Anal. Calcd for $C_{16}H_{25}NO_3S_2$: C, 55.99; H, 7.34; S, 18.97. Found: C, 56.39; H, 7.47; S, 18.70.

Conversion of Sulfoximines IVa and IVb into N-*p*-Toluenesulfonyl Derivatives IIIa and IIIb.—To 3 ml of dry pyridine, 0.1 g of *p*-toluenesulfonyl chloride and 50 mg of free sulfoximine IVa were added; the mixture was stirred at room temperature for 12 hr. The mixture was poured into water and extracted with chloroform; the solvent was evaporated; and the pyridine was removed by azeotropic distillation with toluene. Column chromatography (silica gel-chloroform, then ethyl acetate) provided 92 mg (96%) of the **N-tosylsulfilimine IIIa**, identical in all respects with that obtained above by oxidation.

An analogous reaction with the free sulfoximine IVb gave the **N-tosylsulfilimine IIIb**: 95%; mp 172.5–173.5° (benzene-cyclohexane).

Anal. Calcd for $C_{16}H_{25}NO_3S_2$: C, 55.99; H, 7.34; S, 18.97. Found: C, 56.24; H, 7.37; S, 18.76.

Reaction of *trans*-4-*t*-Butylthiane 1-Oxide with *p*-Toluenesulfonyl Azide.—Following the method of Kwart and Khan, *trans*-sulfoxide Vb (80 mg), *p*-toluenesulfonyl azide (90 mg), and Raney copper (10 mg) in 5 ml of methanol were refluxed for 15 hr. Chromatography of the reaction product revealed unreacted starting sulfoxide and an N-tosylsulfoximine identical in all respects with IIIb obtained above.

Registry No.—I, 768-30-9; IIa, 17604-09-0; IIb, 17659-00-6; IIIa, 17604-10-3; IIIb, 17659-01-7; IVa, 17604-11-4; IVb, 17604-12-5; VI, 17604-13-6.

A Study of Aliphatic Sulfonyl Compounds. IX. Polar Effects in Ethylene- and 2-Propene-1-sulfonyl Chlorides[1a]

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Received May 21, 1968

Rates of ethanolysis of ethylenesulfonyl and 2-propene-1-sulfonyl chloride were found to be significantly faster and only slightly faster, respectively, than that of a saturated sulfonyl chloride. Although infrared and mass spectra suggest that in the case of the former there may be some allylic participation by the α double bond to give the resonance stabilized sulfonylium ion intermediate, enhancement of ethanolysis is not that great and probably is largely polar in origin. There is no evidence in the latter case for homoallylic enhancement to form the conjugated unsaturated sulfonylium ion, and the small increase in rate of ethanolysis probably is entirely due to a polar effect. From the activated state parameters of $\Delta H^* = 15.4$ and 17.7 kcal and $\Delta S^* = -7.5$ and -5.9 eu for ethanolysis of ethylenesulfonyl chloride and 2-propene-1-sulfonyl chloride, respectively, it is clear that the lower enthalpy of activation is responsible for the faster rate of ethanolysis. Alkylation of ethanolic hydrogen chloride with ethyl ethylenesulfonate is somewhat faster than with ethyl 2-propene-1-sulfonate, the former reacting at substantially the same rate as the ethyl ester of a saturated sulfonic acid. There was no spectral evidence for participation of either double bond in the case of these esters. From activated state parameters of $\Delta H^* =$ 21.0 and 23.1 kcal and $\Delta S^* = +4.0$ and $+9.3$ eu, respectively, for ethyl ethylenesulfonate and 2-propene-1-sulfonate, it appears that the considerably greater increase in activation entropy in the case of the latter is more than offset by the increased enthalpy of activation. It was shown that a "polymeric vinylsulfonyl chloride" (obtained from ammonium ethylenesulfonate and phosphorus pentachloride) reported in the literature probably was only 2-chloroethanesulfonyl chloride with an impurity of ethyl ethylenesulfonate.

Previously[3-7] the steric requirements of several branched-chain sulfonyl compounds were compared by a study of the ethanolysis of saturated aliphatic sulfonyl chlorides and alkylation by the corresponding ethyl esters. However, all of the aliphatic compounds studied were saturated and were compared only with analogously branched primary alkyl halides as to steric effects; no important polar contributions could be correlated with those of alkyl halides. In other work, the polar effects of a carbonyl group in *dl*-10-camphorsulfonyl chloride[8] and of a chloro group in 3-chloro-1-propanesulfonyl chloride[9] upon ethanolysis (Table I) have been studied but these are rather special cases. Thus, in the case of the former, the halogen may be displaced by anchimeric assistance from the keto group or its hemiacetal, while in the latter the chain chlorine probably is too far removed to have a significant polar effect on sulfonyl reactivity.

TABLE I

RATES OF ETHANOLYSIS OF SELECTED SULFONYL CHLORIDES AT 84°

Sulfonyl chloride	10^4k, min^{-1}	ΔH^*, kcal mol^{-1}	ΔS^*, cal deg^{-1} mol^{-1}
Ethylene-[a]	880[a]	15.4	−7.5
dl-10-Camphor-[b]	171		
Benzene-[c]	145	16.1	−10.9
2-Propene-1-	102	17.7	−5.9
1-Octane-[d]	89		
3-Chloro-1-propane-[e]	70	8.2	−35.2
α-Toluene-[b]	63		
2,3-Dimethyl-1-butane-[f]	48		
2-Octane-[d]	14		

[a] Calculated for 84° (see Table III for experimentally determined values of *k*). [b] See ref 8. [c] See ref 7. [d] See ref 3. [e] See ref 9. [f] See ref 4.

In the present report the effect of unsaturation was studied in the ethanolysis of ethylene- and 2-propene-1-sulfonyl chlorides. The relative activity of the corresponding ethyl esters as alkylating agents also was investigated.

Results and Discussion

The previous studies[3-9] of the ethanolysis of aliphatic sulfonyl chlorides have led to the conclusion that substituents sterically affect alcoholysis in the same

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[1] (a) From the Ph.D. Dissertation of J. Preston, University of Alabama, 1957. (b) Chemstrand Research Center, Inc., Durham, N. C.

[2] To whom inquiries should be addressed at the Department of Chemistry, The University of Mississippi, University, Miss. 38677.

[3] R. B. Scott, Jr., and R. E. Lutz, *J. Org. Chem.*, **19**, 830 (1954).

[4] R. B. Scott, Jr., and M. S. Heller, *ibid.*, **20**, 1159 (1955).

[5] R. B. Scott, Jr., and M. J. Gordon, *ibid.*, **21**, 385 (1956).

[6] R. B. Scott, Jr., and H. L. McLeod, *ibid.*, **21**, 388 (1956).

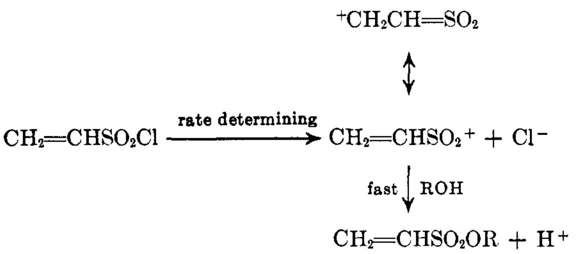
[7] R. B. Scott, Jr., and J. B. Gayle, *ibid.*, **21**, 391 (1956).

[8] J. B. Gayle, Dissertation, University of Alabama, 1953.

[9] M. J. Gordon, Dissertation, University of Alabama, 1960.

general way that they do aliphatic halides, the best analogy being drawn by considering the tetrahedral sulfo group as a pseudomethylene group, but about one-third larger.

An analogy between unsaturated sulfonyl chlorides and alkenyl chlorides also might be anticipated, *i.e.*, the analog for ethylenesulfonyl chloride being allyl chloride and for 2-propene-1-sulfonyl chloride, 4-chloro-1-butene (homoallyl chloride). Thus during solvolysis a resonance-stabilized sulfonylium ion might be expected.



$$\begin{tikzcd} & {}^{+}\text{CH}_2\text{CH}{=}\text{SO}_2 \arrow[d, leftrightarrow] \\ \text{CH}_2{=}\text{CHSO}_2\text{Cl} \arrow[r, "\text{rate determining}"] & \text{CH}_2{=}\text{CHSO}_2^{+} + \text{Cl}^{-} \arrow[d, "\text{fast}"', "\text{ROH}"] \\ & \text{CH}_2{=}\text{CHSO}_2\text{OR} + \text{H}^{+} \end{tikzcd}$$

Although formation of the ethylenesulfonylium ion on bombardment of the sulfonyl chloride in the mass spectrometer cannot be used to prove its existence in solution, this does provide evidence for the possibility. A large peak at *m/e* 91 in the mass spectrum[10] of ethylenesulfonyl chloride indicates fragmentation to form $CH_2{=}CH{-}SO_2^+$. Also, the infrared spectrum shows the double bond shifted to a slightly higher wavelength (6.20 μ) than for a normal double bond, which might be interpreted as contributing to the resonance stabilization of the sulfonylium ion, rather than simple resonance with the sulfonyl group.

However, ethylenesulfonyl chloride undergoes ethanolysis (Table I) only about ten times as fast as a saturated normal sulfonyl chloride, which is not nearly the enhancement expected[11] from appreciable resonance participation in the formation of a sulfonylium ion intermediate.

As the double bond of homoallyl halides does not participate in bimolecular displacement of their halogens, it would not be anticipated that the double bond of 2-propene-1-sulfonyl chloride would participate in a bimolecular displacement. In fact, even less evidence exists for a stabilized sulfonylium ion from this sulfonyl chloride than for one from ethylenesulfonyl chloride.[12] Thus no peak in the mass spectrum of 2-propene-1-sulfonyl chloride is noted at *m/e* 105 due to fragmentation to a sulfonylium ion, and the infrared spectrum shows no shift in the double-bond absorbance (6.09 μ). Upon ethanolysis (Table I), 2-propene-1-sulfonyl chloride reacts only about 10% faster than its saturated counterpart.

The faster rate of ethanolysis of ethylenesulfonyl chloride can be attributed to its lower enthalpy of activation ($\Delta H^* = 15.4$ kcal compared with 17.7 kcal for 2-propene-1-sulfonyl chloride) since the smaller activation entropy ($\Delta S^* = -7.5$ eu compared with -5.9 eu for 2-propene-1-sulfonyl chloride) indicates a more highly ordered activated state than is necessary for the larger molecule.

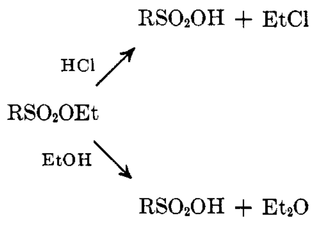
Probably the increased rates with which these unsaturated sulfonyl chlorides undergo ethanolysis simply reflect an inductive withdrawal effect of the unsaturation on the highly electronegative chlorosulfonyl group. The closer proximity of the double bond of ethylenesulfonyl chloride to the chlorosulfonyl group compared with the positions of the corresponding groups of 2-propene-1-sulfonyl chloride probably accounts for the approximately tenfold greater rate of reactivity of the former sulfonyl chloride over the latter.

Although it is perhaps an oversimplification to estimate the rate constants for ethylene- and 2-propenesulfonyl chlorides from other rate data by making some rough assumptions, it was nevertheless interesting that the estimated and determined rate constants were in good agreement.

The estimate of the rate constant for ethylenesulfonyl chloride at reflux was made by consideration of steric and polar effects. Thus as benzenesulfonyl chloride ($k = 0.14$ min^{-1}) reacts ten times as fast at 84° as 2-octanesulfonyl chloride ($k = 0.014$ min^{-1}), then ethylenesulfonyl chloride might be expected to react that much faster than an unbranched primary sulfonyl chloride ($k = 0.089$ min^{-1}). Thereby, the rate constant for ethylenesulfonyl chloride may be estimated to be 0.89 min^{-1}, assuming as a first approximation equivalence of the double bonds of the phenyl and vinyl groups. The experimental rate constant for this compound, calculated for 84° from data at lower temperatures by means of the Arrhenius equation, was 0.88 min^{-1}, agreeing very well with the estimated value and confirming the earlier prediction that this sulfonyl chloride would be quite reactive.

By a similar method an estimate of the rate constant for 2-propene-1-sulfonyl chloride was made. As a saturated sulfonyl chloride having an unbranched chain, such as 1-octanesulfonyl chloride ($k = 0.089$ min^{-1}), reacts 1.94 times as fast at 84° as one having a β-methyl group, such as 2,3-dimethylbutane-1-sulfonyl chloride[4] ($k = 0.48$ min^{-1}), it might be predicted that 2-propene-1-sulfonyl chloride will react 0.089/0.063 times as fast as α-toluenesulfonyl chloride ($k = 0.063$ min^{-1}), if it is assumed that the double bonds of allyl and tolyl groups have approximately equivalent effects. This estimated value of $k = 0.118$ min^{-1} agrees within experimental error with the observed rate constant of 0.102 min^{-1}.

Alkyl sulfonates are known to be good alkylating agents; *e.g.*, the ethyl esters are attacked by hydrogen chloride and ethanol to form free sulfonic acid and, respectively, ethyl chloride and ethyl ether. Solvolysis constitutes a minor part of the reaction when an excess of hydrogen chloride is present. Most previous solvolysis studies reported in the literature have focused



$$\begin{tikzcd} & \text{RSO}_2\text{OH} + \text{EtCl} \\ \text{RSO}_2\text{OEt} \arrow[ur, "\text{HCl}"] \arrow[dr, "\text{EtOH}"'] & \\ & \text{RSO}_2\text{OH} + \text{Et}_2\text{O} \end{tikzcd}$$

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[10] The authors wish to express their appreciation to Dr. R. M. Guedin, Celanese Corp. of America, for mass spectral data.

[11] J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 167, 168.

[12] It has been shown, however, that the double bond does participate in reactions with stronger bases than ethanol, this sulfonyl chloride and the isomeric 1-propene-1-sulfonyl chloride undergoing reaction with triethylamine to give the same products from ketene diethyl acetal, evidently *via* a common sulfene intermediate, $CH_2{=}CH{-}CH{=}SO_2$: W. E. Truce and J. R. Norell, *J. Amer. Chem. Soc.*, **85**, 323 (1963).

on the alcohol moiety, except possibly in the study of aromatic substituent effects, the choice of sulfonic acid apparently being largely one of convenience. From the work of Scott and coworkers, it has become apparent that the sulfonic acid moiety also plays an important role where steric considerations are involved.[3-9]

In the present work, it is seen that unsaturation has little effect on the rates with which the ethyl esters of ethylene- and 2-propene-1-sulfonic acids alkylate refluxing ethanolic hydrogen chloride, the rates being slightly slower than that of an analogous saturated sulfonic acid ester, *e.g.*, ethyl 1-octanesulfonate (Table II). That there is no enhancement in the rate of alkylation of these esters is consistent with their mass spectra and infrared spectra. Unlike the corresponding sulfonyl chlorides, ethyl 2-propene-1-sulfonate and ethyl ethylenesulfonate have very similar mass spectra, and no resonance stabilization is indicated.

TABLE II

RATES OF ALKYLATION OF ETHANOLIC HYDROGEN CHLORIDE WITH SELECTED ETHYL SULFONATES AT 84° [a]

Ethyl sulfonate	10^3k, min^{-1}	ΔH^*, kcal mol^{-1}	ΔS^*, cal deg^{-1} mol^{-1}
1-Octane-[b]	51		
Ethylene-	47[a]	21.0	4.0
2-Propene-1-	39	23.1	9.3

[a] Calculated for 84° (see Table V for experimentally determined values of k). [b] See ref 3.

Although the activated state is much less highly ordered for ethyl 2-propene-1-sulfonate ($\Delta S^* = +9.3$ eu compared to $+4.0$ eu for the ethylenesulfonate), the activation energy of ethyl ethylenesulfonate is sufficiently lower ($\Delta H^* = 21.0$ kcal compared with 23.1 kcal for the 2-propene-1-sulfonate) that the smaller molecule is slightly more reactive.

During the synthesis of ethylenesulfonyl chloride from ammonium ethylenesulfonate and phophorus pentachloride, Landau obtained a high-boiling fraction which he called "possibly a polymeric vinylsulfonyl chloride."[13] From Landau's work, Kern[14] inferred this to be a dimer. No elemental analysis was reported by Landau, and the saponification equivalent reported was somewhat higher than should have been obtained for a "polymer."

Based on the evidence of mass spectra, infrared spectra, physical properties, and saponification equivalent of similar material obtained by us, it is believed that the "polymeric vinylsulfonyl chloride" reported by Landau was in fact a mixture of 2-chloroethanesulfonyl chloride and ethyl ethylenesulfonate. Formation of these substances can be attributed to any ethanol still present in the recrystallized salts of ethylenesulfonyl chloride. Facile additions of this sort are well documented.[15]

$$CH_2{=}CHSO_2ONa \xrightarrow{PCl_5} CH_2{=}CHSO_2Cl$$

$$CH_2{=}CHSO_2Cl \xrightarrow{EtOH} CH_2{=}CHSO_2OEt + HCl$$

$$CH_2{=}CHSO_2Cl \xrightarrow{HCl} ClCH_2CH_2SO_2Cl$$

Experimental Section

Ultimate analyses were made by the Clark Microanalytical Laboratory, Urbana, Ill. Infrared spectra were determined on a Perkin-Elmer Model 21 instrument.

Sodium Ethylenesulfonate.—An aqueous solution of sodium ethylenesulfonate,[16] prepared from 46 g (1.0 mol) of ethanol by the method of Breslow,[17] *et al.*, and treated[16] to remove partially by-product sodium sulfate, was evaporated nearly to dryness under vacuum, the temperature being kept below 55°. The residual paste of salts was extracted with hot absolute ethanol, and the crystallized product was dried at 50° in a vacuum oven for 24 hr. The hard mass was crushed to a fine powder and further dried for 4 hr more. The yield of crude sodium ethylenesulfonate obtained was 107 g (82% of theory based on ethanol). Attempts to remove the ethanol more rapidly often resulted in a hard, glassy, polymeric material.

Ethylenesulfonyl Chloride.—Following a slightly modified procedure of Landau,[13] 98 g of sodium ethylenesulfonate was treated with 166 g of phosphorus pentachloride in 100 ml of chloroform. Neither Landau[13] nor Snyder[18] described the distillation of the sulfonyl chloride, but from our experience with other aliphatic sulfonyl compounds it is unlikely that either used a packed column. We used a 32 × 3 cm Vigreux column with total condensation stillhead and stabilized the distilland with potassium carbonate.[19] It was found necessary to redistil to separate the pure product: n^{20}_{D} 1.4680 (lit. n^{20}_{D} 1.4686,[13] 1.4680[18]); bp 49–50° (10 mm), from a higher boiling fraction.[20]

Ethyl Ethylenesulfonate.—Ethyl ethylenesulfonate, bp 73.5–74° (3 mm), was prepared in 40% yield from free ethylenesulfonic acid[21] and ethyl orthoformate according to a previously reported procedure:[22] n^{28}_{D} 1.4289; d^{28}_{4} 1.180; n^{25}_{D} 1.4295 (lit.[23] n^{25}_{D} 1.4316); n^{20}_{D} 1.4316 (lit.[24] n^{20}_{D} 1.4300); M_{D} 30.3 (calcd 30.1). Discrepancies between these data and previously published data probably can be accounted for by the fact that previous investigators did not stabilize[19] the distilland (we used potassium carbonate) and doubtless some decomposition occurred.[3]

Attempts to prepare this compound by the reaction of ethylenesulfonyl chloride with sodium ethoxide led to a mixture of esters, probably including ethyl 2-ethoxyethanesulfonate, which could not be separated by fractional distillation.

Sodium 2-Propene-1-sulfonate.—The original synthesis of Belous,[25] *et al.*, was modified as follows. A solution of 125 g (1 mol) of sodium sulfite in 500 ml of water was heated under reflux with 121 g (1.0 mol) of freshly distilled allyl bromide for 12 hr, after which time the layer of allyl bromide had disappeared. The yield of product was 98% based on allyl bromide.

A derivative, the benzylisothiouronium 2-propene-1-sulfonate, was prepared with considerable difficulty as follows. A hot solution of 4.6 g of benzylisothiouronium chloride in 14 ml of

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(13) E. F. Landau, *J. Amer. Chem. Soc.*, **69**, 1219 (1947).

(14) W. Kern and R. C. Schulz, *Angew. Chem.*, **69**, 153 (1957).

(15) A. Lambert and J. D. Rose, *J. Chem. Soc.*, 45 (1949).

(16) W. F. Whitmore and E. F. Landau, *J. Amer. Chem. Soc.*, **68**, 1797 (1946).

(17) D. S. Breslow, R. R. Hough, and J. T. Fairclough, *ibid.*, **76**, 5361 (1954).

(18) H. R. Snyder, H. V. Anderson, and D. P. Hallada, *ibid.*, **73**, 3258 (1951).

(19) S. S. Rossander and C. S. Marvel, *ibid.*, **50**, 1491 (1928).

(20) The higher boiling fraction, referred to as a polymer of ethylenesulfonyl chloride by Landau, seems to have been a mixture of 2-chloroethanesulfonyl chloride, produced by HCl addition to ethylenesulfonyl chloride, and ethyl ethylenesulfonate, possibly produced from residual ethanol used in recrystallization of the salt of ethylenesulfonic acid before conversion into the sulfonyl chloride. Thus redistillation of the higher boiling fraction gave a substance [bp 73–74° (4 mm), n^{25}_{D} 1.4848, d^{25}_{4} 1.5169] having a saponification equivalent consistent by chance with the sulfonyl chloride or its polymer, but too high a chloride content. [*Anal.* Calcd for $(C_2H_3ClO_2S)_n$: Cl, 28.1; sapon equiv, 63.3. Found: Cl, 34.0; sapon equiv, 63.1.] The analysis is consistent with a mixture of roughly 80–90% 2-chloroethanesulfonyl chloride and 10–20% ethyl ethylenesulfonate. No attempt was made to refine this mixture, but its mass spectrum was nearly identical with that of an authentic sample of 2-chloroethanesulfonyl chloride: bp 68–70° (6 mm); n^{25}_{D} 1.4910 (lit.[16] n^{20}_{D} 1.4920).

(21) J. Preston and J. K. Lawson, Jr., *J. Polym. Sci., Part A*, **2**, 5364 (1964).

(22) J. Preston and H. G. Clark, III, U. S. Patent 2,928,859 (1960); *Chem. Abstr.*, **55**, 3522 (1961).

(23) V. V. Alder and W. E. Hanford, U. S. Patent 2,348,705 (1944); *Chem. Abstr.*, **39**, 711 (1945).

(24) S. M. McElvain, A. Jeline, and K. Rorig, *J. Amer. Chem. Soc.*, **67**, 1578 (1945).

(25) M. A. Belous and I. Ya. Postovskii, *J. Gen. Chem. USSR*, **20**, 1701 (1950).

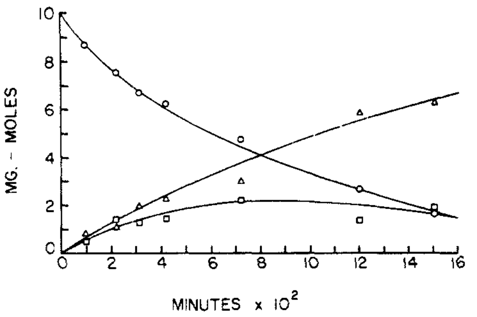

Figure 1.—Ethanolysis of ethylenesulfonyl chloride at 0°: ○, $CH_2{=}CHSO_2Cl$; □, $CH_2{=}CHSO_2OH$; △, $CH_2{=}CHSO_2OEt$.

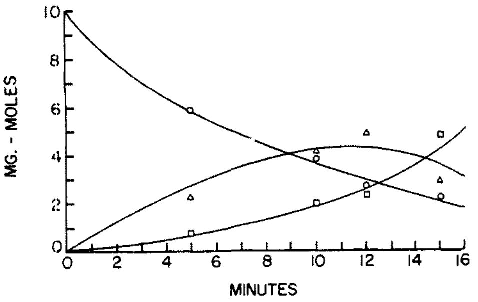

Figure 2.—Ethanolysis of 2-propene-1-sulfonyl chloride at 84°: ○, $CH_2{=}CHCH_2SO_2Cl$; □, $CH_2{=}CHCH_2SO_2OH$; △, $CH_2{=}CHCH_2SO_2OEt$.

water was added to a hot solution of 2.9 g of sodium 2-propene-1-sulfonate in 10 ml of water; an oily layer separated which crystallized when chilled and stirred. Recrystallization from dilute ethanol gave material melting at 121–122°. Further recrystallization from acetone containing a little water gave long needles, mp 130–131°.

Anal. Calcd for $C_{11}H_{16}N_2O_3S_2$: C, 45.81; H, 5.58; N, 9.71. Found: C, 45.63; H, 5.64; N, 9.88, 9.66, 9.51.

2-Propene-1-sulfonyl Chloride.—The procedure of Belous,[25] *et al.*, was used to prepare crude 2-propene-1-sulfonyl chloride: bp 60–61° (4 mm); $n^{20}D$ 1.4768. This material was fractionally distilled in the presence of potassium carbonate as a stabilizer through a 32 × 3 cm Vigreux column equipped with partial condensation stillhead. The heart cut had the following physical properties:[26] bp 61–62° (6.5 mm); $n^{25}D$ 1.4743; $n^{14}D$ 1.4788 (lit.[25] $n^{14}D$ 1.4730); $d^{25}{}_4$ 1.318; MD 30.0 (calcd 29.97).

Anal. Calcd for $C_3H_5ClO_2S$: C, 25.63; H, 3.58; Cl, 25.22; S, 22.81. Found: C, 25.58; H, 3.61; Cl, 25.56; S, 23.23.

Ethyl 2-Propene-1-sulfonate.—Ethanolic sodium ethoxide was prepared from 8.33 g (0.36 g-atom) of sodium and 200 ml of absolute ethyl alcohol. This solution was added in small increments with stirring and cooling to 46.27 g (0.33 mol) of 2-propene-1-sulfonyl chloride in 100 ml of ether. The reaction product was poured into cold water, and the ether layer was washed three times with 50-ml portions of cold 20% sodium chloride solution. The ethereal solution of ester was dried overnight with calcium chloride. After the ether had been removed under vacuum, the ester was distilled in the presence of potassium carbonate as stabilizer from a 50-ml Claisen flask having a Vigreux side arm to give a 41-g yield (82% based on sulfonyl chloride): bp 90–92° (1–2 mm); $n^{20}D$ 1.4420. Fractional distillation through the previously described Vigreux column gave a heart cut having the following physical properties: bp 92–93° (2–3 mm); $n^{25}D$ 1.4415; $d^{25}{}_4$ 1.1442; MD 34.7 (calcd 34.67).

Anal. Calcd for $C_5H_{10}O_3S$: C, 39.98; H, 6.71; sapon equiv, 150.2. Found: C, 40.20; H, 6.67; sapon equiv, 150.3.

Determination of Rates of Ethanolysis of Sulfonyl Chlorides.—An ampoule of the sulfonyl chloride and the calculated amount of ethanol in molar proportions of 1:25 were enclosed in a flask in a constant-temperature bath at selected temperatures for 10–20 min. The ampoule was crushed, and the mixture quickly was made homogeneous by rapidly swirling the flask. Time was recorded from the crushing of the ampoule to subsequent quenching of the sample by plunging the flask into an ice slurry.

The analytical procedures for analysis of the reaction mixtures were described earlier.[7] The amount of unreacted acid chloride was obtained by determination of chloride ion produced upon saponification of the isolated acid chloride. The rate constants are summarized in Tables I, III, and IV while the distribution of products from the ethanolysis of the acid chlorides are shown in Figures 1 and 2.

Table III

Ethanolysis of Ethylenesulfonyl Chloride[a,b]

Temp, °C[c]	k, min^{-1}
0.0	1.12×10^{-3}
20.2	7.27×10^{-3}
35.1	2.90×10^{-2}

[a] Molar ratio of sulfonyl chloride to ethanol initially 1:25 ± 1. [b] Average value of k calculated from a least-squares solution. [c] ±0.1°.

Table IV

Ethanolysis of 2-Propene-1-sulfonyl Chloride[a,b]

Temp, °C	k, min^{-1}
0.0[c]	4.32×10^{-5}
20.2[c]	5.88×10^{-4}
35.1[c]	1.52×10^{-3}
84[d]	9.92×10^{-2}

[a] Molar ratio of sulfonyl chloride to ethanol initially 1:25 ± 1. [b] Average value of k calculated from a least-squares solution. [c] ±0.1°. [d] Reflux.

The rate constants were determined by least-squares solutions of time *vs.* the logarithm of the concentration of residual sulfonyl chloride calculated on the basis of 10.00 mmol initially present. The data collected at a number of temperatures are summarized in Tables III and IV.

Determination of Rates of Alkylation of Ethanolic Hydrogen Chloride with the Ethyl Sulfonates.—The solvent for the alkylation study was an ethanolic solution of dry hydrogen chloride which is more nearly representative of the reaction product medium on ethanolysis of the sulfonyl chloride than ethanol alone, additional hydrogen chloride being used so that its concentration change would be minimized. An amount of the solution was added to the sample such that the molar proportions of ester to hydrogen chloride to ethanol were initially 1:5:50. Unreacted ester was determined by stoichiometric difference from the quantity of sulfonic acid produced; the latter was determined from differential titrations for total acid and chloride ion. Data for the esters are shown in Tables II and V.

Table V

Rates of Alkylation of Ethanolic Hydrogen Chloride by Ethyl Ethylene- and 2-Propene-1-sulfonate[a,b]

Temp, °C	k, min^{-1}
Ethyl Ethylenesulfonate	
35.1[c]	3.62×10^{-4}
50.0[c]	1.86×10^{-3}
Ethyl 2-Propene-1-sulfonate	
35.1[c]	1.58×10^{-4}
50.0[c]	9.58×10^{-4}
84[d]	3.9×10^{-4}

[a] The molar proportions of ester to hydrogen chloride to ethanol initially 1:5:50 ± 2. [b] Average value of k calculated from a least-squares solution. [c] ±0.1°. [d] Reflux.

Registry No.—Ethylenesulfonyl chloride, 6608-47-5; 2-propene-1-sulfonyl chloride, 14418-84-9; benzylisothiouronium 2-propene-1-sulfonate, 17704-11-9; ethyl 2-propene-1-sulfonate, 10602-27-4.

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[26] The elemental analysis reported by Belous,[25] *et al.*, was quite poor, indicating an impure product. Their material was not stabilized with potassium carbonate during the distillation and some decomposition probably occurred, accounting for physical properties which do not correspond to those found by us in the present study.