onto ice, extracted with chloroform, washed with 85% phosphoric acid, then with water, and dried over magnesium sulfate. On removal of the chloroform at room temperature, 3.5 g (95%) of an oil remained. Infrared and vpc analysis indicated the absence of starting alcohol but showed the presence of an impurity (infrared peak at 5.95 μ) which was undoubtedly 1-phenyl-1-butene from either dehydration of the alcohol or dehydrohalogenation of the product. Attempted purification *via* gas chromatography on a UCON polar on firebrick column at 130° resulted in further decomposition to this dehydrohalogenation product in the preheater (130°) and detector sections of the gas chromatography apparatus. The crude oil was therefore distilled under high vacuum. The rotation of the product when taken immediately after distillation was $\alpha^{24.5}\text{D}$ +37.70 ± 0.02° (l = 0.5, neat) but after 26 hr had fallen to $\alpha^{23}\text{D}$ +33.65 ± 0.02° (l = 0.5, neat).

(+)-**1-Phenylbutane-1-*d*** (V). To a solution of lithium aluminum deuteride[31] (0.4 g, 0.0095 mole) in 30 ml of dry tetrahydrofuran (distilled from lithium aluminum hydride) was added 1.8 g (0.0107 mole) of the above (+)-α-chlorobutylbenzene, $\alpha^{24.5}\text{D}$ +33.65 ± 0.02° (l = 0.5, neat), in 10 ml of dry tetrahydrofuran under a dry nitrogen atmosphere. The addition was complete in 10 min and the reaction mixture was refluxed for 29 hr, then decomposed in the cold with a 50:50 mixture of tetrahydrofuran and water. After extraction with 95% pentane and drying over calcium chloride, the solvent was removed on a glass helix packed column and the residue was purified *via* gas chromatography to give 1-phenylbutane-1-*d*, $\alpha^{25.2}\text{D}$ +0.57 ± 0.01 (l = 1, neat).

Rechromatography of this sample on an analytical column showed none of the parent alcohol or chloride and approximately 0.3% of an unknown, low-boiling impurity. The infrared showed a peak at 4.65 μ (C–D) and deuterium analysis by nmr indicated 0.96 ± 0.02 deuterium atom per molecule.

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[31] Metal Hydrides, Inc., reported to be "95% pure."

The Role of Sulfene Intermediates in the Alcoholysis of Sulfonyl Halides in the Presence of Triethylamine[1]

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Contribution from the Department of Chemistry, Purdue University, Lafayette, Indiana. *Received January 12, 1966*

Abstract: Evidence for sulfene formation in the reactions of alkanesulfonyl chlorides, methanesulfonyl bromide, and methanesulfonic anhydride with triethylamine has been obtained, consisting of the formation of monodeuterated esters (in the absence of di- and trideuterated esters) when these reactions are carried out in the presence of methanol- and ethanol-*d*. The effect of the leaving group, the structure of the sulfonyl chloride, and the solvent on the deuterium content of the esters indicate competing elimination and substitution reactions between the sulfonyl halide and triethylamine, eventually giving rise to deuterated and undeuterated esters. Products obtained from the isomeric propenesulfonyl chlorides provide further evidence for this competition.

Sulfene intermediacy has received much attention recently, particularly regarding its apparent role in cycloadditions with various electron-rich olefins.[2] In nearly all cases the sulfene intermediate postulated was generated by treatment of an alkanesulfonyl chloride with triethylamine. Staudinger[3] reported that when sulfur dioxide is bubbled through a methanolic solution of diphenyldiazomethane, a high yield of methyl diphenylmethanesulfonate is obtained. They postulated an initial reaction of the diazo compound with sulfur dioxide to give diphenylsulfene which then added methanol. More recently, deMayo and co-workers[4] proposed the addition of alcohol to a sulfene for the photolytically induced transformation of an unsaturated sultone to a sulfonate ester.

From these results it seemed likely that sulfenes generated by the reaction of sulfonyl chlorides with triethylamine should also add alcohol. These reactions in the presence of alcohol-*d* should give rise to *monodeuterated* sulfonate esters. The absence of *polydeuterated* species would preclude deuterium incorporation by simple exchange.

Results

A number of sulfonyl chlorides, methanesulfonyl bromide, and methanesulfonic anhydride were treated with ordinary and deuterated alcohols in the presence of triethylamine. The reactions were carried out in an inert solvent (benzene or hexane) under anhydrous conditions. A benzene solution of the sulfonyl chloride was added over a 20-min period to a mixture of the alcohol (1.2 equiv) and triethylamine (1.3 equiv) dissolved in benzene. The reactions were worked up after stirring for 1.5 hr at room temperature. The sulfonate esters obtained were characterized by comparison of their physical properties with literature values when available and by their infrared and nmr spectra. The nmr spectra were used to determine the position of deuterium incorporated and the product ratios when mixtures were obtained. Mass spectral analysis[5] was used to determine the deuterium distribution (*mono- vs. polydeuteration*). The parent peak and the alkyl fragment obtained upon cleavage of the carbon–sulfur bond were useful in this respect. In all cases, the esters obtained from deuterio alcohols were found to be *monodeuterated* only. These spectra will be discussed in a future publication. The amount of deuteration was determined by combustion analysis.[6]

(1) Abstracted from the Ph.D Thesis of Robert W. Campbell, Purdue University, 1966.

(2) (a) G. Stork and I. J. Borowitz, *J. Am. Chem. Soc.*, **84**, 313 (1962); (b) G. Opitz and H. Adolph, *Angew. Chem.*, **74**, 77 (1962); (c) W. E. Truce, *et al.*, *J. Am. Chem. Soc.*, **84**, 3030 (1962).

(3) H. Staudinger and F. Pfenninger, *Chem. Ber.*, **49**, 1941 (1916).

(4) J. F. King, *et al.*, *Can. J. Chem.*, **41**, 100 (1963).

(5) Mass spectra were measured with a Hitachi RMU-6A instrument.

(6) Analyzed by J. Nemeth, University of Illinois.

Table I. Nmr Data for the Esters Obtained[a]

$$\underset{c}{\mathrm{C}}-\underset{b}{\mathrm{C}}-\underset{a}{\mathrm{C}}-\mathrm{SO_2}-\mathrm{O}-\underset{d}{\mathrm{C}}-\underset{e}{\mathrm{C}}$$

Ester	a	b	c	d	e	Relative area of a:b:c:d:e
$CH_3SO_3CH_3$	2.98 (s)	. . .	. . .	3.87 (s)	. . .	3:3
$CH_2DSO_3CH_3$	3.00 (s)[b,c]	. . .	. . .	3.90 (s)	. . .	2.5:3
$CH_3SO_3CH_2CH_3$	3.03 (s)	. . .	. . .	4.36 (q)	1.45 (t)	3:2:3
$CH_2DSO_3CH_2CH_3$	3.03 (s)	. . .	. . .	4.36 (q)	1.45 (t)	2.6:2:3
$CH_3CH_2SO_3CH_3$	3.12 (q)	1.38 (t)	. . .	3.86 (s)	. . .	2:3:3
$CH_3CHDSO_3CH_3$	3.14 (q)	1.41 (m)[d]	. . .	3.88 (s)	. . .	1.6:3:3
$CH_3CH_2CH_2SO_3CH_3$	3.14 (t)	1.92 (m)	1.10 (t)	3.93 (s)	. . .	2:2:3:3
$CH_3CH_2CHDSO_3CH_3$	3.14 (t)	1.92 (m)	1.10 (t)	3.93 (s)	. . .	1.6:2:3:3
$(CH_3)_2CHSO_3CH_3$	3.36 (p)[e]	1.45 (d)	. . .	3.93 (s)	. . .	1:6:3
$(CH_3)_2CDSO_3CH_3$	3.36 (p)	1.45 (t)[f]	. . .	3.93 (s)	. . .	0.4:6:3
$CH_2{=}CHCH_2SO_3CH_3$	3.87 (d)	5.60 (m)		3.92 (s)	. . .	2:3:3
$CH_2{=}CHCHDSO_3CH_3$	3.87 (d)	5.60 (m)		3.92 (s)	. . .	1.7:3:3
$CH_2{=}CHCH_2SO_3CH_2CH_3$	3.88 (d)	5.63 (m)		4.36 (q)	1.41 (t)	2:3:2:3
$C_6H_5CH_2SO_3CH_3$	4.34 (s)	7.42 (s)[g]	. . .	3.73 (s)	. . .	2:5:3
$C_6H_5CHDSO_3CH_3$	4.34 (s)	7.42 (s)	. . .	3.73 (s)	. . .	1.5:5:3
p-$NO_2C_6H_4CH_2SO_3CH_3$	4.50 (s)	7.99 (q)	. . .	3.89 (s)	. . .	2:4:3
p-$NO_2C_6H_4CHDSO_3CH_3$	4.50 (s)	7.99 q)	. . .	3.89 (s)	. . .	1.6:4:3

[a] The multiplicity is expressed as: (s) singlet, (d) doublet, (t) triplet, (q) quartet, (p) quintet, (m) multiplet. [b] Hydrogen–deuterium coupling was not completely resolved in any of the deuterated esters, probably due to the presence of undeuterated ester. [c] Ester obtained from methanesulfonyl chloride. [d] Triplet overlaying a doublet. [e] Signal was weak, hence expected septet was not observed. [f] Doublet overlaying a singlet. [g] Aromatic protons.

Table II. Deuterium Content of Sulfonate Esters

R	X	R′	Atom % excess D	% Mono-deuterated ester
CH_3	Cl	CH_3	7.95	47.7
CH_3	Br	CH_3	8.03	48.3
CH_3	CH_3SO_3[a]	CH_3	8.83	53.0
CH_3	Cl	CH_3[b]	13.55	81.4
CH_3	Cl	CH_3[c]		45[d]
CH_3CH_2	Cl	CH_3	5.00	40.0
$CH_3CH_2CH_2$	Cl	CH_3	4.75	47.5
$(CH_3)_2CH$	Cl	CH_3	5.70	57.0
$C_6H_5CH_2$[a]	Cl	CH_3	3.99	39.9
p-$NO_2C_6H_4CH_2$[a]	Cl	CH_3	4.48	40.1
$CH_2{=}CHCH_2$	Cl	CH_3	3.94	31.6
$CH_3CH{=}CH$[e]	Cl	CH_3	3.92	31.4
CH_3	Cl	CH_2CH_3	5.97	47.7
$CH_3CH{=}CH$[e]	Cl	CH_2CH_3	4.90	49.0

[a] Small amount of THF used in addition funnel to attain dissolution. [b] Reaction carried out with 4 equiv of MeOD. [c] Hexane as solvent. [d] Analyzed from plot of (*m*/*e* 15)/(*m*/*e* 16) *vs.* % deuterated ester from combustion analysis of previously obtained methyl methanesulfonates. [e] Ester mixture.

The yields of methyl esters are quite low, due to a facile alkylation of the tertiary amine by the sulfonate ester produced. Since a portion of the amine is used up in this manner, a 30% excess of the amine was used to get complete conversion of the sulfonyl chloride.

The infrared spectra of the methyl esters exhibited major bands at 7.4 and 8.6 μ, due to the sulfonyl group, and at 10.1 μ, attributed to carbon–oxygen stretch. In the ethyl esters, the sulfonyl absorption remains nearly the same, while the band in the 10–11-μ region appears at 10.9 μ. These three bands were the most intense peaks present in all of the esters prepared and were unaffected by the presence of deuterium.

The nmr data from these esters are compiled in Table I.[7] In all cases, the signal corresponding to the protons α to the sulfonyl group showed a decrease in relative area, indicating approximately the same amount of deuterium incorporated as the analytical data.

Results from the deuterium analyses are given in Table II. The data pertain to esters obtained *via* the reaction

$$\mathrm{RSO_2X + Et_3N + R'OD \xrightarrow{benzene} RSO_3R'}$$

The following experimental observations appear to rule out hydrogen–deuterium exchange between methanol-*d* and triethylammonium chloride under our reaction conditions. When methanol-*d*, triethylamine, and triethylammonium chloride were allowed to stir in benzene, no detectable deuterium was incorporated into the triethylammonium salt, as shown by its infrared spectrum. In another experiment, methanol-*d* was added to a reaction mixture of methanesulfonyl chloride, methanol, and triethylamine which had stirred for 1 hr. Again the triethylammonium chloride obtained upon work-up appeared to be undeuterated. These results indicate a negligible solubility of this salt in benzene, since its exchange[8] with methanol-*d* in a homogeneous system is complete in less than 34 sec at 0°.

The ester obtained from propene-1-sulfonyl chloride, methanol-*d*, and triethylamine was found to be a mixture of 33% methyl propene-1-sulfonate (undeuterated) and 67% methyl propene-3-sulfonate (partially deuterated) by nmr. For the methyl propene-1-sulfonate in the ester mixture, the vinylmethyl appeared as a closely split doublet at δ 2.1 (relative area 3), the vinyl protons as a complex at δ 6.8 (relative area 2), and the methoxyl group as a singlet at δ 3.87 (relative area 3).

From the reaction of this same sulfonyl chloride with ethanol-*d* and triethylamine, an ester mixture consisting of 9% ethyl propene-1-sulfonate (undeuterated) and 91% ethyl propene-3-sulfonate (partially deuterated)

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(7) The nmr spectra were obtained using a Varian A-60 spectrometer at a sweep width of 500 cps with TMS as an internal standard. The chemical shifts are given in δ units.

(8) C. G. Swain, *et al.*, *J. Am. Chem. Soc.*, **76**, 4243 (1954).

was obtained. That the product ratio did not change with time was established by allowing a similar reaction to run for only 15 min; the resulting ester mixture was of the same composition as that from the 1.5-hr run.

When propene-1-sulfonyl chloride was allowed to stir with 0.25 equiv of triethylamine the sulfonyl chloride recovered was the 1 isomer only (74% recovery) as shown by the infrared spectrum. Strong bands at 12.4 for propene-1-sulfonyl chloride and 11.5 μ for propene-3-sulfonyl chloride are present exclusively in each isomer.

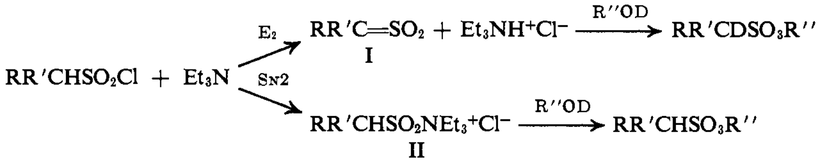
Discussion

The formation of monodeuterated sulfonate esters in these reactions provides unequivocal evidence for sulfene formation under these conditions.[9-12]

The fact that the esters produced were partially undeuterated, coupled with the observation that exchange between alcohol and the ammonium chloride does not occur under the reaction conditions, leads to the conclusion that competing sulfene and "nonsulfene" reactions are taking place.

Effect of the leaving group, the solvent, and the structure of the sulfonyl chloride on the amount of deuterium incorporated are all in accord with competing elimination and substitution reactions between the sulfonyl chloride and triethylamine. The product of elimination, a sulfene, could then add methanol-*d*, giving rise to monodeuterated ester, while the substitution product, a quaternary sulfonyltriethylammonium salt, would undergo displacement of triethylamine by alcohol, forming undeuterated ester (Scheme I).

Scheme I



Evidence for the intermediate sulfene (I) has been discussed previously. The formation of a sulfonylammonium salt (II) is not without precedent. For example, a very rapid reaction takes place[13] when benzenesulfonyl chloride is treated with trimethylamine in benzene, giving rise to a salt-like material (very hygroscopic). In the presence of excess trimethylamine, this 1:1 adduct yields tetramethylammonium chloride and N,N-dimethylbenzenesulfonamide. The most likely structure of this adduct is benzenesulfonyltrimethylammonium chloride, an analog of II. In addition, Majda and Okon[14] have isolated and characterized a number of N-benzenesulfonylammonium chlorides from the reactions of benzenesulfonyl chloride with a series of tertiary aromatic amines.

Solvolysis of alkanesulfonyl chlorides[15] (where sulfene intermediacy is possible), as well as solvolysis of arenesulfonyl chlorides[16] (where SN2 attack on sulfur is presumably involved), proceeds too rapidly to be measured conveniently when bases such as hydroxide or alkoxide are involved. This lends support to the hypothesis that nucleophilic displacement on sulfur can compete with an elimination–addition sequence.

When the leaving group is changed from chloride to bromide to methanesulfonate a small increase in deuterated ester is observed (Table II). In a study of competing E2–SN2 reactions, Hughes and Shapiro[17] noted that in 80% ethanol, isopropyl chloride and isopropyl bromide give 58 and 61% olefin, respectively, and that in 60% ethanol, isopropyl bromide and iodide give 58 and 74% olefin, respectively. These results and others suggest that the ratio E2/SN2 increases slightly for the series RCl, RBr, and RI. Our results are in agreement with this trend.

The E2/SN2 ratio has also been shown to be influenced by the polarity of the solvent. When a negatively charged base reacts with a neutral substrate, charge is dispersed over a larger area in the transition state of an E2 reaction than an SN2 reaction; therefore low solvent polarity favors elimination at the expense of substitution. Typically, for the reaction of isopropyl bromide with sodium hydroxide, the ratio E2/SN2 increases from 1.17 to 1.44 when the solvent is changed from 60% ethanol to 80% ethanol.[18] In our system, where a neutral base attacks neutral substrate, greater charge separation is present in the transition state of the E2 reaction; therefore, low solvent polarity should favor substitution. In fact, when hexane was used as solvent, a decrease in the deuterium content of the ester was observed (Table II). A more complete investigation of the effect of solvent was ruled out by the fact that triethylammonium chloride has significant solubility in solvents of higher dielectric constant (*e.g.*, diethyl ether).

The decrease in deuterated ester produced upon going from methane to ethanesulfonyl chloride (47.7 to 40.0%) is readily explained by the decrease in acidity of the α hydrogens. The acidity of these hydrogens in 1-propanesulfonyl chloride should be comparable to the ethane analog; however, the extended methyl group might be expected to decrease the rate of attack on sulfur. For example, Geiseler[19] noted a marked decrease in the rate of hydrolysis of alkanesulfonyl chlorides on going from ethanesulfonyl chloride to propanesulfonyl chloride. Hence the increase in deuterated ester from 1-propanesulfonyl chloride (from 40.0 to 47.5%) can be accounted for on the basis of

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(9) Fusco and co-workers,[10] Opitz and Fischer,[11] and Borowitz[12] have obtained evidence ruling out the most likely alternative mechanism (*i.e.*, involving $>CHSO_2C—C=NR_2^+$ as an intermediate) for the formation of thietane 1,1-dioxide derivatives from the reactions of alkanesulfonyl chlorides with triethylamine and enamines and thereby providing indirect evidence for intermediate sulfenes in these transformations.

(10) R. Fusco, S. Rossi, and S. Maiorana, *Chim. Ind.* (Milan), **44**, 873 (1962).

(11) G. Opitz and K. Fischer, *Z. Naturforsch.*, **18b** 775 (1963).

(12) I. J. Borowitz, *J. Am. Chem. Soc.*, **86**, 1146 (1964).

(13) L. W. Jones and H. F. Whalen, *ibid.*, **47**, 1343 (1925).

(14) H. Majda and K. Okon, *Biul. Wojskowej Akad. Tech.*, **10**, 101 (1961); *Chem. Abstr.*, **57**, 11161 (1962).

(15) H. K. Hall, *J. Am. Chem. Soc.*, 78, 1450 (1956).

(16) P. Hirsjarvi and E. Tommila, *Acta Chem. Scand.*, **5**, 1097 (1951).

(17) E. D. Hughes and U. G. Shapiro, *J. Chem. Soc.*, 1177 (1937).

(18) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., Inc., New York, N. Y., 1962, p 488.

(19) G. Geiseler and F. Asinger, *Chem. Ber.*, **89**, 1100 (1956).

steric inhibition, by the added methyl group, toward the SN2 process.

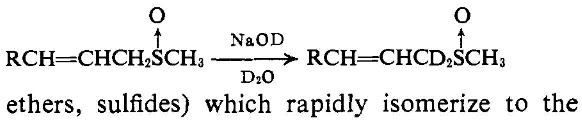
Asinger and co-workers[20] found that in long-chain sulfonyl chlorides, the rate of hydrolysis in aqueous dioxane decreased by a factor of 10 when an α-methyl group is present. It was also reported[21] that in a large variety of solvents, the alcoholysis of 2-propanesulfonyl chloride was as much as 20 times slower than that of the straight-chain isomer. This steric factor apparently outweighs the further decrease in acidity of the α hydrogens, since the ester from 2-propanesulfonyl chloride is 57.0% deuterated.

The reaction of methanesulfonyl chloride with excess methanol-*d* seems to indicate that a considerable amount of sulfene (I) formed initially collapses with the triethylammonium chloride produced, yielding the quaternary ammonium intermediate (II) which then reacts with methanol-*d* producing undeuterated ester. In the presence of excess methanol-*d* more of the sulfene is trapped out by the alcohol, as evidenced by the large increase in deuterated ester. With large excesses of deuterated alcohol, amine, or water in the presence of triethylamine, King and Durst obtained solvolysis products which are highly monodeuterated.[22-24]

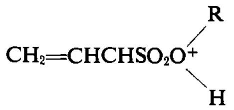
The decreased deuterium content of the esters obtained from sulfonyl chlorides, which have groups ($CH_2{=}CH^-$, $C_6H_5^-$, *p*-$NO_2C_6H_4^-$) substituted on the α carbon that are capable of giving resonance stabilization to, for example, an adjacent carbanion center, may be due to a slower reaction of methanol-*d* with these sulfenes as a result of their increased stability. The over-all result would be formation of more undeuterated ester from collapse of these sulfenes with triethylammonium chloride. Greater stability of these sulfenes is expected since the orientation of their cycloadditions with ketene acetals and enamines indicates the following polarization.

$$RR'C{=}SO_2 \qquad RR'C^-SO_2^+$$

The isomeric propenesulfonyl chlorides give further indication of competing elimination and substitution. The fact that propene-3-sulfonyl chloride gives only propene-3-sulfonate ester clearly shows that the conjugated sulfene which forms, $CH_2{=}CHCHSO_2$ (III), undergoes 1,2 addition of alcohol only. O'Connor and Broaddus[25] have found that upon treatment of β,γ-unsaturated sulfoxides with sodium deuterioxide in deuterium oxide, exchange occurs only at the methylene between the sulfoxide group and the double bond with no isomerization. This is in direct contrast with behavior of other β,γ-unsaturated systems (*e.g.*, amines, ethers, sulfides) which rapidly isomerize to the α,β-unsaturated compounds.[26-29] The sulfoxide data were rationalized as resulting from a more rapid protonation of an allylic carbanion intermediate at the center of highest electron density, namely the methylene adjacent to the electron-withdrawing sulfoxide group. The carbanionic property of this sulfene (III) in a concerted addition of alcohol, or a carbanion intermediate in a stepwise process, would be expected, for the same reason, to yield the β,γ isomer as observed.



$$\mathrm{RCH{=}CHCH_2\overset{O}{\overset{\uparrow}{S}}CH_3 \xrightarrow[D_2O]{NaOD} RCH{=}CHCD_2\overset{O}{\overset{\uparrow}{S}}CH_3}$$



The products from elimination and substitution reactions of propene-1-sulfonyl chloride differ in structure as well as isotopic composition. In view of the large rate differences between solvolysis reactions with and without base present, it is unlikely that the methyl propene-1-sulfonate is produced from attack of sulfonyl chloride by alcohol. The undeuterated methyl propene-3-sulfonate probably arises from conversion of III to the β,γ-unsaturated sulfonyl triethylammonium salt. It cannot be arising from an SN2 reaction of isomerized sulfonyl chloride since an appropriate control showed no isomerization taking place under these conditions.

The ester mixture obtained from the reaction of propene-1-sulfonyl chloride and ethanol-*d* was only 9% ethyl propene-1-sulfonate, indicating the reaction of ethanol with the quaternary ammonium intermediate (II) is slower than with methanol. Under these conditions equilibrium between I and II may be attained,[11] as evidenced by the increase from 31.4 (with methanol-*d*) to 50.0% (with ethanol-*d*) of deuterated ester from propene-1-sulfonyl chloride, while with methanesulfonyl chloride the per cent deuterated ester increases from 47.7 (with methanol-*d*) to only 48.7 (with ethanol-*d*). In other words, the sulfonyl chloride capable of forming a resonance-stabilized sulfene intermediate benefits most, in terms of deuterated ester produced, from equilibrium between I and II.

The results from these propenesulfonyl chloride reactions are summarized in Table III.

Summary

Evidence was obtained for sulfene formation in the reaction of alkanesulfonyl chlorides with triethylamine. This evidence consisted of the isolation of monodeuterated sulfonate esters when these reactions were carried out in the presence of deuterated alcohols. Also, sulfene was shown to be involved as an intermediate in like reactions of methanesulfonyl bromide and methanesulfonic anhydride.

The effect of the leaving group, the solvent, and the structure of the sulfonyl chloride on the deuterium content of the ester indicate that displacement by triethylamine on sulfur is in competition with the elimination reaction. The results of the reaction with an excess of methanol-*d*, product distributions from the

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[20] F. Asinger, G. Geiseler, and H. Eckholdt, *Chem. Ber.*, **89**, 1233 (1956).

[21] G. Geiseler and P. Lane, *ibid.*, **95**, 867 (1962).

[22] After the initiation of this work, we learned that King and Durst had independently developed a method similar to ours, for providing evidence of sulfene intermediacy in the solvolysis of alkanesulfonyl chlorides. It was arranged that the two preliminary communications should appear simultaneously.[23,24]

[23] J. F. King and T. Durst, *J. Am. Chem. Soc.*, **86**, 287 (1964); **87**, 5684 (1965).

[24] W. E. Truce, R. W. Campbell, and J. R. Norell, *ibid.*, **86**, 288 (1964).

[25] D. E. O'Connor and C. D. Broaddus, *ibid.*, **86**, 2267 (1964).

[26] T. J. Prosser, *ibid.*, **83**, 1701 (1961); C. C. Price and W H. Snyder, *ibid.*, **83**, 1773 (1961).

[27] C. C. Price and W. H. Snyder, *Tetrahedron Letters*, 69 (1962).

[28] C. C. Price and W. H. Snyder, *J. Org. Chem.*, **27**, 4639 (1962).

[29] E. A. Rabinovich, I. V. Astaf'ev, and A. I. Shatenshtein, *Zh. Obshch. Khim.*, **32**, 748 (1962).

Table III. Alcoholysis of Propenesulfonyl Chlorides

Sulfonyl chloride	Alcohol	Reaction time, hr	% $CH_2{=}CHCH_2SO_3R$	% $CH_3CH{=}CHSO_3R$	% deuterated ester
$CH_2{=}CHCH_2SO_2Cl$	CH_3OD	1.5	100	0	31.6
$CH_3CH{=}CHSO_2Cl$	CH_3OD	1.5	67	33	31.4
$CH_3CH{=}CHSO_2Cl$	CH_3CH_2OD	1.5	91	9	50.0[a]
$CH_3CH{=}CHSO_2Cl$	CH_3CH_2OD	0.25	91	9	...

[a] Corrected for the presence of 2% EtOH in the starting alcohol.

Table IV. Physical Constants of the Esters Obtained *via* RSO_2X + Alcohol + $Et_3N(C_6H_6) \xrightarrow{1.5\ \text{hr}}$ Sulfonate Ester

R	X	Alcohol	Bp, °C (mm)	n_D (°C)	Lit. bp, °C (mm)
CH_3	Cl	MeOH	78 (10)	1.4151 (19.5)[a]	101 (26)[f]
CH_3	Cl	MeOD	75 (8)	1.4148 (19.5)	...
CH_3	Cl[b]	MeOD	76 (8)	...	...
CH_3	Cl	MeOD[c]	78 (10)	...	...
CH_3	Br	MeOD	78 (10)	...	...
CH_3	CH_3SO_3	MeOD	72 (7)	1.4151 (20.5)	...
CH_3CH_2	Cl	MeOH	80 (9)	1.4199 (27)	78 (6)[g]
CH_3CH_2	Cl	MeOD	78 (8)	1.4199 (27)	...
$CH_3CH_2CH_2$	Cl	MeOH	62 (2)	1.4264 (20.5)	...
$CH_3CH_2CH_2$	Cl	MeOD	42 (0.08)	1.4264 (20.5)	...
$(CH_3)_2CH$	Cl	MeOH	74 (7.5)	1.4242 (20)	...
$(CH_3)_2CH$	Cl	MeOD	73 (7)	1.4246 (20.5)	...
$C_6H_5CH_2$	Cl	MeOH	60–62[d]	...	61–62[h]
$C_6H_5CH_2$	Cl	MeOD	59–61[d]	...	...
p-$NO_2C_6H_4CH_2$	Cl	MeOH	110–111[d]	...	111–113[h]
p-$NO_2C_6H_4CH_2$	Cl	MeOD	109–111[d]	...	...
$CH_2{=}CHCH_2$	Cl	MeOH	89 (9)	1.4457 (21)	...
$CH_2{=}CHCH_2$	Cl	MeOD	88 (8)	1.4430 (30.5)	...
$CH_2{=}CHCH_2$	Cl	EtOH	54 (0.1)	1.4444 (21)	...
$CH_3CH{=}CH$	Cl	MeOD	52 (0.5)	...	110 (10)[i]
$CH_3CH{=}CH$	Cl	EtOD	57 (0.8)	1.4447 (21)	...
$CH_3CH{=}CH$	Cl	EtOH[e]	57 (0.8)	1.4447 (21)	...
CH_3	Cl	EtOH	78 (7.5)	1.4174 (21)	86 (10)[j]
CH_3	Cl	EtOD	78 (7.5)	1.4174 (21)	...

[a] Lit. $n^{17.6}_D$ 1.4158. [b] Hexane as solvent. [c] Four equivalents of MeOD used. [d] Melting point. [e] Reaction time of 15 min. [f] W. E. Bissinger, F. E. King, and C. W. Hamilton, *J. Am. Chem. Soc.*, **70**, 3940 (1948). [g] A. Simon and H. Kreigsman, *Z. Physik. Chem.* (Leipzig), **204**, 369 (1955). [h] C. K. Ingold, E. H. Ingold, and F. R. Shaw, *J. Chem. Soc.*, 813 (1927). [i] A. Lambert and J. D. Rose, *ibid.*, 49 (1949). [j] H. Billeter, *Chem. Ber.*, **38**, 2018 (1905).

isomeric propenesulfonyl chlorides, and the effect of the nature of the alcohol on the per cent of deuterated ester point to partial collapse of the elimination product (sulfene) and triethylammonium chloride to give the substitution product (sulfonyltriethylammonium chloride) when methanol is used, and attainment of equilibrium between these intermediates with ethanol-*d*.

Experimental Section[30]

Materials. Triethylamine (Matheson Coleman and Bell reagent), methanol-*d* (Volk, 100% O–D deuterated by combustion analysis), ethanol-*d* (Volk, 98.0% O–D deuterated by combustion analysis), benzene (Baker spectrophotometric reagent), hexane (Fisher chemical reagent), methanesulfonyl chloride (Eastman White Label), ethanesulfonyl chloride (Eastman White Label), 1-propanesulfonyl chloride (Eastman White Label), phenylmethanesulfonyl chloride (Eastman White Label), and methanesulfonic anhydride (Eastman White Label) were used as obtained. Methanol and ethanol were dried over magnesium and distilled prior to use. A number of sulfonyl chlorides was prepared according to the references cited below and the physical constants agreed well with with those reported in the literature. These include: 2-propanesulfonyl chloride,[31] bp 57° (7.5 mm); *p*-nitrophenylmethanesulfonyl chloride,[32] mp 90–92°; propene-3-sulfonyl chloride,[33] bp 72° (11 mm); propene-1-sulfonyl chloride,[34] bp 62° (7 mm); methanesulfonyl bromide,[35] bp 66° (11 mm).

General Procedure for the Reaction of Sulfonyl Halides with Alcohol and Triethylamine. To avoid needless repetition of experimental conditions, the following general procedure is described.

The sulfonyl halide (0.10 mole) dissolved in benzene (30 ml) was slowly added (20 min) to a benzene solution (100 ml) of triethylamine (0.13 mole) and the alcohol (0.12 mole) in a 300-ml, three-neck, round-bottom flask equipped with an addition funnel, mechanical stirrer, and reflux condenser. The system was flame dried prior to the addition and the reactions were run under nitrogen. After stirring for a total of 1.5 hr at room temperature, the triethylammonium chloride produced was removed by filtration (mp 251–257°, 85–98% yield). The benzene filtrate, usually containing a lower layer of triethylammonium salts, was washed with water (40 ml) and dried over magnesium sulfate, and the solvent was removed *in vacuo*. When a liquid sulfonate ester was obtained, the residue was distilled through a 10-cm Vigreux column at reduced pressure. When a solid product was obtained, it was recrystallized from an ethyl acetate–hexane mixture. The yields of the methyl esters were in the range 20–45%; the ethyl esters were obtained in 67–76% yield. Physical constants of the esters obtained from the reaction

$$RSO_2X + \text{alcohol} + Et_3N \xrightarrow[1.5\ \text{hr}]{C_6H_6} \text{products}$$

are listed in Table IV.

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(30) All melting points and boiling points are uncorrected.

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Hydrogen–Deuterium Exchange between Triethylammonium Chloride and Methanol-*d* in Benzene. Triethylammonium chloride (1.5 g, 11 mmoles; prepared by passing dry hydrogen chloride through an ethereal solution of triethylamine; recrystallized from a chloroform–ether mixture; mp 255–256°), triethylamine (1.1 g, 11 mmoles), and methanol-*d* (0.3 g, 11 mmoles) were added to 30 ml of benzene and allowed to stir for 1 hr under nitrogen. The triethylammonium chloride was collected by filtration and dried *in vacuo*. The infrared spectrum of this salt indicated no deuterium incorporation.

Check on Hydrogen–Deuterium Exchange between Triethylammonium Chloride and Methanol-*d* under the Exact Reaction Conditions. Methanesulfonyl chloride (11.4 g, 0.10 mole) was added to methanol (3.8 g, 0.12 mole) and triethylamine (13.1 g, 0.13 mole) in the usual manner. After stirring for 1 hr, methanol-*d* (2.0 g, 0.06 mole) was added and the reaction mixture was stirred for an additional 30 min. The triethylammonium chloride was isolated by filtration, washed with benzene, and dried *in vacuo*. The infrared spectrum showed no exchange.

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A Study of Chemiluminescence from Reactions of Oxalyl Chloride, Hydrogen Peroxide, and Fluorescent Compounds[1]

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Abstract: The chemiluminescent reaction between oxalyl chloride and hydrogen peroxide in the presence of a fluorescer was investigated with respect to the emitting species, the reaction products, the effects of reactant concentrations on absolute quantum yields and reaction rates, and the effects of free-radical chain inhibitors. Water was found to be a critical reactant in the chemiluminescent process. The system was found to be the most efficient nonbiological chemiluminescent system yet reported, providing quantum yields on the order of 5%. A mechanism involving the decomposition of monoperoxyoxalic acid in a key step is proposed.

Although the direct conversion of chemical energy to light has been observed in a wide variety of chemical reactions,[2] only a few reactions are known which provide moderately high chemiluminescent light intensities indicative of quantum yields above 10^{-3}. Prominent examples of such "bright" chemiluminescence include the reactions of hydrogen peroxide or oxygen with certain phthalhydrazide derivatives,[3,4] imidazole derivatives,[5,6] and acridinium salts.[7-9] Investigation of the mechanisms by which light is produced in such reactions has proved to be difficult because of the complex multistep processes involved and because of low quantum yields of emission. Thus, the identity of the key reaction step that produces the emitting singlet excited state in these reactions tends to be obscured by earlier reaction steps, subsequent reaction steps, and by competing nonluminescent side reactions. Even the identification of the emitting species in these reactions is subject to uncertainty[10] since the available assignments rest entirely on comparisons of chemiluminescence and fluorescence spectral distributions in systems which lack well-defined and uniquely characteristic emission bands.[4,6,8,9]

With these difficulties in mind, we have sought a model chemiluminescent reaction more suitable for mechanistic studies. The chemiluminescent reaction between oxalyl chloride, hydrogen peroxide, and various fluorescent compounds, discovered by Chandross,[11] appeared particularly attractive in this regard. Using aqueous hydrogen peroxide and a fluorescent aromatic hydrocarbon such as anthracene in an organic solvent, Chandross reported the emission as a bright flash having a color matching the fluorescence of the fluorescent additive. Thus, the emitting species, as

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