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The Reactions of Carbyl Sulfate with Weak Organic Bases

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THE REACTIONS OF CARBYL SULFATE WITH WEAK ORGANIC BASES

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THE REACTIONS OF CARBYL SULFATE

WITH WEAK ORGANIC BASES

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Cheryl J. Geiger

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I. INTRODUCTION

The objective of this thesis is the study of the reactions of carbyl sulfate with two classes of weak bases: alcohols and nitriles. Of lesser magnitude the thesis will present a synopsis of the probable mechanisms of the reactions of carbyl sulfate.

Carbyl sulfate is a cyclic organic sulfur compound. The structure is most often represented as is shown in Figure 1.

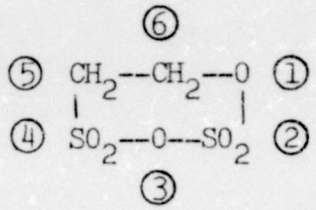


Figure 1. Carbyl Sulfate

Carbyl sulfate has the systematic name of 2,2,4,4-tetraoxo-1,3,2,4-dioxadithiane. The name encountered most often is 2-hydroxy-ethanesulfonic acid hydrogen sulfate-cyclic anhydride, and, less frequently, ethionic acid anhydride.

To facilitate identification of the reaction sites, the atoms are numbered, starting with the oxygen in the ring next to the carbon as number one. Sulfur-2 is known as the "sulfate" sulfur and sulfur-4 as the "sulfonyl" sulfur.

II. LITERATURE

The preparations, the properties, and the reactions of carbyl sulfate will be briefly examined in this section.

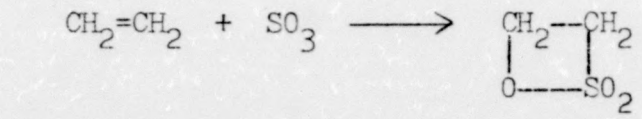
There are three reported methods of preparation of carbyl sulfate. The first synthesis was reported by G. Magnus in 1833.[1] He reacted anhydrous ethanol with excess sulfur trioxide. This synthesis was later modified by the use of liquid sulfur dioxide as the solvent.[2, 3, 8] The mechanism can be reasoned as follows: the electron deficient sulfur of the sulfur trioxide attacks the electron pair on the oxygen of the alcohol, forming ethyl hydrogen sulfate; the ethyl hydrogen sulfate eliminates sulfuric acid to yield ethylene; and this reacts with two moles of the sulfur trioxide to give the cyclic structure of carbyl sulfate.[13]

The second synthesis reacts isethionic acid (2-hydroxyethane-sulfonic acid) with two moles of sulfur trioxide.[4] This preparation has little use.

The last synthesis has the widest applicability. It was reported by V. Regnault in 1838.[4] In this synthesis, ethylene is reacted with sulfur trioxide in an anhydrous atmosphere at 160-180°C.[5-7] Air Products and Chemicals uses this method to manufacture the carbyl sulfate used in this work.

$$CH_2{=}CH_2 + \cdot 2SO_3 \longrightarrow \overline{OSO_2CH_2CH_2OSO_2} \qquad (1)$$

There have been two mechanisms proposed for this reaction. Gilbert proposed a four membered sultone as the intermediate, which undergoes reaction with another mole of sulfur trioxide to yield carbyl sulfate.[5, 37]



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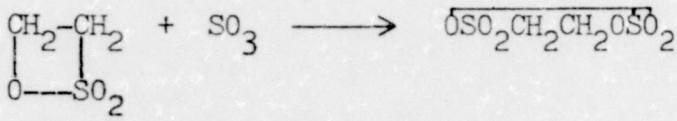
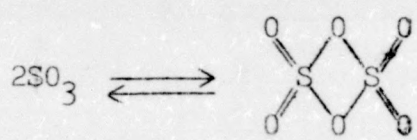


(3)

The evidence for the cyclic intermediate is based upon hydrolysis to 2-hydroxysulfonic acids,[6] and the isolation of the sultone itself when styrene is used as the starting compound.[5, 37]

Michael and Weiner postulated the formation of a sulfur trioxide dimer which reacts with ethylene to yield carbyl sulfate.[11]



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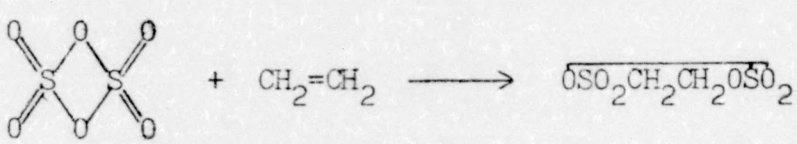


(5)

The reasoning for this mechanism is based upon the fact that polymerization of sulfur trioxide is known, and also on the fact that the sultone of Gilbert's mechanism has not been isolated.[11]

Carbyl sulfate is an extremely deliquescent, colorless crystalline solid. When completely free of solvent, the white needles melt at

107-108°C.[9, 13] The heat of formation is 158 kcal per mole, and its heat of combustion is 1240 cal per gram.[9] Carbyl sulfate's neutralization equivalent is calculated to be 94.1 based upon the expected ratio:

$$\overline{OSO_2CH_2CH_2OSO_2} + 2KOH \longrightarrow KOSO_2CH_2CH_2OSO_3K + H_2O \qquad (6)$$

Carbyl sulfate reacts with Lewis bases in a ring-opening reaction. The site of the ring opening depends upon the type of base. Water, alcohols, primary and secondary amines react in a similar fashion. Tertiary amines are distinctly different.

With water as the most common Lewis base, carbyl sulfate reacts to form ethionic acid.[1-4, 7, 8, 12, 13] The ethionic acid can then react further to isethionic acid in acidic solutions.[12, 13]

$$\overline{OSO_2CH_2CH_2OSO_2} + H_2O \longrightarrow HOSO_2CH_2CH_2OSO_3H \qquad (7)$$

$$H_2O + HOSO_2CH_2CH_2OSO_3H \xrightarrow{H^+} HOCH_2CH_2SO_3H + H_2SO_4 \qquad (8)$$

Alcohols, from the simple methyl alcohol to the complex cellulose, have been reacted with carbyl sulfate.[14-21] The general reaction is noted below:

$$\overline{OSO_2CH_2CH_2OSO_2} + ROH \longrightarrow ROSO_2CH_2CH_2OSO_3H \qquad (9)$$

In mildly alkaline solutions, alkyl esters formed in the above reaction can further react.[21]

$$ROSO_2CH_2CH_2OSO_3H + KHCO_3 \longrightarrow ROSO_2CH_2CH_2OSO_3K + H_2CO_3 \qquad (10)$$

In strongly basic solutions, aromatic and long chain alkyl esters eliminate sulfuric acid to form vinylsulfonate ester.[14-16, 20]

$$2NaOH + ArOSO_2CH_2CH_2OSO_3H \longrightarrow ArOSO_2CH{=}CH_2 + Na_2SO_4 + H_2O \quad (11)$$

Primary and secondary amines react analogously to alcohols and water, when in a ratio of one to one.[23-30]

$$\overline{OSO_2CH_2CH_2OSO_2} + RNH_2 \longrightarrow RHNSO_2CH_2CH_2OSO_3H \quad (12)$$

Mixed products result when the ratio of amine to carbyl sulfate is varied. A ratio of one to one results in the formation of the sulfonamide while a ratio of two to one yields the amine salt of the sulfonamide.[23, 29, 30]

$$\overline{OSO_2CH_2CH_2OSO_2} + R_2NH \longrightarrow R_2NSO_2CH_2CH_2OSO_3H \quad (13)$$

$$\overline{OSO_2CH_2CH_2OSO_2} + 2R_2NH \longrightarrow R_2NSO_2CH_2CH_2OSO_3^- \; NH_2R_2^+ \quad (14)$$

The sulfonamide, in the presence of base, forms a vinylsulfonamide.[23, 29, 30]

$$R_2NSO_2CH_2CH_2OSO_3H + NaOH \longrightarrow R_2NSO_2CH{=}CH_2 + NaHSO_4 + H_2O \quad (15)$$

Tertiary amines do not react in the same manner as the preceeding examples.[24, 26, 30] Using pyridine, Klass found the reaction product to be 2-(1-proto-1-pyridyl)-1-ethanesulfonate.[31]

$$\overline{OSO_2CH_2CH_2OSO_2} + \text{C}_5\text{H}_5\text{N} \longrightarrow \text{C}_5\text{H}_5\overset{+}{\text{N}}CH_2CH_2SO_3^- + SO_3 \quad (16)$$

Breslow and Hough,[9] and Wooton[13] report that when a strong base (NaOH) is added to carbyl sulfate, the vinylsulfonate results.

$$\overline{OSO_2CH_2CH_2OSO_2} + 3NaOH \longrightarrow CH_2{=}CHSO_3Na + Na_2SO_4 + 2H_2O \quad (17)$$

Carbyl sulfate in a sodium chloride melt yields the sodium vinylsulfonate.[35]

$$\overline{OSO_2CH_2CH_2OSO_2} + NaCl_{(l)} \longrightarrow CH_2{=}CHSO_3Na + HCl + SO_3 \quad (18)$$

Carbyl sulfate and aromatic compounds in the presence of a Friedel-Crafts catalyst will give a diaromatic compound.[32]

Wooton explained the reaction mechanism as follows: the Friedel-Crafts catalyst complexes sulfur dioxide in the carbyl sulfate ring, opening it; the adduct then reacts with one mole of the aromatic compound to form the ethylphenyl sulfate intermediate; this then eliminates hydrogen sulfate ion to give styrene, which reacts with another mole of the aromatic compound in a conventional alkylation reaction.[13]

Carbyl sulfate reacts with aqueous hydrochloric acid to give 2-chloroethanesulfonic acid.[33] The same product is observed in the reaction of isethionic acid and hydrochloric acid. Consequently, it is hypothesized that the reacting species is really isethionic acid. Reactions (7) and (8) show the relationship of carbyl sulfate and isethionic acid.

III. EXPERIMENTAL

A. Introduction

This research was roughly divided into two segments: one on the study of the reaction of carbyl sulfate with alcohols, and the other on the study of the reaction of carbyl sulfate with nitriles. There was a two-fold purpose for this. One reason was to attempt to elucidate the mechanism(s) of the reactions that carbyl sulfate can undergo. The second reason was to explore the possibility of reactions of carbyl sulfate and nitriles.

The first area of difficulty encountered is in handling and purification of carbyl sulfate.

The next area studied is carbyl sulfate's reaction with various alcohols. Methyl alcohol, ethyl alcohol, isopropyl alcohol, and tert-butyl alcohol were used in this study. Two problems were confronted in the alcohol work. One was the development of a handling procedure, a problem that was alleviated by the use of the serum bottle technique. The second problem was that of improvising a method for the determination of equivalents of free acid in the alcohol solutions.

The last segment deals with the reaction of carbyl sulfate with nitriles. The nitriles used in thus study were acetonitrile, acrylonitrile, and benzonitrile. Procedures were developed for the reaction, for the subsequent purification of the product, for the hydrolysis of the product, and for identification of the hydrolysis products.

B. Purification and Handling of Carbyl Sulfate

Since quantitative information was desired from the reactions of carbyl sulfate, especially from the reactions with the alcohols, a method of obtaining fairly pure samples was needed. The first handling problem had to do with the bulk of the crude carbyl sulfate that was supplied by Air Products and Chemicals. This was solved by liquifying the crude carbyl sulfate with an infrared lamp and then transferring to smaller bottles.

The crude carbyl sulfate is liquified with moderate heating. The liquid is then poured into a warm solution of 1,2-dichloroethane. There is an immediate separation into two phases, with the 1,2-dichloroethane on the top. The top layer is decanted and cooled. If the carbyl sulfate is too hot, the 1,2-dichloroethane solution will be darkly colored. There is, of course, some carbyl sulfate in the bottom layer, but heating of the two phases only decreases the purity of the top layer, and, thus, increases the number of recrystallizations needed to get pure carbyl sulfate. When crystallization is complete, the 1,2-dichloroethane is poured off. The crystals are transferred to another flask with fresh 1,2-dichloroethane and are slowly heated to about 70°. Most of the carbyl sulfate dissolves. A small lower liquid layer contains the impurities. The top layer is again decanted and cooled. Purity is enhanced when the solution is allowed to cool slowly. If further purification is required, the last step can be repeated.

To get the small quantities of highly pure carbyl sulfate, a modification of the serum bottle technique[38] was developed. The solvent-wet crystals of carbyl sulfate were transferred to sixty-ml serum bottles with fast solvent flashing at 60° and 20 mm in a vacuum oven.

The vacuum was then slowly vented through a drying tube packed with anhydrous calcium chloride. The serum bottles were then promptly sealed with pharmaceutical pullover bottle caps. The colorless crystals thus obtained were stable at room temperature for several days. Normally samples were prepared in this manner on the same day that the subsequent reactions were run.

C. Alcohol Reactions With Carbyl Sulfate

The target compounds of alcohol addition to carbyl sulfate in this study were the slightly volatile alkyl vinylsulfonates. See Plate 1.

(a) Initial attempts. (i) Using a Soxhlet apparatus, approximately ten grams of carbyl sulfate was extracted into one hundred milliliters of 1,2-dichloroethane. Fifty milliliters of a twenty per cent (by volume) solution of methanol in 1,2-dichloroethane was added to the carbyl sulfate solution. An exothermic reaction was noted. Analysis of the solution by gas chromatography revealed only the expected solvent and methanol components. (ii) A series of bases was employed to bring about the elimination of sulfuric acid. Sodium bicarbonate, tetramethylammonium hydroxide, and piperidine were added to separate solutions in small amounts. The solutions were analyzed before and after refluxing, but again there were only the expected volatile components. (iii) There was some indication in the hydrolysis work of Wooton[13] that the pH of the reaction medium was crucial in determining the path of the reaction. Using a titration procedure with a pH meter, aliquots at various "pH's" were taken and analyzed. Chromatographic analysis of these aliquots did not show any extra peaks. The columns used were polyphenyl ether 10%, Carbowax 20M, Carbowax 20M 10%, Porapak Q, and SE-30. The column temperatures were varied from 70° to 225°C.

(b) Quantitative studies with alcohols and carbyl sulfate. Having had little success with the non-quantitative procedure, a quantitative method[38] was modified. Direct titration of the carbyl sulfate-methanol solution with standardized methanolic potassium hydroxide using phenolphthalein as the indicator was attempted first. The ratios of base to carbyl sulfate were not reproducible, due to a fading endpoint. (Though not reproducible, the first color change from acid to base would be indicative of the initial free acid present in the solution.)

The procedure developed and consequently used was as follows: to the pure, preweighed sample of carbyl sulfate in the capped serum bottle, the alcohol was injected into the serum bottle, which was then weighed, heated twenty minutes in a 50° water bath, and reweighed for weight loss due to evaporation. Excess methanolic potassium hydroxide was then injected into the serum bottle which was weighed, heated in the 50° water bath for two to four hours, cooled and reweighed. The excess base was then titrated with standardized hydrochloric acid until the phenolphthalein pink disappeared. The serum bottle was again weighed.

To determine whether the alcohol addition or the base addition was the slow step, two experiments were attempted for clarification. For one set of duplicate runs, the time of heating the alcohol—carbyl sulfate solution was varied with all other times kept constant. In the other set, the time of heating after neutralization was varied. The heating periods were for five minutes, thirty minutes, one hour, and four hours. It was determined that the slow step was a neutralization (elimination or saponification) by base. Methanol and ethanol solvation (ring opening) of carbyl sulfate were very fast.

A neutralization of carbyl sulfate was done using the alcoholic base without prior addition of methanol, assaying by the back titration procedure. The ratio of base to carbyl sulfate was three to one under these conditions.

(c) Thermal elimination. Since no volatile components were found in the analysis of the quantitative runs, a straightforward addition and twenty-four hour reflux of the alcohol—carbyl sulfate reaction mixtures was attempted. Gas chromatographic analysis of these solutions indicated the presence of volatile components. A methanol—carbyl sulfate solution was subjected to vacuum distillation with a component distilling over in the range of 60-65° at approximately 1 mm pressure. Gas chromatographic analysis of this solution on an SE-30 column and a column temperature of 96° showed two components present. An unsaturation test (Br_2/CCl_4) was positive. An N.M.R. spectrum was taken of the distilled fraction and its most likely contaminant, dimethyl sulfate.

D. Nitrile Reactions With Carbyl Sulfate

Three nitriles were reacted with carbyl sulfate. Acetonitrile, acrylonitrile, and benzonitrile were used.

(a) General procedure. Pure, dry nitrile is added in five-fold excess to carbyl sulfate, either in 1,2-dichloroethane or in the absence of solvent. The solution is refluxed one to three hours. The yellow salt formed is separated by decantation and washed with 1,2-dichloroethane. The salt is added to cold water and neutralized with dilute sodium hydroxide. After evaporating the water under reduced pressure, the sodium salt is extracted with an azeotrope of acetone and methanol.

(b) Specific example. To 21.7 grams of dry, pure carbyl sulfate, freshly recrystallized from 1,2-dichloroethane, is added 45 ml of dry redistilled acrylonitrile and 20 ml of reagent 1,2-dichloroethane. The mixture is slurried to yield a clear, colorless solution. The solution is refluxed overnight, and then cooled. The reaction mixture now consists of a heavy yellow precipitate and a light yellow liquid phase. The salt is separated from the organic phase by decantation, then washed with warm 1,2-dichloroethane. The salt is then dissolved in thirty-five milliliters of cold water. A small amount of organic phase consisting of 1,2-dichloroethane and unreacted acrylonitrile is also present. The strongly acidic solution is then neutralized to pH 8 with dilute sodium hydroxide. The water is removed by evaporation under reduced pressure to yield a bright yellow crystalline mass, which is a mixture of sodium acryloyltaurate and inorganic salts. The yellow mass is extracted with hot methanol-acetone azeotrope, which yields a white crystalline solid.

(c) Hydrolysis of sodium N-acryloyltaurate. A portion of the crude sodium N-acryloyltaurate was dissolved in water and brought to pH 9 with dilute sodium hydroxide. The solution was then heated overnight. The water was evaporated under reduced pressure, and the residue was treated with hot methanol to remove the excess base. The residue was divided into two portions.

(d) Derivatives of the hydrolysis products. (i) To one portion of the residue, dilute hydrochloric acid was added and then the solution was extracted with ether. The ether was evaporated, and the liquid left was distilled. The distillate came over at 140°. Acrylic acid

boils at 141°. The derivatives of acrylic acid were prepared following the procedure in Pasto and Johnson.[39]

> In a 25-ml, round bottomed flask fitted with a condenser and a calcium chloride tube to exclude moisture, place 0.5 g of the anhydrous acid and add 2.5 ml of thionyl chloride. Reflux the mixture gently thirty minutes. To destroy the excess thionyl chloride, add formic acid. Divide the product into two fractions. To one fraction, add 7.5 ice-cold ammonium hydroxide. The precipitated amide can be recrystallized from water. To the other fraction, add 2.5 ml of benzene and add this to 1 g of aniline in 7.5 ml of benzene. Shake the reaction mixture with 3 ml of dilute hydrochloric acid to remove the excess aniline, wash the benzene layer with 3 ml of water, evaporate the solvent, and recrystallize the anilide from water.

(ii) The other portion of the residue was tested for the presence of taurine. Feigl's spot test[40] was used. The procedure is as follows:

> A small amount of the salt is mixed with several cgs of paraformaldehyde and heated to 140° to insure complete removal of the paraformaldehyde. Several cgs of benzoin are added, and the test tube is placed in an oil bath pre-heated to 130°. The open end of the test tube is covered with a disk of filter paper moistened with a solution of .08 g ferric chloride and .10 g of potassium ferricyanide in 100 ml of water. A positive response is shown by the appearance of a blue stain on the paper.

(e) Benzonitrile--Carbyl Sulfate Reaction. Whereas acetonitrile and acrylonitrile reacted similarly, benzonitrile differed from the two. After the refluxing period noted in the general procedure, the benzonitrile--carbyl sulfate reaction products crystallize upon cooling. All attempts to dissolve substantial amounts of the salt in water were futile. Some of the product did go into water to form an acidic solution, but not nearly as much as in the cases of the other two nitrile products. The product that did not dissolve in water sublimed at 170° at approximately 1mm of pressure. The atmospheric melting point was 232°.

All attempts to hydrolyze the sublimation product failed to give any other compound. The water soluble product was recovered by concentrating and cooling the solution. This compound had a melting point of 122°. The range of the mixed melting point using benzoic acid and the product was 116-119°. The amide derivative of the water soluble compound (as prepared according to the procedure noted in part (d)) had a melting point of 130°. Benzoic acid's amide derivative melts at the same temperature. Further data on these compounds are presented in the next section.

IV. RESULTS

A. Introduction

The data from this research divides along the alcohol and nitrile lines again. The alcohol section includes the mathematical method used to calculate the base to carbyl sulfate ratio, the table of the direct titration determination of the ratio (Table I), the table of the base: carbyl sulfate ratio using the back titration method (Table II), and the N.M.R. data on the distillate of the extended reflux (Table III). The nitrile section includes the elemental analyses of the reaction products of the carbyl sulfate-nitrile reactions.

B. Alcohol Analysis

The gravimetric determination of the base to carbyl sulfate ratio is shown below:

$$\text{mmoles of carbyl sulfate} = A = \frac{\text{weight of carbyl sulfate (g)}}{\text{molecular weight of carbyl sulfate}} \times 1000$$

$$\text{mmoles of total base} = B = \frac{\text{weight of standardized KOH (g)}}{\text{density of the solution}} \times \text{normality}$$

$$\text{mmoles of excess base} = C = \frac{\text{weight of standardized HCl (g)}}{\text{density of the solution}} \times \text{normality}$$

The ratio of equivalents of base per mole of carbyl sulfate equals (B-C)/A.

TABLE I

BASE: CARBYL SULFATE RATIOS WITH VARIOUS ALCOHOLS BY THE DIRECT TITRATION PROCEDURE AT 50°

Alcohol	mmoles of Carbyl Sulfate	mmoles of KOH (net)	Ratio Base: Carbyl Sulfate
methyl	1.61	1.87	1.16
ethyl	1.36	1.60	1.17
isopropyl	1.19	1.37	1.14
tert-butyl	1.25	3.11	2.56

TABLE II

BASE: CARBYL SULFATE RATIOS WITH VARIOUS ALCOHOLS AT 50°
AND REACTION TIME OF TWO HOURS

Alcohol	mmoles of Carbyl Sulfate	mmoles of KOH (net)	Ratio Base: Carbyl Sulfate
methyl	2.33	4.46	1.92
ethyl	1.73	3.21	1.86
isopropyl	.86	1.53	1.79
tert-butyl	1.25	3.53	2.82

TABLE III

N.M.R. SPECTRAL CORRELATIONS

Compound	Chemical Shift (δ)	Splitting
Methyl vinylsulfone[42], a		
vinylic group	5.8 - 7.32	multiplet (9)
methyl group	2.62	singlet
Sodium vinylsulfonate[13], b		
vinylic group	5.85 - 7.0	multiplet (7)
Methyl vinylsulfonate[15], c		
vinylic group	6.0 - 6.6	multiplet
Methyl vinylsulfonate[d]		
vinylic group	5.95 - 6.70	multiplet (8)
methyl group	3.82	singlet
Dimethyl sulfate[e]		
methyl group	3.92	singlet

[a] tetramethylsilane internal standard, CCl_4 solvent

[b] tetramethylsilane external standard, H_2O solvent

[c] tetramethylsilane internal standard, $CDCl_3$ solvent, only values given

[d] tetramethylsilane internal standard, CCl_4 solvent, present work, vinylic: methyl ratio is 1:1

[e] tetramethylsilane internal standard, CCl_4 solvent, present work

A few observations made during the alcohol work should be enumerated for later discussion. In the quantitative studies, a salt was formed during the neutralization of the alcohol--carbyl sulfate solutions. This salt was not identified in any case, but it was at least partially organic.

The tertiary alcohol--carbyl sulfate solutions developed a gas that had a sharp odor characteristic of unsaturation and gave a positive bromine-in-carbon-tetrachloride test. This gas was assumed to be isobutylene.

Using dry carbyl sulfate and methanolic potassium hydroxide without first opening the ring with an alcohol, a base to carbyl sulfate ratio of three to one was obtained.

The results of the extended reflux of the methyl alcohol--carbyl sulfate solution were consistent with the expected product, methyl vinylsulfonate. The positive bromine-in-carbon-tetrachloride test indicated unsaturation. The N.M.R. that was taken of the distillate had a multiplet in the vinylic region, and a doublet upfield. A singlet was expected for the methoxy group so it was suspected that one of the peaks of the doublet was really a contaminant's singlet. Dimethyl sulfate was added to the solution and an increase in only one of the peak's area was noted. It was thus reasoned that there were two components in the distilled fraction. This was substantiated by the gas chromatographic analysis of the fraction. The area under the integration curves, excluding the contaminant, agreed with the compound expected.

C. Nitrile Analysis

Three samples were analyzed by elemental analysis: one acetonitrile--carbyl sulfate sodium salt, one acrylonitrile--carbyl sulfate sodium salt, and the last the sublimation product from the benzonitrile reaction.

(a) Acetonitrile--carbyl sulfate sodium salt analysis.

Element	Found	45% sodium acetyltaurate*
C	11.44, 11.32	11.43
H	1.92, 1.91	1.92
N	3.81, 3.86	3.33

*balance inorganic salt, i.e. sodium sulfate

(b) Acrylonitrile--carbyl sulfate sodium salt analysis.

Element	Found	69% sodium acryloyltaurate*
C	20.32, 20.31	20.60
H	3.49, 3.49	3.45
N	5.03, 4.97	4.80
S	18.93, 18.79	18.20
Na	12.66, 12.65	13.04
O**	39.57, 39.79	39.91

*balance as $NaHSO_4 \cdot H_2O$

**by difference

(c) Benzonitrile--carbyl sulfate sublimation product analysis.

Element	Found	Predicted for 2,4,6-triphenyl-s-triazine monohydrate
C	77.09, 77.14	77.04
H	5.30, 5.25	5.23
N	12.79, 12.78	12.84
O	4.83, 4.89	4.89

V. DISCUSSION

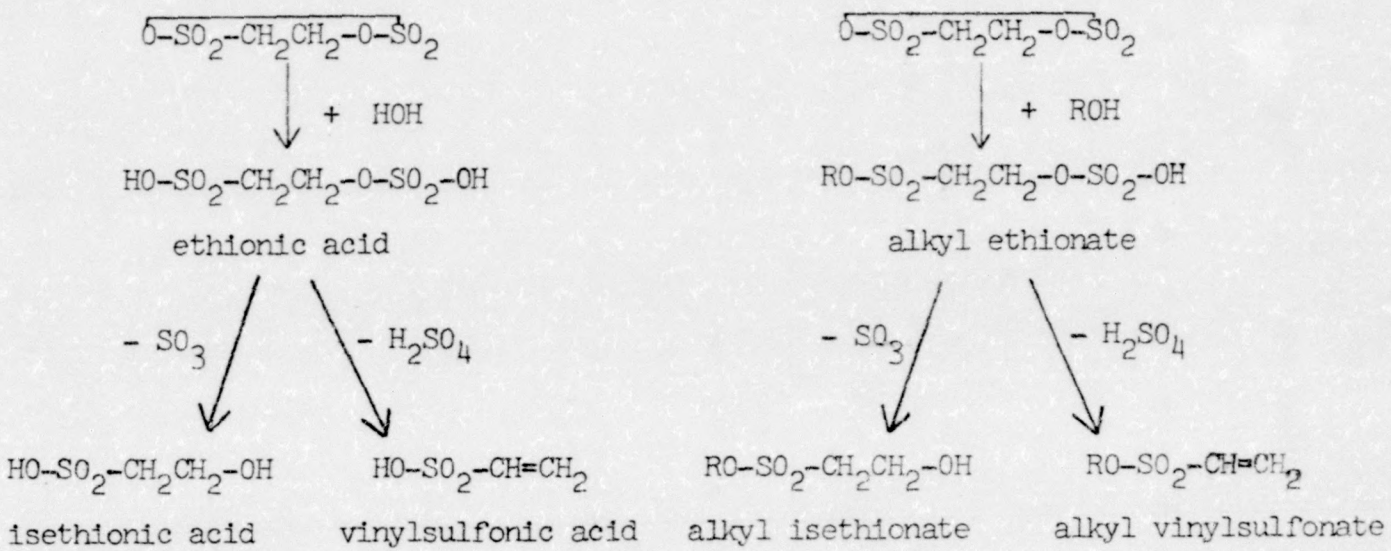
Since the alcohol study was initiated assuming there was similarity with the hydrolysis work of Wooton,[13] a brief examination of his work and the proposed similarities with alcohols is in order. Plate 1 illustrates the reaction paths of hydrolysis and the hypothesized reaction paths of alcoholysis.

Carbyl sulfate hydrolyzes to ethionic acid. Since carbyl sulfate is extremely deliquescent, ethionic acid was reported in the first publications of the syntheses of carbyl sulfate.[1-4] This acid cannot be isolated in the pure state due to its instability. Ethionic acid slowly reacts to form isethionic acid in acidic solutions. At intermediate pH's (6-10), ethionic acid readily eliminates to vinylsulfonic acid. Isethionic acid can be converted to vinylsulfonic acid by reaction with sulfuric acid to the ethionic acid, then neutralization to the vinylsulfonic acid.

(a) General observations. To apply this reaction scheme to alcoholysis, the first step should be the formation of the alkyl ester. As with hydrolysis, this step is rapid. This was tested during the quantitative analysis investigation by allowing different heating periods of the alcohol—carbyl sulfate solution. After solvation was complete, the length of the heating period did not affect the base to carbyl sulfate ratio. The addition of the alcohol to carbyl sulfate was exothermic, most noticeably with methanol and ethanol. While isolation and characterization of this alkyl ester were unsuccessful,

PLATE 1

PROPOSED REACTION SCHEME RELATING HYDROLYSIS AND ALCOHOLYSIS



the literature supports its presence by isolation of the potassium salt.[21] In the pure state, the ethionic esters are as unstable as is ethionic acid itself.

The target compound of the alcohol work was methyl vinylsulfonate. Thus some of these observations are only valid for the methanol--carbyl sulfate solutions.

The initial attempts noted under the experimental section can be summarized as follows: (1) the methyl ethionate ester does not spontaneously eliminate sulfuric acid to give the methyl vinylsulfonate. (2) The methyl ethionate ester does not form the vinylsulfonate ester in the presence of catalytic amounts of weak organic bases. (3) The ethionate ester, when titrated with base, does not form vinylsulfonate ester even in the presence of excess base.

Spontaneous elimination of sulfuric acid was not expected from the hydrolysis work; thus it was not surprising that the first few attempts to synthesize methyl vinylsulfonate failed. The second and third observations were somewhat unexpected though. Literature sources validate long chain and aryl vinylsulfonate ester formation from solutions of the alcohol and carbyl sulfate.[14-16, 20]

A few observations on alkyl vinylsulfonates, and methyl vinylsulfonate, in particular, are needed. Methyl vinylsulfonate is a toxic alkylating agent resembling dimethyl sulfate.[15] Methyl vinylsulfonate has a reported boiling point range of 54°-60°C at .2-.4 mm of pressure.[15] Methyl vinylsulfonate hydrolyzes easily to vinylsulfonic acid and methanol. In fact, a preparation of technically pure vinylsulfonic acid is made in this manner. The most common preparation of the alkyl vinylsulfonate esters involves basic catalysis of 2-chloroethanesul-

fonyl chloride in the alcohol.[41] With excess base, the alcohol adds to the double bond of the vinylsulfonate,[15] to form the methoxyethanesulfonic acid (anion). Aryl vinylsulfonate esters are stable toward hydrolysis. In fact, aryl vinylsulfonates can be synthesized in aqueous base.[14]

The second finding, that methyl ethionate does not eliminate with catalytic amounts of base present, must be due to the nature of the vinylsulfonate ester itself. The smallness of the methyl group permits S_N2 substitution, which in this case is easier than elimination of the sulfuric acid.[15]

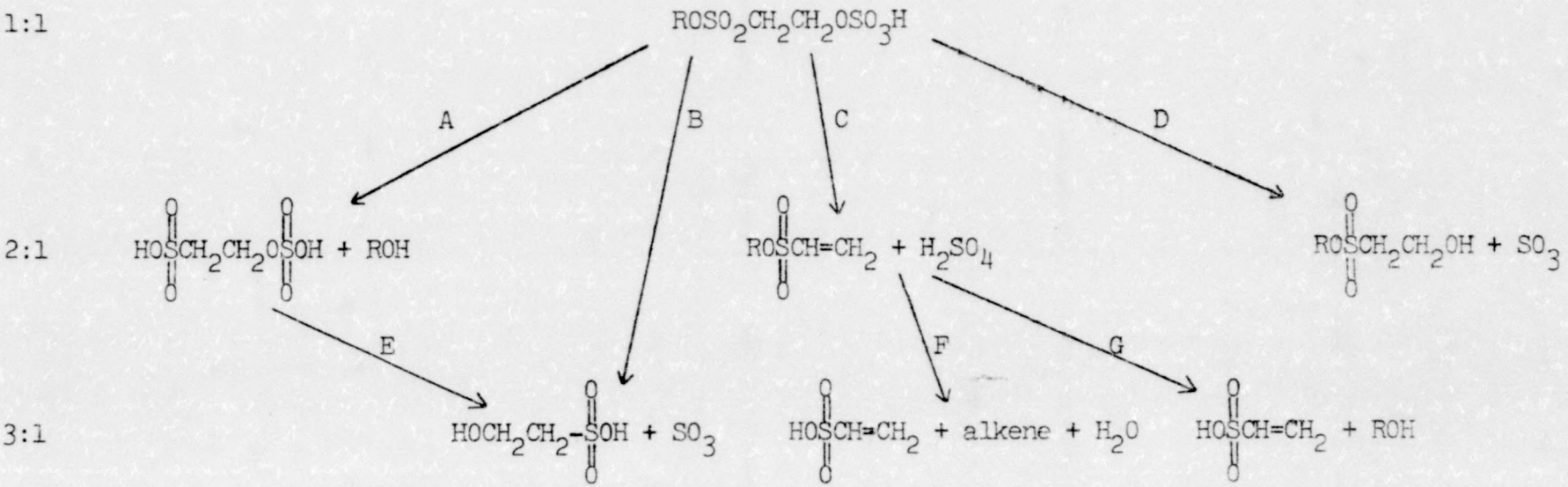
The third attempt, that of titration with a strong base, failed because of the abovementioned propensity for substitution rather than elimination and, perhaps, because of the tendency of the excess alcohol to add to the double bond in the presence of excess base.

Reconciliation of the literature claims of vinylsulfonate ester formation with these results can be accomplished by examining the actual procedures involved. The alkyl vinylsulfonates that have been made from carbyl sulfate have been derivatives of long chain alcohols. These substituents are not sterically open for nucleophilic substitution. Not being generally susceptible to nucleophilic substitution, aryl vinylsulfonates are not easily attacked either.

(b) Quantitative studies with alcohols and carbyl sulfate. These studies were initiated to try to deduce the reaction scheme in the alcohol--carbyl sulfate solutions upon addition of base. Two primary alcohols, a secondary alcohol, and a tertiary alcohol were used to see if the course of the reaction were related to the alkoxy substituent. See Plate 2 for the probable reactions. The expected salts formed

PLATE 2

REACTION PATHS



from neutralization are listed in Table IV. In all alcohol--carbyl sulfate solutions, the initial step was considered to be the ring opening reaction forming the alkyl ethionate ester. If the methyl ethionate product is stable, then the base to carbyl sulfate ratio would be one to one. There would be no ratio dependence on the alkoxy substituent. There is literature evidence that with low concentrations of base this is true.[21]

If the methyl sulfonate ester linkage is hydrolyzed (A), forming the ethionate dianion, then the ratio of base to carbyl sulfate would be two to one. The hydrolysis work of Wooton predicts elimination of sulfur trioxide from the ethionate dianion (E) in intermediate pH's. This would give a ratio of three to one. The hydrolysis of the ester linkages would be rate determining. The methyl ethionate ester would hydrolyze the easiest; thus the ratio would decrease from methyl to ethyl to isopropyl alcohol.

If both ester linkages are hydrolyzed (B), forming the isethionate anion and inorganic sulfate, the ratio would be three to one. Again the ratio from methyl to isopropyl alcohol would decrease.

If the alkyl ethionate ester eliminates sulfuric acid (C), forming the vinylsulfonate ester, the ratio would be two to one. Path C is valid for aryl and long chain alkyl groups as supported by literature.[14-16, 20] Also primary and secondary amines react with carbyl sulfate and in the presence of strong base eliminate to the vinylsulfonamide. The amide linkage is not easily hydrolyzed.[22] If path C occurs, a possible side product in the tertiary alcohol--carbyl sulfate solutions would be isobutylene (F). If after elimination, hydrolysis occurs (G), forming the vinylsulfonic acid, the base to carbyl sulfate

TABLE IV

NEUTRALIZATION SALTS

Path	Salt	Ratio Base: Carbyl Sulfate
A	$KOSO_2CH_2CH_2OSO_3K$	2:1
B, E	$HOCH_2CH_2OSO_3K$, K_2SO_4	3:1
C, D	K_2SO_4	2:1
F, G	$KOSO_2CH{=}CH_2$, K_2SO_4	3:1

ratio would be three to one. Since a tertiary alcohol would be harder to hydrolyze (the second step (F or G) would be rate determining), the ratio would decrease.

If the sulfate ester linkage is hydrolyzed (D), forming the isethionic ester and inorganic sulfate, the ratio would be three to one. In this case, the ratios from primary to secondary to tertiary alcohol would not change, because the alkoxy linkage is undisturbed. Path D would be expected to occur under acid conditions if the correlation with hydrolysis is valid. The reaction conditions are not acidic though, but basic.

Considering the direct titration data (Table I), it is apparent that methanol, ethanol, and isopropanol have similar ratios. The fading endpoint in this experiment points to an easily hydrolyzable ester function. Also apparent is the fact that all the ratios are greater than one; thus the alkyl ethionate is not the stable product. The fact that three values are similar points to either the hydrolysis of the same sulfate ester linkage in each case, or that there is little difference in the case of hydrolysis of the sulfonate ester functions. The tertiary alcohol value is much greater, indicating a different path, probably C-F or G.

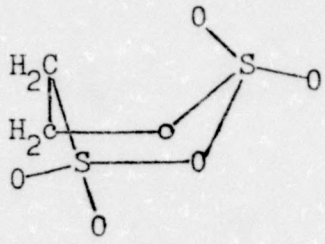
The back titration data (Table II) shows an overall increase in the ratio from primary to tertiary alcohol, but a slight decrease in going from methyl to ethyl to isopropyl alcohol. Accepting path C for the tertiary alcohol appears valid based on the actual ratio found plus the production of isobutylene in the acid solution before neutralization. Path C cannot be accepted for the primary and secondary alcohols, because it would lead to a ratio of three to one, while the upper limit

of the ratio actually found is two. (The short chain alkyl esters hydrolyze easily; so path F or G would also occur with these esters.)[15] Path D is unacceptable for primary or secondary alcohols since such a path would be independent of the nature of the alcohol while the data shows a consistent and significant dependency. Path B has a ratio of three to one whereas the data's upper limit appears to be two to one. Path A seems to fit the data the best. It was found upon extended reflux that the methyl, ethyl, and isopropyl alcohol ratios could be pushed over two to one, but the conditions were so severe, that the data gathered were suspect. It is not unlikely though that the ethionate dianion could undergo further hydrolysis under these conditions.

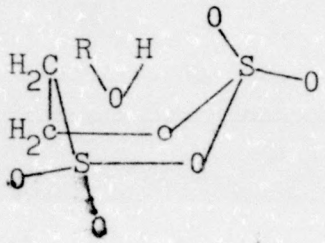
In summary on this part of the quantitative section, there seems to be two different paths indicated. No final determination was made in this study.

One reaction study was done using the standardized methanolic potassium hydroxide and dry carbyl sulfate without first adding methanol. The base to carbyl sulfate ratio was found to be three to one. The ratio found when methanol was used to open the ring then neutralized with methanolic base was two to one. The difference here is in the mechanism of ring opening. In the reaction with the ratio of three to one, the attacking species is the hydroxide ion, forming the vinylsulfonate anion and inorganic sulfate. The attacking species of the reaction with the ratio of two to one is the soft base, methanol, forming the ethionate dianion. Using water as a soft base, Breslow and Hough found the ratio to be two to one.[9] Here the acid being neutralized was ethionic acid, not carbyl sulfate.

(c) Thermal elimination. The elimination of hydrogen sulfate from the methyl ethionate ester yields the methyl vinylsulfonate. The by-product, dimethyl sulfate, can be explained as the reaction of the hydrogen sulfate and methanol in the solution under the severe reaction conditions. The presence of methyl vinylsulfonate substantiates the expected mode of addition. This reaction, which can be conveniently viewed with carbyl sulfate in the boat conformation,



is illustrated below:



$$\longrightarrow \quad R\text{-}O\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{-}CH_2\text{-}CH_2\text{-}O\text{-}SO_3H \qquad (19)$$

$$R\text{-}O\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{-}CH_2CH_2\text{-}O\text{-}SO_3H \longrightarrow R\text{-}O\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{-}CH{=}CH_2 + H_2SO_4 \qquad (20)$$

(where R = methyl). The bond cleavage must be between the "sulfonyl" sulfur and the "sulfate" sulfur. The oxygen of the alcohol attacks the "sulfonyl" sulfur and the hydrogen of the alcohol becomes attached to the oxygen of the "sulfate" sulfur.

This attack was predicted from the literature using phenol and long chain alcohols as precursors.[14-16, 20] This is also the familiar ring opening reaction in hydrolysis.[13]

(d) Acetonitrile and acrylonitrile reactions with carbyl sulfate. The most thorough analysis was made on the reaction product of acrylonitrile and carbyl sulfate, but it is assumed that the analysis of acetonitrile--carbyl sulfate reaction product would yield similar results. The reaction scheme for the acrylonitrile reaction is shown in equations (21) and (22).

$$\overline{OSO_2CH_2CH_2OSO_2} + CH_2{=}CHC{\equiv}N: + H_2O \longrightarrow CH_2{=}CHCONHCH_2CH_2SO_3H + H_2SO_4 \quad (21)$$

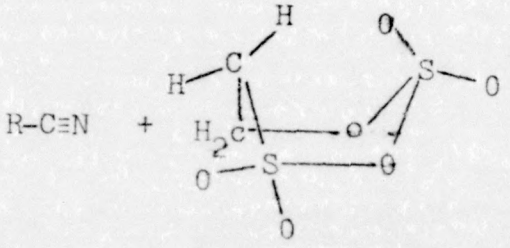
$$CH_2{=}CHCONHCH_2CH_2SO_3H + NaOH \longrightarrow CH_2{=}CHCONHCH_2CH_2SO_3Na + H_2O \quad (22)$$

Hydrolysis of sodium N-acryloyltaurate involves cleavage of the acyl group from the taurine.

$$CH_2{=}CHCONHCH_2CH_2SO_3Na + NaOH \longrightarrow CH_2{=}CHCO_2Na + NH_2CH_2CH_2SO_3Na \quad (23)$$

$$CH_2{=}CHCOONa + HCl \longrightarrow CH_2{=}CHCOOH + NaCl \quad (24)$$

The bond cleavage is between carbon-six and oxygen-one in the ring. The products obtained here involve cleavage at the same bond found in Klass's work with pyridine.[31]



$$\longrightarrow R\text{-}C{\equiv}\overset{(+)}{N}\text{-}CH_2CH_2SO_3^{(-)} + SO_3 \quad (25)$$

$$R\text{-}C{\equiv}\overset{(+)}{N}\text{-}CH_2CH_2SO_3^{(-)} \rightleftharpoons R\text{-}\overset{(+)}{C}{=}N\text{-}CH_2CH_2SO_3^{(-)} \quad (26)$$

$$R\text{-}\overset{(+)}{C}\!=\!\ddot{N}\text{-}CH_2CH_2SO_3^{(-)} + H_2O \longrightarrow R\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH\text{-}CH_2CH_2SO_3H \qquad (27)$$

N-acyltaurines have usually been synthesized via the Schotten-Baumann reaction:[43, 44]

$$R\text{-}COCl + H_2NCH_2CH_2SO_3^- + OH^- \longrightarrow R\text{-}CONH\text{-}CH_2CH_2SO_3^- + H_2O + Cl^- \qquad (28)$$

Another standard method to prepare the taurine makes use of the acid anhydride:

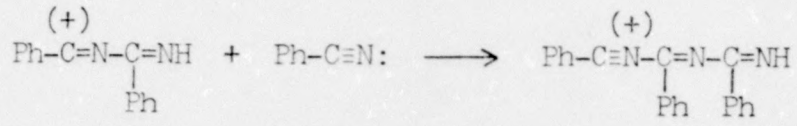
$$(R\text{-}CO)_2O + H_2N\text{-}CH_2CH_2SO_3^- + OH^- \longrightarrow R\text{-}CONH\text{-}CH_2CH_2SO_3^- + H_2O + RCOO^- \qquad (29)$$

There are two preparations for N-acryloyltaurine noted in the literature. Both are Schotten-Baumann syntheses. One is the Schotten-Baumann reaction of 3-chloropropanoyl chloride with taurine, presumably to give the intermediate N-(3-chloropropanoyl)taurine, followed by treatment with strong base at room temperature, to effect dehydrohalogenation.[46] The other preparation reacts acryloyl chloride with taurine in the presence of base.[47]

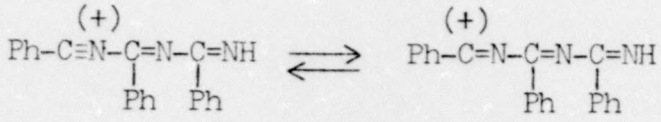
(e) Benzonitrile reaction with carbyl sulfate. The benzonitrile--carbyl sulfate reaction is thought to differ from the preceeding reactions because of the severity of the reaction conditions. The formation of 2,4,6-triphenyl-s-triazine occurs with the acid catalyzed trimerization of benzonitrile.[48, 49]

$$Ph\text{-}\overset{(+)}{C}\!=\!\ddot{N}H + Ph\text{-}C\equiv N: \longrightarrow Ph\text{-}\overset{(+)}{C}\equiv N\text{-}\underset{\displaystyle Ph}{\underset{|}{C}}\!=\!NH \qquad (30)$$

$$Ph\text{-}\overset{(+)}{C}\equiv N\text{-}\underset{\displaystyle Ph}{\underset{|}{C}}\!=\!NH \rightleftharpoons Ph\text{-}\overset{(+)}{C}\!=\!\ddot{N}\text{-}\underset{\displaystyle Ph}{\underset{|}{C}}\!=\!NH \qquad (31)$$



(32)



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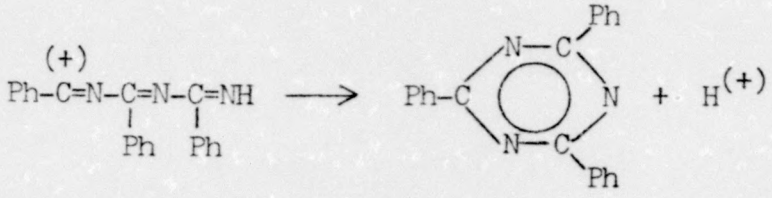
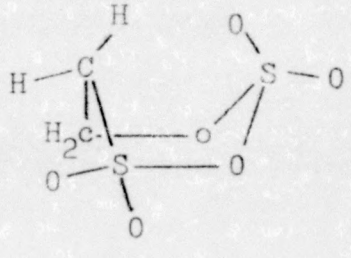


(34)

The other product, benzoic acid, was formed from the acid hydrolysis of the nitrile. Isolation of the N-benzoyltaurine was not accomplished at this time.

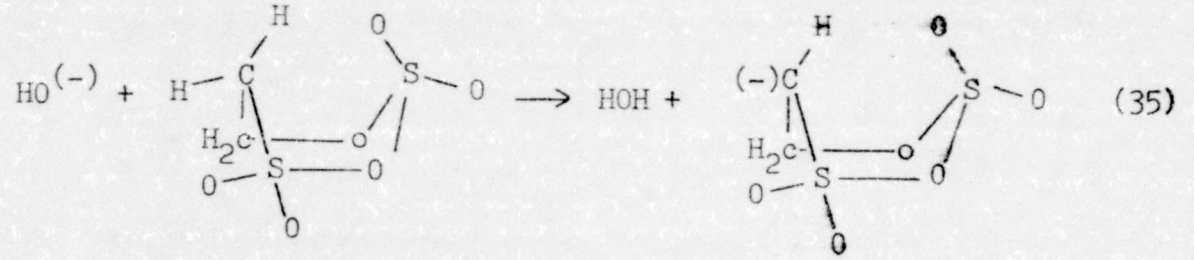
(f) Synopsis of proposed ring-opening mechanisms. A three-dimensional structural representation of carbyl sulfate is useful in understanding its ring-opening reactions with Lewis bases.

A six-membered, non-aromatic ring is normally pictured in the chair conformation, this being the most stable. However, the boat conformation is expected to be the most stable for carbyl sulfate. The chair conformation has, as seen by space filling models, considerable axial repulsion between two sulfur-attached oxygen atoms, whereas the boat conformation minimizes this interaction and may possibly have some extra stabilization due to an oxygen-hydrogen interaction (carbon-five's flagpole hydrogen with sulfur-two's oxygen).

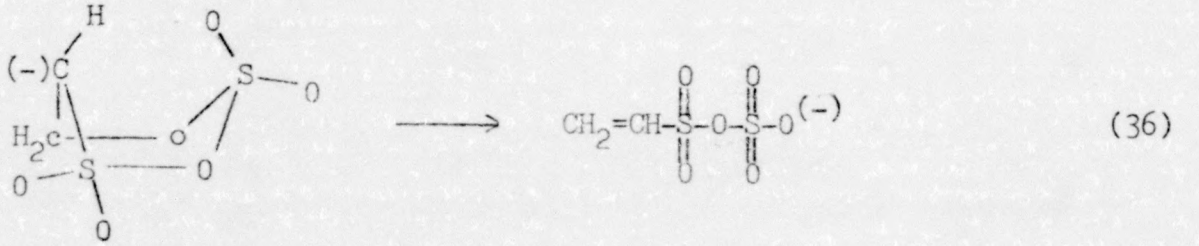


The terms 'hard' and 'soft' in the next few paragraphs are applied to Lewis acids and bases in the sense first introduced by Ralph Pearson.[50] Hardness refers to these factors, or a combination of them: small size, low polarizability, high electronegativity, and empty orbitals of high energy. Softness refers to: large size, greater polarizability, and low lying orbitals. In Pearson's concept, hard will prefer hard and soft will prefer soft.

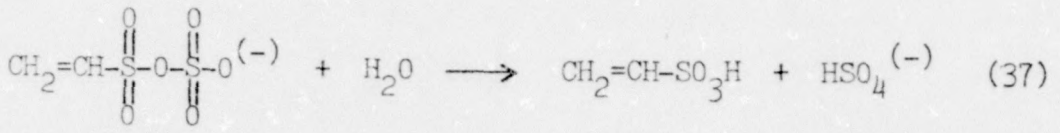
The first base---carbyl sulfate reaction mechanism to be considered involves the hard Lewis base, for example, the hydroxide ion, the amide anion, or the phenoxide anion. Attack of a hard base is thought to proceed via the ElcB mechanism. With hydroxide ion as the hard base, the reaction products are the vinylsulfonate anion and the inorganic salt. The attack is on the equatorial hydrogen of carbon-five. This hydrogen is the harder of the two at carbon-five, due to the interaction of the "sulfate" oxygen and the flagpole hydrogen. The hard base first abstracts a proton; this is followed by ring opening and elimination of sulfate. Reactions (35), (36), and (37) illustrate this mechanism.



(35)



(36)



(Alternately, reactions (35) and (36) may occur simultaneously, in an E2 mechanism.)

The next mechanism to be considered entails attack by a soft Lewis base with active hydrogens available. Examples of these types of bases are primary and secondary amines, alcohols and water. The attack is on the "sulfonyl" sulfur (S-4). This is the most familiar ring opening reaction. This attack is favored by the favorable stereochemistry of the intermediate. There is a strainless-concerted, acid-base type interaction with the "sulfonyl" sulfur and the flagpole oxygen attached to the "sulfate" sulfur. This mechanism is shown in reactions (19) and (20).

The third mechanism is an S_N2 displacement on carbon-six, brought about by the attack by a neutral Lewis base with no active hydrogens. This low energy attack is on the carbon with the best leaving group available, namely, sulfate. The types of bases that fall into this category are nitriles, tertiary amines, and, possibly, disubstituted amides. Klass's work with pyridine, and the current work with nitriles, exemplify the mechanism. The product is zwitterionic. This mechanism is illustrated in reaction (25).

In summary, the reactions of carbyl sulfate are dependent upon the type of base effecting the reaction. A hard base will bring about elimination to the vinylsulfonate anion and the sulfate anion. A soft base with active hydrogens will yield the ethionate intermediate. A soft base without active hydrogens reacts to give a zwitterionic product and sulfur trioxide.

VI. CONCLUSION

This study has examined the reactions of carbyl sulfate with two classes of weak organic bases: nitriles and alcohols. This thesis has presented probable mechanisms for the reactions of carbyl sulfate with Lewis bases.

The first synthesis of short chain alkyl vinylsulfonates via the alcohol reaction with carbyl sulfate is described. The proof of the methyl vinylsulfonate ester is based on the N.M.R. spectrum, the close correlation of the reported boiling point, and the positive unsaturation test.

This is the first reported study of the reactions of carbyl sulfate with nitriles. The first known preparation of N-acyltaurines via carbyl sulfate is disclosed.

A synopsis of the proposed mechanisms of carbyl sulfate reactions with Lewis bases concludes the study. Ring opening occurs by an ElcB-type mechanism with hard bases; soft Lewis bases without active hydrogens elicit an S_N2-type ring opening; and soft Lewis bases with active hydrogens take advantage of the favorable stereochemistry of the carbyl sulfate ring to effect a 3,4-ring opening.

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APPENDIX A

CHEMICALS USED

1. Carbyl sulfate, technical grade, Air Products and Chemicals.
2. 1,2-dichloroethane, spectro grade, Matheson, Coleman, and Bell.
3. Methanol, spectro grade, Matheson, Coleman, and Bell.
4. Ethanol (Abs.)
5. Isopropyl alcohol, reagent grade, Baker Chemicals.
6. tert-Butyl alcohol, reagent grade, Baker Chemicals.
7. Potassium hydroxide, reagent, 45%, Matheson, Coleman, and Bell; Baker Chemicals.
8. Hydrochloric acid, reagent, Baker Chemicals.
9. Sodium hydroxide, 50% soln., reagent, Matheson, Coleman, and Bell.
10. Benzonitrile, reagent, Baker Chemicals.
11. Acrylonitrile, reagent, Matheson, Coleman, and Bell.
12. Acetonitrile, reagent, Matheson, Coleman, and Bell.
13. Magnesium sulfate, anhydrous reagent, Matheson, Coleman, and Bell.
14. Piperidine, reagent, Matheson, Coleman, and Bell.
15. Tetramethylammonium hydroxide, 24% in methanol, Matheson, Coleman, and Bell.
16. Sodium bicarbonate, reagent, Fisher Scientific.
17. Acetone, N.F. purified, Baker Chemicals.
18. Calcium chloride, anhydrous, Matheson, Coleman, and Bell.
19. Phenolphthalein, reagent, ACS, powder.
20. Thionyl chloride, practical, Matheson, Coleman, and Bell.

APPENDIX A, CONTINUED

21. Ammonium hydroxide, reagent, Baker Chemicals.
22. Aniline, practical, Matheson, Coleman, and Bell.
23. Ferric chloride, reagent, Fisher Scientific.
24. Potassium ferricyanide, reagent, Matheson, Coleman, and Bell.
25. Paraformaldehyde, 95%, Matheson, Coleman, and Bell.
26. Benzoin, practical, Matheson, Coleman, and Bell.

APPENDIX B

INSTRUMENTS USED

1. Gas chromatograph: Varian Aerograph 202-1C
2. N.M.R. spectrometer: Varian A-60A