent yields of chlorosulfates are reported from the reaction of chlorine with alkyl sulfites; the chlorosulfates derived from several primary alcohols (methyl, ethyl, propyl, and 2-chloroethyl)⁶⁶ as well as secondary alcohols (ethyl 2-hydroxypropionate⁶⁷ and 2-octanol⁶⁸) have been prepared by this method.

If this reaction proceeded solely by a cyclic mechanism (eq 17), then the resulting alkyl chloride would be expected to be formed with retention of configuration. However, the 2-

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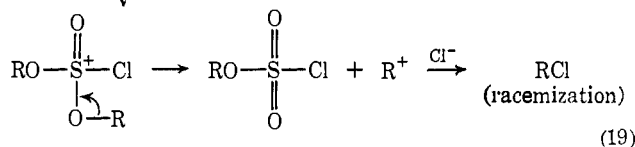
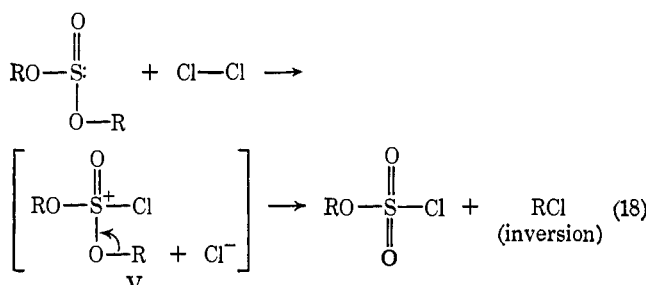
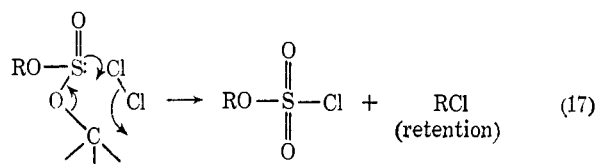
(65) D. E. Young, L. R. Anderson, D. E. Gould, and W. B. Fox, *Tetrahedron Lett.*, **9**, 723 (1969).

(66) R. Levaillant, *C. R. Acad. Sci., Paris*, **189**, 465 (1929).

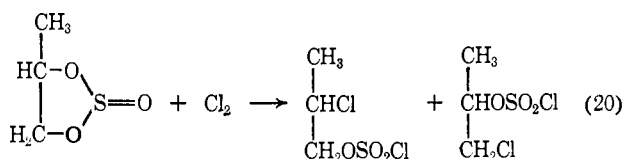
(67) W. Gerrard, *J. Chem. Soc.*, 218 (1940).

(68) A. H. J. Cross and W. Gerrard, *ibid.*, 2686 (1949).

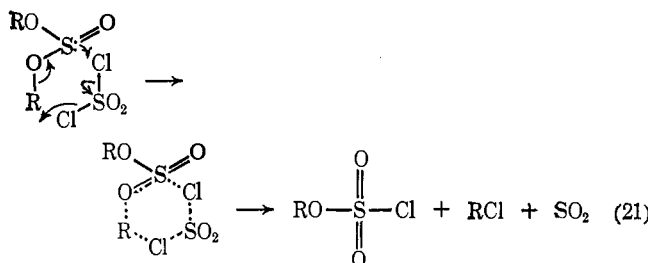
chlorooctane obtained from optically active di-(–)-octan-2-ol sulfite had predominantly *inverted* configuration.⁶⁸ It was therefore suggested⁶⁸ that the main reaction route is an ionic process (electrophilic attack by chlorine on sulfur followed by backside displacement on carbon) leading to inversion (eq 18). To account for the lack of complete optical purity in the 2-chlorooctane it was proposed⁶⁸ that competing with the process of eq 18, there are two further concurrent processes: (i) the intermediate (V) formed in the main reaction (eq 18) may also react unimolecularly, resulting in racemization (eq 19); (ii) a cyclic process (eq 17) giving retention of configuration. The chlorination of cyclic sulfites gives rise to chloroalkyl



chlorosulfates.⁶⁹ Methylene sulfite thus gave a mixture of two products.⁶⁹



The reported formation of butyl⁷⁰ and 2-bromoethyl⁷¹ chlorosulfates in the reaction of the dialkyl sulfites with sulfur chloride may also be formulated by a cyclic mechanism.



E. FROM ALKYL HYDROGEN SULFATE AND A HALOGENATING AGENT

The reaction of phosphorus pentachloride with ethyl hydrogen sulfate^{21,72} or with its potassium salt⁶² gives rise to ethyl chlorosulfate (eq 22); these processes are clearly analogous to the conversion of alcohols or carboxylic acids to the alkyl or acyl halides.



III. Structure and Properties

The available evidence points to a close relationship between the structures of alkyl chlorosulfates and alkane sulfonyl chlorides, on the one hand, and alkyl sulfonates, on the other hand. For instance, the Raman frequencies of $\text{CH}_3\text{OSO}_2\text{Cl}$ were noted^{73,74} to correlate well with those of HOSO_2Cl , $\text{CH}_3\text{SO}_2\text{Cl}$, and $\text{CH}_3\text{OSO}_2\text{CH}_3$, which were all ascribed the C_s symmetry. Raman⁷³ and infrared²³ measurements on a series of simple alkyl chlorosulfates showed the expected⁷⁵ characteristic frequencies.

Characteristic ultraviolet spectra are reported for the polyfluoroalkyl chlorosulfates,⁴⁶ and fluorine-19 nmr data have also been obtained.⁶⁵ Aryl chlorosulfates have been examined by ultraviolet³⁴ and infrared^{34,76} spectroscopy. Correlations have been given between vibrational stretching frequencies, force constants, bond lengths, and bond orders (of the sulfur-oxygen bonds) among the various structural types (XSO_2Y), including the chlorosulfates.⁷⁵⁻⁷⁷ (For related spectroscopic studies the reader is referred to ref 78-80.)

The simple primary alkyl chlorosulfates are all colorless liquids and are usually strong lachrymators. The lower alkyl chlorosulfates, as well as the phenyl chlorosulfates, can be distilled under reduced pressure. Attempted distillation at atmospheric pressure usually leads to decomposition; for example, ethyl chlorosulfate decomposes⁸¹ at 160° to ethylene, sulfur dioxide, sulfuric acid, and hydrogen chloride. Ethyl chlorosulfate also decomposes on heating in a sealed tube at 100°, to ether, sulfuric acid, and hydrogen chloride.⁶² The higher molecular weight chlorosulfates, such as 2-octyl⁶⁸ and 2-chloro-cyclohexyl³⁵ chlorosulfates, could not be distilled without decomposition, even under reduced pressure.

The alkyl chlorosulfates have a remarkably low solubility in water, and as a result they are practically unaffected by cold water. They react readily with hot water to give a variety of products; these products as well as the products of reaction with alcohols, alkoxides, and other reagents will be described in detail in subsequent sections.

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(73) R. Vogel-Högler, *Acta Phys. Austriaca*, **1**, 323 (1948).

(74) A. Simon, H. Kriegsmann, and H. Dutz, *Chem. Ber.*, **89**, 2378 (1956).

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(77) R. J. Gillespie and E. A. Robinson, *Can. J. Chem.*, **41**, 2074 (1963).

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(69) P. A. Bristow, R. G. Jones, and J. G. Tillett, *J. Chem. Soc.*, **C**, 314 (1967).

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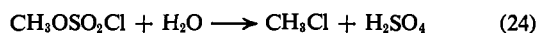
(71) R. Levilliant, *C. R. Acad. Sci., Paris*, **197**, 648 (1933).

IV. Reactions of Alkyl and Aryl Chlorosulfates

A. CARBON-OXYGEN SCISSION VS. SULFUR-CHLORINE SCISSION

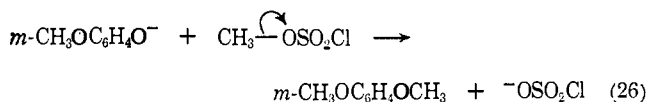
1. Hydrolysis and Related Nucleophilic Processes of Some Alkyl Chlorosulfates

In an early study⁸² of the reaction of methyl chlorosulfate with water, several products were observed: methanol, methyl chloride, methyl hydrogen sulfate, dimethyl ether, and sulfuric and hydrochloric acids. The authors formulated three main concurrent reactions.



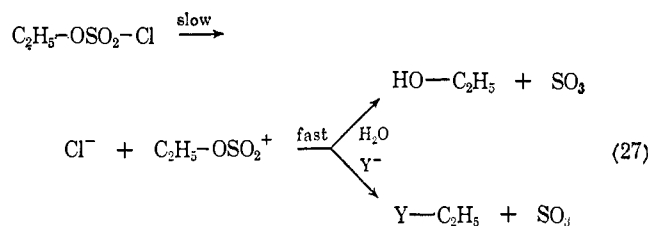
It was also noted⁸² that the proportion of products depended on the initial ratio of the two reactants. With a 1000-fold excess of water the products represented by eq 23–25 were in the proportion 0.87:0.06:0.07; with 100-fold excess of water these proportions were 0.64:0.28:0.08. These reactions were, however, carried out under heterogenous conditions. Hall⁸³ investigated the hydrolysis reaction under homogenous conditions, by using aqueous dioxane as the reaction medium, and found that reaction proceeded quantitatively according to eq 23; the chlorosulfate concentration in this work was of the order of 0.001 *M*. It appears, therefore, that the reaction products according to eq 24 and 25 are the results of the heterogenous reaction conditions and the higher substrate concentrations used in the former study.⁸²

The first kinetic study with an alkyl chlorosulfate was also carried out by Hall,⁸³ with the purpose of comparing the mechanism of hydrolysis of alkyl chlorosulfates with the sulfonyl chlorides, as well as with other acyl derivatives. The rate of reaction, in 86.1% water–13.9% dioxane (v/v), was followed by an alkalimetric titration method and also by electrometric measurement of chloride ion. The two methods gave identical rate constants, which showed that reaction could not proceed *via* an intermediate methyl hydrogen sulfate, since hydrolysis of the latter was known⁸⁴ to be slow under the reaction conditions. The effect of added nucleophilic reagents was also examined.⁸³ The reaction rate was increased by added sodium hydroxide, sodium *m*-cresoxide and by pyrrolidine, and in addition 1-methylpyrrolidine and *m*-methylanisole were isolated from the corresponding reaction mixtures. It was concluded that these reactions proceed by direct displacement on carbon, *e.g.*

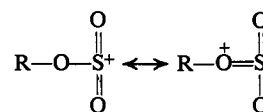


The displaced $^-\text{OSO}_2\text{Cl}$ ion would react rapidly with water. The reaction of ethyl chlorosulfate was also studied,⁸⁵ but it was concluded that this compound reacts by a different mechanism, rate-determining ionization at the sulfur–chlorine

bond followed by fast reaction of the nucleophile with the ethoxysulfonylium ion intermediate *at carbon*, with SO_3 as the displaced group.



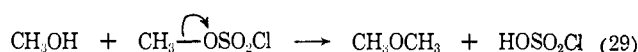
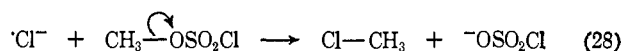
The driving force for this process would be the considerable stabilization derived in separation of the sulfur trioxide molecule. The possibility of resonance stabilization in the alkoxy-sulfonylium cation



would cause ionization of the type considered in eq 27 to be more likely for the solvolysis of ROSO_2Cl than for RSO_2Cl .

In a subsequent study⁸⁵ the hydrolysis of *n*-propyl chlorosulfate was examined, using a less polar reaction medium, 85.3% dioxane–14.7% water (w/w). With 0.01 *M* chlorosulfate reaction proceeded quantitatively to give the alcohol, sulfuric acid, and hydrochloric acid, according to eq 23. The rate of hydrolysis was measured conductimetrically and electrometrically for chloride ion, giving identical results. Added halide ions increased the rate of reaction, in the order $\text{I}^- > \text{Br}^- > \text{Cl}^-$, as did hydroxide ion and pyrrolidine. The observed reactivity order with respect to halide is typical of bimolecular nucleophilic displacement processes at saturated carbon in aqueous media.^{86,87} A satisfactory correlation⁸⁸ between the nucleophilic parameter *n* of Swain and Scott⁸⁹ and the rate constant ratio $\log k_{\text{X}} - \log k_{\text{H}_2\text{O}}$ for the three halide ions is also in accord with substitution at carbon, with $^-\text{OSO}_2\text{Cl}$ as the leaving group.

The observation by the early workers of a variety of products in the reaction of alkyl chlorosulfates with water can be interpreted on the basis of carbon displacement as the principal primary process. The increased yield of methyl chloride reported by Guyot and Simon⁸² as the concentration of methyl chlorosulfate was increased would arise due to the greater ability of chloride ion, formed in the primary reaction (eq 23), to compete with water in nucleophilic displacement on carbon (eq 28). The formation of dimethyl ether would similarly result owing to methanol acting as the nucleophile (eq 29).



(82) J. Guyot and L.-J. Simon, *C. R. Acad. Sci., Paris*, 170, 326 (1920).

(83) H. K. Hall, Jr., *J. Amer. Chem. Soc.*, 78, 1450 (1956).

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(85) E. Buncel and J. P. Millington, *Can. J. Chem.*, 43, 547 (1965).

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(87) C. A. Bunton, "Nucleophilic Substitution at a Saturated Carbon Atom," Elsevier Publishing Co., New York, N. Y., 1963, p 75.

(88) J. P. Millington, Ph.D. Thesis, Queen's University, 1965.

(89) C. G. Swain and C. B. Scott, *J. Amer. Chem. Soc.*, 75, 141 (1953).

Table I
Relative Rates of Solvolytic Reactions

Reaction	Relative rate					Ref
	CH ₃	CH ₃ CH ₂	CH ₃ CH ₂ CH ₂	(CH ₃) ₂ CHCH ₂	(CH ₃) ₃ CCH ₂	
1. ROTs, EtOH, 75°	2.3	1.0		0.046	0.00057	96
2. ROSO ₂ Cl, 85.3% aq dioxane, 25°	2.93	1.0	0.555	0.043	0.00235	23
3. RBr, 50% aq EtOH, 95°	1.94	1.0		0.075	0.00625	97
4. RBr, 70% aq EtOH, Ag ⁺ , 64°	0.81	1.0		0.085	0.013	97
5. ROTs, HCOOH, 75°	0.56	1.0		1.22	1.0	96

Although methyl hydrogen sulfate would be formed by reaction of sulfuric acid (eq 23) or chlorosulfonic acid (eq 29) with methanol, it is not obvious why the relative yield of this product should remain constant, as the proportions of the reactants are varied. Some of the methyl hydrogen sulfate may possibly result from nucleophilic displacement by H₂O at sulfur. The reported⁶² formation of diethyl ether and sulfuric and hydrochloric acids from ethyl chlorosulfate when heated with water in a closed system at 100° can be explained analogously. There appears to be no requirement to postulate an intramolecular S_Ni process for the formation of methyl chloride in the above studies.^{62,82}

In support of the general feasibility of the ⁻OSO₂Cl leaving group can be cited the corresponding ionization of the inorganic chlorosulfates (MOSO₂Cl ⇌ M⁺ + ⁻OSO₂Cl) in dimethyl sulfoxide,⁹⁰ hydrogen chloride,⁹¹ and chlorosulfonic acid.⁹² Some analogy for this type of process is provided by reactions of alkyl chlorosulfites, where the structurally related leaving group ⁻OSOC_l has been invoked.¹⁵ Reactions of alkyl fluorosulfates with nucleophiles have similarly been interpreted as displacements on carbon with ⁻OSO₂F as the leaving group.⁹³

The facility of the chlorosulfate moiety as a leaving group has been of value in synthesis. Reaction of the polyfluoroalkyl chlorosulfates with fluoride, chloride, and bromide ions gives the respective fluoroalkyl halides.^{29,94,95} It was noted²⁹ that reaction of fluoroalkyl chlorosulfates occurred under considerably milder conditions than with the corresponding tosylates. (Some of the fluoroalkyl halides are useful⁹⁶ as "solvents, heat exchange media, hydraulic fluids, dielectrics, fire extinguishing agents, intermediates, and especially inhalation anesthetics.")

Reactions of alcohols, etc., with sulfuryl chloride often produce alkyl chlorides, and it can be reasonably assumed that the intermediate chlorosulfates have undergone displacement by chloride ion present in the reaction mixture (*e.g.*, ref 26). The observation³⁸ of predominant formation of *cis*-1,2-dichlorocyclohexane in the reaction of cyclohexane epoxide with sulfuryl chloride is in accord with chloride substitution on an intermediate *trans*-2-chlorocyclohexyl chlorosulfate (*cf.* ref 35).

(90) R. J. Gillespie and E. A. Robinson, *Can. J. Chem.*, **40**, 644 (1962); J. A. Ciruna and E. A. Robinson, *ibid.*, **46**, 1715 (1968).

(91) T. C. Waddington and F. Klanberg, *J. Chem. Soc.*, 2332 (1960).

(92) R. C. Paul, S. K. Vashisht, K. C. Malhotra, and S. S. Pahil, *J. Sci. Ind. Res.*, **21B**, 528 (1962).

(93) M. G. Ahmed, R. W. Alder, G. H. James, M. L. Sinnott, and M. C. Whiting, *Chem. Commun.*, 1533 (1968).

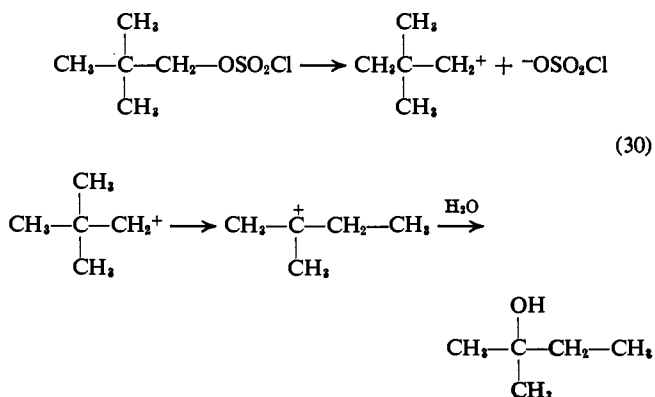
(94) A. Zappel and H. Jonas, U. S. Patent 3,080,431; *Chem. Abstr.*, **59**, 5021b (1963).

(95) W. V. Cohen, U. S. Patent 3,080,430; *Chem. Abstr.*, **59**, 7373 (1963).

2. Study of a Reaction Series

Further insight into the mechanism of substitution was gained from a solvolytic study of the series of primary alkyl chlorosulfates, methyl, ethyl, *n*-propyl, isobutyl, and neopentyl.²³ It is of interest to compare relative reactivities within the series, and also with other series of alkyl derivatives. These data, given in Table I,^{23,96,97} show that the alkyl chlorosulfates fit very satisfactorily with other series of alkyl derivatives. Since the other series are known to solvolyze by nucleophilic substitution at carbon, it is highly likely that hydrolysis of the alkyl chlorosulfates proceeds by the same mechanism.

The question of mechanistic types in such series of derivatives (bimolecular or unimolecular solvolytic mechanisms) has been discussed,⁹⁸ particularly as the ionizing power of the medium is increased, *i.e.*, on going downward from reaction 1-5 in Table I. In the alkyl chlorosulfate series the steady decrease in rate from methyl to the neopentyl derivative is strongly suggestive of a bimolecular process for the first several members. In the neopentyl case such a mechanism would be disfavored by the very great increase in steric hindrance to the approach of the nucleophile, so that a unimolecular mechanism might be preferred. The latter alternative was in fact demonstrated by the observation that added hydroxide ions did not increase the rate of hydrolysis and that the alcoholic product of the reaction was not neopentyl alcohol but the rearranged *t*-pentyl alcohol.



Rearrangement in the solvolysis of neopentyl derivatives had been observed previously⁹⁷ (*cf.* ref 99). Several discussions

(96) S. Winstein and H. Marshall, *J. Amer. Chem. Soc.*, **74**, 1120 (1952).

(97) I. Dostrovsky, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 173 (1946).

(98) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 73, 135.

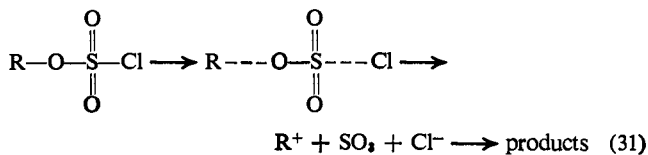
(99) G. M. Fraser and H. M. R. Hoffmann, *Chem. Commun.*, 561 (1967).

have been given on the question of the timing of the ionization and rearrangement steps in such processes.⁹⁸⁻¹⁰¹

Unimolecular processes are usually characterized by entropy of activation values which are about 20 eu greater than those of the corresponding bimolecular processes.¹⁰² This situation was found exactly in chlorosulfate solvolysis: ΔS^\ddagger for the neopentyl derivative was more positive, by 15-26 eu, than for the other members of the series.²³

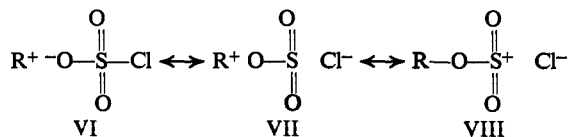
3. Multiple Bond Fission

The derived activation parameters in chlorosulfate solvolysis revealed one further point of note: for a particular mechanism of solvolysis, bimolecular or unimolecular, the entropy of activation for chlorosulfate solvolysis was greater, by 10-20 eu, than for solvolysis of other alkyl derivatives. For example, in 10 M aqueous dioxane the unimolecularly hydrolyzing *t*-butyl chloride¹⁰³ and isopropyl benzenesulfonate¹⁰⁴ have ΔS^\ddagger values of -12.7 and -14.6 eu, respectively, while neopentyl chlorosulfate has $\Delta S^\ddagger = 0.1$ eu. It was suggested¹⁰⁵ that in the neopentyl case there might be *simultaneous* bond weakening of both carbon-oxygen and sulfur-chlorine bonds, leading to the formation of three fragments. This would result in an increased ΔS^\ddagger due to the gain of vibrational and rotational degrees of freedom, over cases such as *t*-butyl chloride or isopropyl benzenesulfonate where only two particles are formed. Chlorosulfate solvolysis would thus be represented by



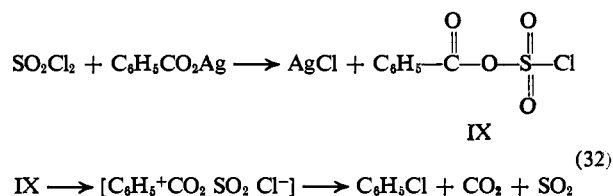
While fragmentation reactions have been well documented,¹⁰⁶ not all such processes need be characterized by abnormally large ΔS^\ddagger values. It is conceivable that multiple bond rupture may create steric *restrictions* in the transition state, as in the case of a departing phenyl group, which stabilizes the transition state by charge delocalization and is consequently restricted to a given spatial orientation; such a case has been reported.¹⁰⁷ However, this situation is not likely to be present in chlorosulfate solvolysis so that the "abnormal entropy criterion" may well apply here. Extension of the criterion to some other processes was considered.²³

The transition state for chlorosulfate solvolysis may then be represented by several resonance structures.



Contribution by structure VIII would reflect reactivity by sulfur-chlorine fission (*e.g.*, eq 27) while contribution by structures VI and VII would account for the carbonium ion type behavior of alkyl chlorosulfates. Noteworthy is the marked instability of simple secondary and tertiary alkyl chlorosulfates; the only reported¹⁰⁸ tertiary derivative, *t*-butyl chlorosulfate, is said to decompose spontaneously above 0°. The attempted preparation of benzyl chlorosulfate resulted in the formation of polybenzyl,¹⁰⁹ a reaction presumably proceeding *via* benzyl carbonium ions derived from the intermediate chlorosulfate.

The reaction of silver benzoate with sulfonyl chloride was reported¹¹⁰ as a novel method for the preparation of chlorobenzene. It seems possible that this reaction proceeds *via* an intermediate benzoyl chlorosulfate (IX), which fragments, and the products form by recombination in an internal ion pair.



An alternative mechanism involving a cyclic transition state, akin to the S_Ni reaction of alkyl chlorosulfites or alkyl chloroformates, is, of course, also possible.

Multiple bond fission has been invoked^{106,111} in other reactions involving organosulfur compounds (see also section IV.C). It should be stressed that postulates of multiple bond fission require support by independent criteria, in addition to ΔS^\ddagger . For example, the kinetic isotope effect, Cl³⁶/Cl³⁷, for chlorosulfate solvolysis (eq 31) would constitute an independent criterion of multiple bond fission.

4. Alcoholysis

The reaction of alcohols with chlorosulfates was one of the first to be examined. Claesson reported⁴¹ that ethyl chlorosulfate reacted with ethanol to yield ethyl chloride, diethyl ether, ethyl hydrogen sulfate, diethyl sulfate, and hydrochloric acid. The corresponding products, with the exception of the dialkyl ether, were reported¹¹² to be formed from the reaction of methyl chlorosulfate with methanol. Interestingly, the yield of dialkyl sulfate in these reactions never exceeded 20% of the theoretical value. The reaction of ethyl chlorosulfate with several sodium alkoxides was reported²¹ to yield the following products: ethyl alkyl ether, ethyl alkyl sulfate, alkyl sodium sulfate, sodium sulfate, and sodium chloride.

In order to clarify the origin of the various products the alcoholysis reaction was reexamined.¹¹³ The reaction of *n*-propyl chlorosulfate with *n*-propyl alcohol was chosen for study, the advantage of this combination being that the number of organic products would be kept to a minimum and

(100) J. E. Nordlander, S. P. Jindal, P. von R. Schleyer, R. C. Fort, Jr., J. J. Harper, and R. D. Nicholas, *J. Amer. Chem. Soc.*, **88**, 4475 (1966).

(101) J. E. Nordlander and W. J. Kelly, *J. Org. Chem.*, **32**, 4122 (1967).

(102) L. L. Schlager and F. A. Long, *Advan. Phys. Org. Chem.*, **1**, 1 (1963).

(103) S. Winstein and A. H. Fainberg, *J. Amer. Chem. Soc.*, **79**, 5937 (1957).

(104) E. Tommila and E. Merikallio, *Suomen Kemistilehti*, **B**, **26**, 79 (1953); E. Tommila, *Acta Chem. Scand.*, **9**, 975 (1955).

(105) E. Buncel and J. P. Millington, *Proc. Chem. Soc.*, 406 (1964).

(106) C. A. Grob, *Angew. Chem. Intern. Ed. Engl.*, **6**, 1 (1967).

(107) S. Seltzer and F. T. Dunne, *J. Amer. Chem. Soc.*, **87**, 2628 (1965).

(108) W. H. Brader, Jr., U. S. Patent 3,083,221; *Chem. Abstr.*, **59**, 8595 (1963).

(109) R. A. Gibbons, M. N. Gibbons, and M. L. Wolfrom, *J. Amer. Chem. Soc.*, **77**, 6374 (1955).

(110) G. Ciustea, C. Demetrescu, and L. Ivan, *Rev. Chim. (Bucharest)*, **13**, 757 (1962); *Chem. Abstr.*, **59**, 6214 (1963).

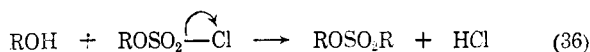
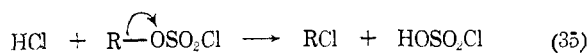
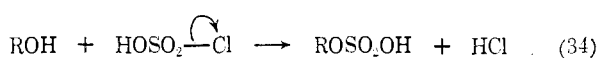
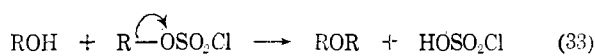
(111) J. F. King and D. J. H. Smith, *J. Amer. Chem. Soc.*, **89**, 4803 (1967).

(112) R. Levailant and L.-J. Simon, *C. R. Acad. Sci., Paris*, **169**, 854 (1919).

(113) E. Buncel and J. P. Millington, *Can. J. Chem.*, **47**, 2145 (1969).

could be conveniently analyzed by vapor phase chromatography. It was observed that as the chlorosulfate concentration was increased gradually from 0.01 to 2.0 *M* the yield of di-*n*-propyl ether decreased steadily from 96 to 23%; the yield of *n*-propyl chloride increased from 5 to 65%, with a corresponding decrease in the yield of hydrogen chloride (isopropyl chloride was formed only at the highest chlorosulfate concentration, to the extent of a few per cent); di-*n*-propyl sulfate was formed in small yield, 3 to 9%; *n*-propyl hydrogen sulfate was formed to the extent of 94 to 97%.

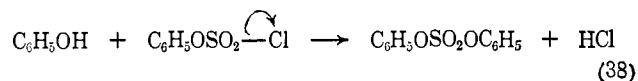
The following interpretation is suggested by the above results. The primary reaction is a typical alcoholysis process, that is nucleophilic displacement by alcohol on carbon with formation of ether and chlorosulfonic acid (eq 33). The chlorosulfonic acid product is solvolyzed to *n*-propyl hydrogen sulfate and HCl (eq 34). Alkyl chloride is formed from reaction of chloride ion (derived from HCl) with alkyl chlorosulfate, again by displacement at carbon (eq 35); the chlorosulfonic acid so formed will react to give more alkyl hydrogen sulfate, whose total yield therefore will equal the sum of the yields of ether and alkyl chloride. Dialkyl sulfate would be formed as in eq 36. The effect of initial substrate concentration on the product



distribution is readily seen: an increasing substrate concentration will give rise to an increasing chloride ion concentration (reactions 33 and 34) which can then successfully compete for substrate (reaction 35). It is noteworthy that of the various products obtained in the alcoholysis of the alkyl chlorosulfate, only the dialkyl sulfate is formed by nucleophilic displacement on sulfur.

Diisopropyl sulfate¹¹⁴ and di-*t*-butyl sulfate¹⁰⁸ are formed in good yield from the alcohols and SO_2Cl_2 ; these reactions presumably proceed *via* the intermediate chlorosulfates. However, in general, dialkyl sulfates are formed only as minor products in the reaction of alcohols with alkyl chlorosulfates. Yields of dialkyl sulfate may be improved by use of alkoxides²¹ as in the case of the bisfluoroalkyl sulfates.²⁹ Other methods for the preparation of alkyl sulfates are given under section IV.C.

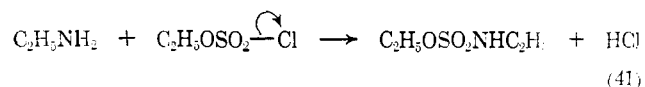
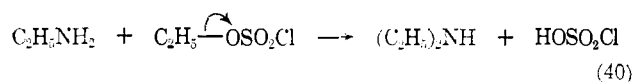
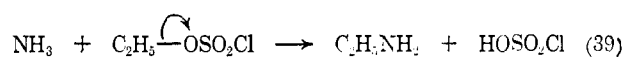
Phenols are alkylated by alkyl chlorosulfates in basic solution. The reaction of methyl chlorosulfate with an aqueous solution of sodium phenoxide was reported¹¹⁵ to give anisole in 75% yield. Similarly, phenetole was obtained⁸¹ from the reaction of ethyl chlorosulfate with an ether suspension of the phenolic salt (eq 37). In contrast, phenols react with aryl chlorosulfates by displacement on sulfur with formation of aryl sulfates. Diphenyl sulfate was obtained¹¹⁶ from the reaction of phenol with phenyl chlorosulfate in the presence of pyridine (eq 38); the methyl-,¹¹⁶ chloro-, and nitroaryl³³ sulfates were prepared similarly. The possibility of a competing



sulfur-oxygen bond fission in the reaction of alkoxides with aryl chlorosulfates will be considered subsequently (section IV.B).

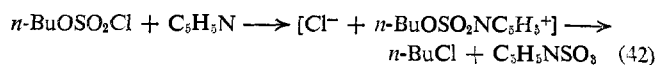
5. Reaction with Amines

Ethyl chlorosulfate was reported^{62,81,116} to react violently with ammonia to give a mixture of products, though in ether or in benzene solution the reaction was more moderate. Products isolated from the reaction mixtures included mono-, di-, and triethylamine, and di-, tri-, and tetraethylammonium chlorides; these products clearly result from nucleophilic displacement on carbon, *e.g.*, reactions 39 and 40. Other products isolated were $\text{C}_2\text{H}_5\text{NHSO}_2\text{OC}_2\text{H}_5$ and $(\text{C}_2\text{H}_5)_2\text{NSO}_2\text{OC}_2\text{H}_5$; these must result from substitution by the amines at sulfur, *e.g.*, reaction 41. The reaction of dimethylamine with methyl



chlorosulfate¹¹⁷ yielded $\text{CH}_3\text{OSO}_2\text{NMe}_2$, and reaction of other dialkylamines with alkyl chlorosulfates¹¹⁸ yielded the corresponding dialkylamine sulfonates, again by nucleophilic displacement at sulfur.

The formation of alkyl chloride in the reaction of alkyl chlorosulfates with tertiary amines has been observed;^{22,67,81,119a} a detailed study of the pyridine-triethylamine reaction was presented.²² *n*-Butyl chlorosulfate reacted rapidly with both bases, even at -80° , giving *n*-butyl chloride as the volatile product. It was suggested²² that a pyridinium salt is formed as an intermediate (reaction at sulfur), which then undergoes displacement by chloride ion (reaction at carbon).



However, isobutyl chlorosulfate, which required a higher temperature (0°) for reaction, yielded isobutyl chloride (67%), as well as *t*-butyl chloride (30%) and butenes (3%) as the volatile products, which would suggest that with this substrate a carbonium ion mechanism is, at least in part, operative. Neopentyl chlorosulfate reacted very slowly with pyridine at 20° and no volatile products were observed.²²

Gerrard, *et al.*,²² also studied the reaction of pyridine with optically active chlorosulfates. The chlorosulfate derived from (–)-ethyl lactate yielded ethyl α -chloropropionate of "pre-

(114) R. Levaillant, *C. R. Acad. Sci., Paris*, 188, 261 (1929).

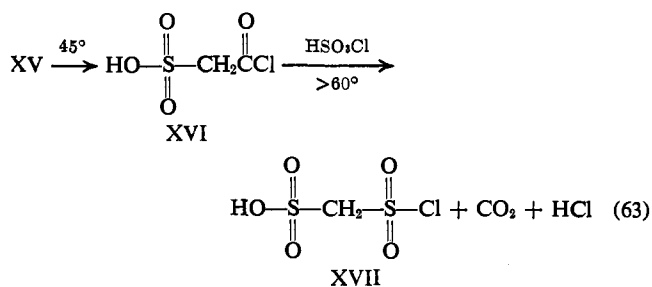
(115) W. Traube, *Z. Angew. Chem.*, 38, 441 (1925).

(116) L. Denivelle, *C. R. Acad. Sci., Paris*, 199, 211 (1934).

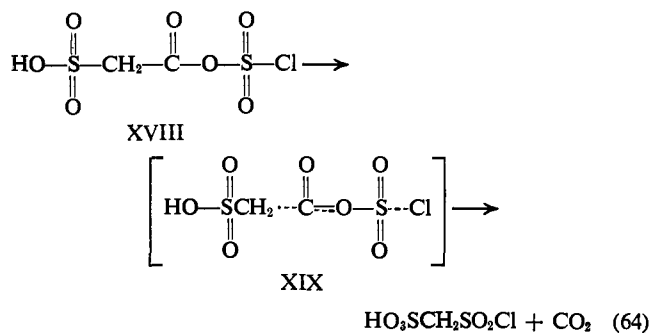
(117) M. Delépine and R. Demars, *Bull. Sci. Pharmacol.*, 30, 577 (1923).

(118) W. W. Binkley and E. F. Degering, *J. Amer. Chem. Soc.*, 61, 3250 (1939).

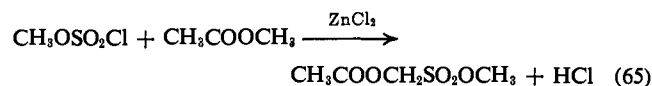
(119) (a) P. Baumgarten, *Chem. Ber.*, 59, 1166 (1926); (b) W. J. Spillane and F. L. Scott, *Tetrahedron Lett.*, 14, 1251 (1967).



with chlorosulfonic acid proceeds *via* an intermediate chlorosulfate XVIII which undergoes fragmentation (XIX) to give XVII and CO₂.

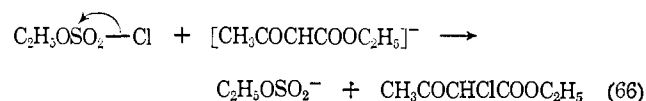


Somewhat related to the last instance is the reported¹³⁷ formation of methyl acetoxyethanesulfonate in 25% yield from the reaction of methyl chlorosulfate with methyl acetate in presence of zinc chloride.



An insertion process appears to be involved, as in the rearrangement of XV to XVI. A mechanism involving the intermediate formation of an acetoxysonylium ion has been proposed.⁸³

The reaction of ethyl chlorosulfate with sodio ethyl acetoacetate or with sodio malonate⁸¹ takes a quite unexpected course. Whereas one might have expected an alkylation to occur, the observed products are those of chlorination.



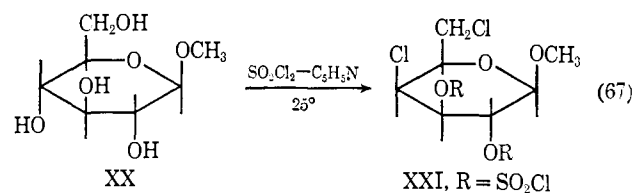
It appears that the acetoacetate and malonate anions act as nucleophiles toward chlorine. Further processes of this type are discussed in section V.

V. Carbohydrate Chlorosulfates

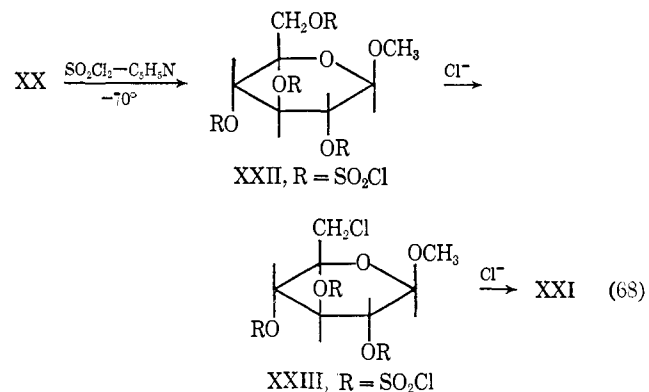
The reaction of sulfuryl chloride with carbohydrate derivatives was first investigated by Helferich and coworkers.¹³⁸⁻¹⁴⁰ The reagent apparently caused the substitution of hydroxyl groups by chlorine atoms or bridging by cyclic sulfate groups. Jones, Buncel, and coworkers elucidated the stereochemistry of the above reactions and extended the sulfuryl chloride-

sugar reaction to a large number of sugar derivatives.¹⁴¹⁻¹⁴⁶ This work has given rise to many chloro sugars and has cast new light on the mechanism of reaction of chlorosulfates. Some selected examples¹⁴³⁻¹⁴⁶ of the sugar chlorosulfate chemistry will be presented here to illustrate the stereochemical principles as well as the various bond scissions.

When methyl β-D-glucopyranoside (XX) is treated with sulfuryl chloride and pyridine in chloroform solution at room temperature, one obtains methyl 4,6-dichloro-4,6-dideoxy-β-D-galactopyranoside 2,3-dichlorosulfate (XXI); thus two hydroxyls have been replaced by chlorosulfate groups and two by chlorine atoms, the ring hydroxyl being replaced with inversion of configuration.^{143,144} When the reaction is carried



out at -70° and the reaction mixture carefully acidified at -30°, the product isolated is methyl β-D-glucopyranoside 2,3,4,6-tetrachlorosulfate (XXII). Reaction of XXII with 1 mole of chloride ion (pyridinium chloride or *n*-Bu₄NCl) yields methyl 6-chloro-6-deoxy-β-D-glucopyranoside 2,3,4-trichlorosulfate (XXIII). Reaction of either XXII or XXIII with excess chloride gives XXI. This series of reactions shows that (i) a



fully chlorosulfated sugar can be formed (it is quite a stable, nicely crystalline, compound); (ii) the primary chlorosulfate group on C₆ is first displaced, as expected for a nucleophilic substitution process; (iii) the one-step conversion of XX to XXI (eq 67) takes place *via* XXII, by reaction with the liberated chloride ion.

The fact that the chlorosulfate group at C₄ is preferentially displaced, relative to the other ring positions, is paralleled in the displacement of mesyl or tosyl groups and is due to both electronic and conformational factors. The transition state

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(138) B. Helferich, *Chem. Ber.*, 54, 1082 (1921).

(139) B. Helferich, A. Lova, W. Nippe, and H. Riedel, *ibid.*, 56, 1083 (1923).

(140) B. Helferich, G. Sprock, and E. Besler, *ibid.*, 58, 886 (1925).

(141) P. D. Bragg, J. K. N. Jones, and J. C. Turner, *Can. J. Chem.*, 37, 1412 (1959).

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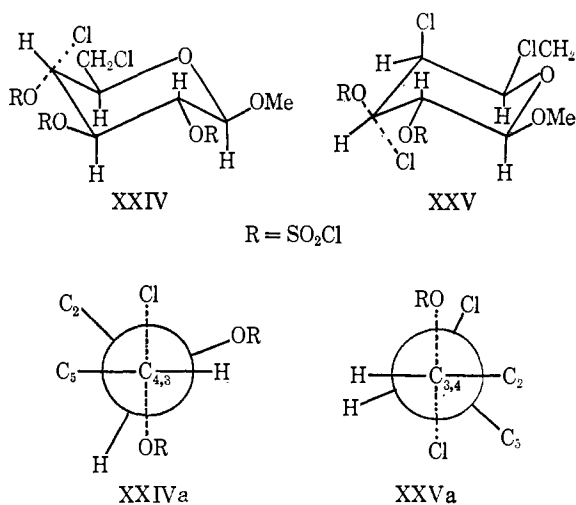
(143) H. J. Jennings and J. K. N. Jones, *ibid.*, 40, 1408 (1962); 41, 1151 (1963); 43, 2372, 3018 (1965).

(144) A. G. Cottrell, E. Buncel, and J. K. N. Jones, *Chem. Ind. (London)*, 522, (1966); *Can. J. Chem.*, 44, 1483 (1966).

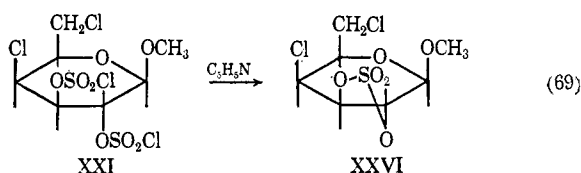
(145) S. S. Ali, T. J. Mephram, I. M. E. Thiel, E. Buncel, and J. K. N. Jones, *Carbohydr. Res.*, 5, 118 (1967).

(146) E. Buncel, H. J. Jennings, J. K. N. Jones, and I. M. E. Thiel, *ibid.*, 10, 331 (1969).

for substitution of OSO_2Cl by chloride at C_4 (XXIV and the end-on representation along the $\text{C}_4\text{-C}_3$ bond, XXIVa) may be compared with the corresponding structures XXV and XXVa for displacement at C_3 . It is apparent that the considerable skew interactions between the $\text{C}_4\text{-Cl}$ and $\text{C}_3\text{-OSO}_2\text{Cl}$ groups in XXV will cause that transition state to be energetically unfavorable with respect to XXIV for substitution at C_4 . Similarly, substitution of OSO_2Cl at C_2 in XXI is disfavored as a result of a 1,3 interaction between the axially disposed $\text{C}_4\text{-Cl}$ and the incoming chloride ion.



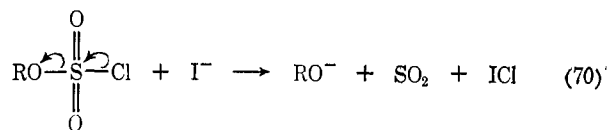
In contrast to the displacement process at carbon, observed in the above reactions, a different type of process occurs when XXI is treated with pyridine.¹⁴³



The product is a cyclic sulfate (XXVI), which is formed with retention at C_2 and C_3 . It is probable that one of the chlorosulfate groups is first hydrolyzed with retention (S-O bond scission); the free hydroxyl so formed undergoes displacement on the remaining chlorosulfate grouping (S-Cl bond scission) to give the product. The spatial requirement for the latter process is a very favorable one, since the two chlorosulfate groups in XXI are equatorially oriented. The conversion of several carbohydrate chlorosulfates into the fluorosulfate analogs by reaction with silver fluoride in aqueous methanol¹⁴⁶ provides another instance of sulfur-chlorine scission. By analogy with other systems involving silver ion catalysis⁹² this process can be presumed to have appreciable $\text{S}_\text{N}1$ character.

As the last illustration of the mode of reaction of sugar chlorosulfates, the reaction with iodide ion is considered. When a solution of a carbohydrate chlorosulfate in methanol is treated with sodium iodide in aqueous methanol, there is an immediate formation of iodine and an evolution of sulfur dioxide. The product of such a reaction is the original carbohydrate derivative that was caused to react with SO_2Cl_2 (apart from the $\text{C}_5\text{-OH}$ which is generally replaced by Cl); e.g., XXIII ($\text{R} = \text{SO}_2\text{Cl}$) when so treated gives methyl 6-chloro-6-

deoxy- β -D-glucopyranoside (XXIII, $\text{R} = \text{H}$), and XXI ($\text{R} = \text{SO}_2\text{Cl}$) gives methyl 4,6-dichloro-4,6-dideoxy- β -D-galactopyranoside (XXI, $\text{R} = \text{H}$). The chief point of interest is that the "dechlorosulfation" reaction takes place with retention of configuration. A possible mechanism of this reaction is displacement by iodide at chlorine (the ICl first formed would react with I^- to give I_2 and Cl^-).

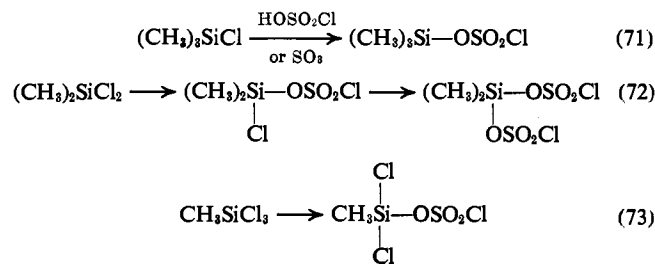


Sulfonyl halides are also known to undergo displacement on chlorine by iodide¹⁴⁶ and cyanide ion.¹⁴⁷ An alternative mechanism to the above (eq 70) would be formation of an intermediate, unstable, iodosulfate.

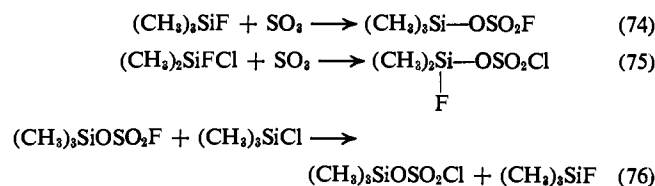
Studies with cyclohexyl chlorosulfates have been undertaken¹⁴⁸ with the purpose of finding a simpler reaction system but which will nevertheless have the characteristic structural features of the carbohydrate chlorosulfates, and thus to bridge the gap between the latter and their simple alkyl analogs.

VI. Organosilicon and Titanium Chlorosulfates

Organosilicon chlorosulfates have been investigated by several workers. Trimethylsilyl chlorosulfate, $(\text{CH}_3)_3\text{SiOSO}_2\text{Cl}$, is formed in excellent yield by the action of sulfur trioxide or chlorosulfonic acid on trimethylchlorosilane (eq 71).¹⁴⁹ Dimethyldichlorosilane when similarly treated gave first a mono- and then a dichlorosulfate (eq 72), but with methyltrichlorosilane only one chlorine could be substituted (eq 73). Reaction



of trimethylfluorosilane with sulfur trioxide gave¹⁵⁰ trimethylsilyl fluorosulfate (eq 74), but dimethylfluorochlorosilane yielded a chlorosulfate (eq 75). Interestingly, halogen exchange occurs between trimethylchlorosilane and trimethylsilyl fluorosulfate (eq 76).



Trimethylbromosilane or trimethyliodosilane did not yield the corresponding halosulfates on reaction with sulfur tri-

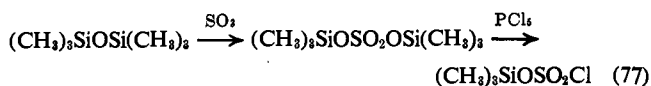
(147) B. Saville, *Chem. Ind.* (London), 660 (1956).

(148) E. Bunzel, work in progress.

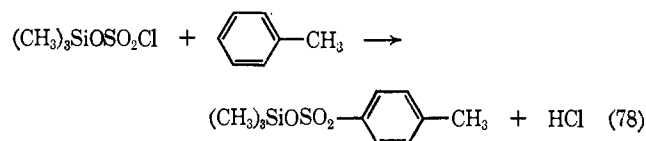
(149) M. Schmidt and H. Schmidbauer, *Angew. Chem.*, 70, 657 (1958).

(150) H. Schmidbauer, *Chem. Ber.*, 98, 83 (1965).

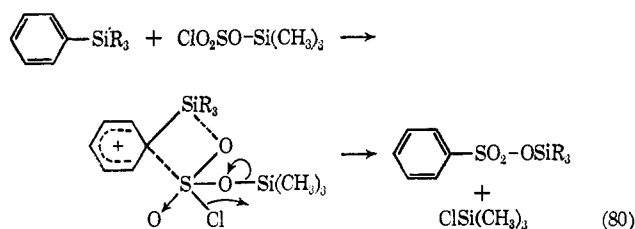
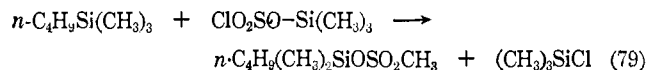
oxide.¹⁶⁰ An alternative route to trimethylsilyl chlorosulfate starts with hexamethyldisiloxane.¹⁵¹



The organosilicon chlorosulfates can be used^{149,151} as sulfonating agents toward aliphatic and aromatic compounds. For example, trimethylsilyl chlorosulfate reacts with toluene to give a silyl sulfonate ester (eq 78) which can readily be hydrolyzed to the sulfonic acid.



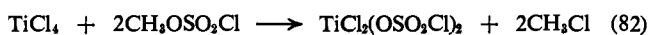
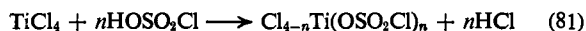
Reaction of trimethylsilyl chlorosulfate with alkylsilanes gives rise to silyl sulfonates,¹⁵² e.g., eq 79. The mechanism indicated in eq 80 was proposed¹⁵² for the reaction of phenylsilanes with trimethylsilyl chlorosulfate.



The hydrolysis of trimethylsilyl chlorosulfate (using 1 equiv of H₂O in ether) gave rise to trimethylsilyl hydrogen sulfate, by displacement of chloride.¹⁵³ Interestingly, hydrolysis of Me₂ClSiOSO₂Cl occurred¹⁵³ with stepwise bond cleavage in the order S-Cl, Si-Cl, and Si-O-S. Reaction of trimethylsilyl chlorosulfate with ammonia¹⁵³ gave (Me₃SiOSO₂)₂NH.

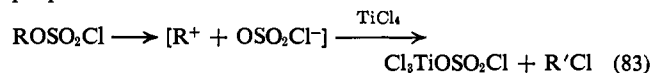
Reaction of tetramethyl titanate, (CH₃O)₄Ti, with excess sulfuryl chloride yields dimethyl dichlorosulfuryl titanate, (CH₃O)₂Ti(OSO₂Cl)₂.¹⁵⁴ When an equimolar proportion of sulfuryl chloride was used, dimethyl ether and methyl chloride were the only identifiable products.

Reaction between titanium tetrachloride and chlorosulfonic acid¹⁵⁵ gives rise to the series of chlorotitanyl chlorosulfates Cl_{4-n}Ti(OSO₂Cl)_n with n = 1, 2, or 3 (eq 81). Titanium sulfate, Ti(SO₄)₂, is also formed in this reaction. The chlorosulfates (n = 1 or 2) are also obtained from methyl chlorosulfate and titanium tetrachloride (e.g., eq 82). Reaction of n-propyl and



n-butyl chlorosulfates with TiCl₄ likewise yielded the chlorotitanyl chlorosulfates, but the resulting alkyl halide showed

almost complete rearrangement (e.g., n-BuCl yielded 95% of sec-BuCl, 5% n-BuCl). A carbonium ion process was hence proposed.¹⁵⁵



In accord with this mechanism, phenyl chlorosulfate and trichloroethyl chlorosulfate did not react with titanium tetrachloride.

Some analogous processes have been observed with aluminum trichloride.¹⁵⁶ Reaction with ethyl chlorosulfate yields AlCl₃(OSO₂Cl) and AlCl(OSO₂Cl)₂. These compounds are effective catalysts in the polymerization of isoprene or isobutylene.¹⁵⁶

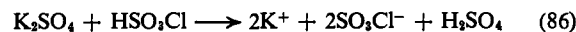
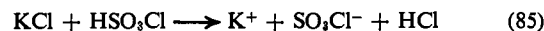
VII. Ionic Chlorosulfates

Chlorosulfates of metals (MSO₃Cl) have been extensively investigated. They were originally obtained¹⁵⁷⁻¹⁶² from the metal halides and gaseous or liquid sulfur trioxide; in addition to the alkali metal salts, compounds such as Cd(SO₃Cl)₂, Co(SO₃Cl)₃, and UO₂(SO₃Cl)₂ were so prepared. Further, in the metal halide-SO₃ reaction products of varying composition were reported: 2NaCl·SO₃ to NaCl·2SO₃,¹⁵⁸ or even to NaCl·3SO₃¹⁶¹ for the alkali metal halide addition products; NiCl₂·2SO₃, CuCl₂·2SO₃¹⁵⁹ for some of the other halides.

Recent preparative and structural studies show conclusively that the MCl·SO₃ addition products are the salts of chlorosulfonic acid. Thus the alkali metal and alkali earth metal salts can be prepared⁹⁰ simply from the metal halide and chlorosulfonic acid, e.g.



The more exotic chlorosulfates (CH₃)₄NSO₃Cl and PCl₄SO₃Cl were obtained⁹¹ by neutralization of tetramethylammonium chloride and phosphorus pentachloride, respectively, with chlorosulfonic acid in liquid hydrogen chloride. The salts are obtained as white solids on evaporation of the solvent. The tetramethylammonium and tetrachlorophosphonium chlorosulfates were investigated by infrared spectroscopy¹⁶³ and the alkali metal chlorosulfates by Raman spectroscopy.⁹⁰ The studies (see also ref 164 and 165) ascribe a tetrahedral structure to the chlorosulfate anion and identify the six fundamental vibrational frequencies associated with the C_{3v} symmetry; analogy with the related tetrahedral anions HSO₄⁻, SO₃F⁻, and CH₃SO₃⁻ was also pointed out. The Raman study⁹⁰ showed that KCl and K₂SO₄ in chlorosulfonic acid give rise to the chlorosulfate ion.



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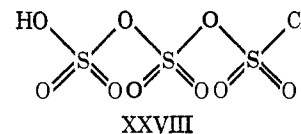
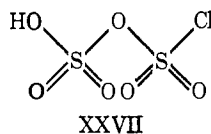
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Conductivity data of sodium and potassium chlorosulfates in chlorosulfonic acid were similarly interpreted.^{92, 166} Some ionic reactions of chlorosulfates were investigated.^{167, 168} Comparison has been made between the physical properties (magnetic moment, etc.) of chlorosulfates and their fluorosulfate analogs in the transition metal series.¹⁶⁹ Fluorosulfates have been contrasted with the parent fluorides.¹⁷⁰

Information on the structures of the addition products of the $\text{NaCl} \cdot 2\text{SO}_3$ type was obtained from Raman studies of the $\text{SO}_3\text{-HSO}_3\text{Cl}$ and $\text{NaSO}_3\text{Cl-SO}_3\text{-HSO}_3\text{Cl}$ systems.¹⁷¹ In the former case, the species present with small SO_3 concentrations is chlorodisulfuric acid (XXVII), while a trisulfuryl compound (XXVIII) forms when the SO_3 concentration is increased. Addition of NaSO_3Cl to a dilute solution of SO_3 in chlorosulfonic acid gave rise to the chlorodisulfate ion, $^-\text{OSO}_2\text{-}$



OSO_2Cl . The addition products $\text{NaCl} \cdot \text{SO}_3$, $\text{NaCl} \cdot 2\text{SO}_3$, and $\text{NaCl} \cdot 3\text{SO}_3$ were therefore formulated¹⁷¹ as salts of chlorosulfonic acid, chlorodisulfuric acid, and chlorotrisulfuric acid, respectively.

Nitrosyl chlorosulfate, which is prepared from nitrosyl chloride and sulfur trioxide¹⁷² or from nitrosyl chloride and chlorosulfonic acid,¹⁷³ has a crystal structure¹⁷³ corresponding to discrete NO^+ and SO_3Cl^- ions.

Acknowledgments. Thanks are due to Professor J. K. N. Jones and Dr. H. K. Hall, Jr., for discussion. Financial support by the National Research Council of Canada is gratefully acknowledged.

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