

A STUDY OF ALIPHATIC SULFONYL COMPOUNDS. I. OCTANE-1- AND -2-SULFONYL CHLORIDES¹

ROBERT B. SCOTT, JR.,² AND ROBERT E. LUTZ

Received October 30, 1953

Some time ago Goubau (1) found that the solvolysis of aromatic sulfonyl chlorides is essentially first order when carried out with a large excess of alcohol at 0° to 50°. Recent investigations by Tommila (2) indicate that the reaction takes place by a bimolecular (S_N2) mechanism). Except for Goubau's reference to some unpublished work with phenylmethanesulfonyl chloride and its *p*-nitro derivative, kinetic studies of the alcoholysis of aliphatic sulfonyl halides have not heretofore been reported.

Since alcoholysis of aliphatic sulfonyl chlorides very probably also proceeds in a bimolecular manner, the mechanisms of reactions of aliphatic sulfonyl halides should be comparable to those of primary alkyl halides and thus subject to steric and polar influences which affect primary alkyl halides. An investigation of the effects of substituent groups on the rate of alcoholysis in boiling ethanol therefore was undertaken.

This report is concerned with data obtained for octane-1- and -2-sulfonyl chlorides which are known, and it represents the first of a series of studies on the magnitude of steric and polar influences on reactions of aliphatic sulfonyl compounds. New preparations and determinations of physical constants are described herein because previous investigators (3, 4) did not report density determinations and referred to slight decomposition taking place during distillation.

Octane-1-sulfonyl chloride was prepared by oxidative chlorination of the corresponding mercaptan according to Ziegler (3), by sulfonylation of *n*-octylmagnesium chloride with excess ethereal sulfuryl chloride according to Cherbuliez (5), and by heating the mercaptan-derived sulfonic acid with either phosphorus pentachloride or thionyl chloride. The products from these three routes had identical physical properties (m.p. 15.5–16.5°, b.p. 94°/1 mm., n_D^{20} 1.4591, n_D^{25} 1.4570, d_4^{25} 1.0817, M_D 53.56) and yielded the same amide. No decomposition occurred during distillation when crystals of potassium carbonate were used as boiling stones. The refractive index is in agreement with that reported in the literature (3).

Octane-2-sulfonyl chloride was prepared by sulfonylation of 2-octylmagnesium chloride (5). Distillation under a vacuum without decomposition was made pos-

¹ Principally from the 1949 dissertation presented by Robert B. Scott, Jr., in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Virginia. A minor part of this work was completed at the University of Alabama as a contribution to project NR 055 222 under contract N9 onr 96100 with the Office of Naval Research. Rights reserved for reproduction in whole or in part for any purpose by the United States Government.

² E. I. du Pont de Nemours Research Fellow 1947–1948, University of Virginia. Present Address: Department of Chemistry, University of Alabama, University, Alabama.

sible by potassium carbonate stabilization of the distilland and by using an unpacked distillation column (b.p. $90^{\circ}/1$ mm., n_D^{25} 1.4599, d_4^{25} 1.0834, M_D 53.77, mobile liquid at about -70°). The literature value for the refractive index (4) is substantially the same.

Potassium carbonate stabilizes these sulfonyl chlorides (and also their ethyl esters) against decomposition during reduced pressure distillation but it is necessary to use an unpacked column such as a Vigreux, and probably partial condensation reflux is preferred to total condensation. Whitmore (6) observed that *tert*-alkyl chlorides can similarly be stabilized against autocatalytic decomposition and Gilman (7) found that sulfonic esters reported to be thermally unstable can be distilled without decomposition after drying with potassium carbonate. Rossander (8) also reported having used this compound for drying esters of sulfonic acids.

Although the *ethyl sulfonates* can be prepared directly from these sulfonyl chlorides in the presence of cold pyridine (9) a more satisfactory synthesis is the essentially quantitative reaction of the sulfonic acids with excess ethereal diazoethane, analogous to the preparation of methyl sulfonates using diazomethane (10). Like the sulfonyl chlorides, these esters can be distilled under reduced pressure in the presence of potassium carbonate without decomposition.

Only one derivative of octane-1-sulfonic acid has been previously reported, namely, the phenylhydrazine salt (11), and none has been reported for octane-2-sulfonic acid. Consequently, a number of new characterizing derivatives were prepared and these are listed in Table II.

EXPERIMENTAL

Ethanolysis of the sulfonyl chlorides. A mixture of 2.13 g. (0.0100 mole) of the particular sulfonyl chloride, 0.50 g. (0.014 mole) of hydrogen chloride, and 11.2 g. (0.24 mole) of dry ethanol, was refluxed. Weighed aliquots were periodically removed and quenched in cold water. The composition of the mixture of sulfonyl chloride and sulfonic ester remaining after aqueous extraction of the sulfonic acid was estimated from the weight of the mixture and its refractive index after total distillation in a small electrically-heated static type molecular still (5-10 mm. distillation path, 0.02-0.05 mm. pressure) equipped with a U-shaped condenser instead of the conventional cold-finger in order to increase the rate of distillation. Temperatures in excess of 50° were avoided and the material balance of the distillations was good. The aqueous extract containing sulfonic acid was concentrated and treated with barium chloride solution. The amount of sulfonic acid in the alcoholysis mass then was calculated from the dry weight (75° *in vacuo*) of barium sulfonate precipitated. It also was calculated by stoichiometric difference from the amounts of sulfonyl chloride and ester. The material balance was good in the case of the primary sulfonyl chloride but only fair in the case of the secondary one because of the appreciable solubility of its barium sulfonate. The results are recorded in parts A and B of Table I.

Ethyl octane-1-sulfonate was prepared in 62% conversion by ethanolysis of the sulfonyl chloride in the presence of cold pyridine and in essentially quantitative yield by distilling ethereal diazoethane into an ether solution of the sulfonic acid; it was distilled through a 36 cm. \times 16 mm. Vigreux column fitted with a partial-condensation still head. In order to avoid possible decomposition during the reduced pressure distillation, crystals of potassium carbonate were used as boiling stones. Physical characteristics are: b.p. $113^{\circ}/1$ mm., n_D^{25} 1.4382, d_4^{25} 1.0009, M_D 58.3.

Anal. Calc'd for $C_{10}H_{22}O_3S$: C, 54.02; H, 9.98.

Found: C, 54.00; H, 9.83.

Ethyl octane-2-sulfonate was prepared in an analogous manner by reacting the sulfonic acid with diazoethane (b.p. $101^\circ/1$ mm., n_D^{25} 1.4338, d_4^{25} 1.0029, M_D 58.3).

Anal. Calc'd for $C_{10}H_{22}O_3S$: C, 54.02; H, 9.98.

Found: C, 54.09; H, 9.76.

Action of alcoholic hydrogen chloride on the sulfonic esters. Rates of attack on the intermediate ethyl esters by ethanolic hydrogen chloride were determined in a manner somewhat like that described for ethanolysis of the sulfonyl chlorides. A mixture of 2.22 g. (0.0100 mole) of the ethyl octanesulfonate, 0.83 g. (0.023 mole) of hydrogen chloride, and 11.0 g. (0.24 mole) of dry ethanol was refluxed. Periodically, weighed aliquots were removed and treated as for ethanolysis of the sulfonyl chlorides except that the absence of sulfonyl chloride obviated distillation of recovered ester. The results are recorded in parts C and D of Table I.

Solvolysis of the sulfonic esters. Rates of attack by the solvent were estimated by refluxing a mixture of 1.11 g. (0.0050 mole) of ethyl ester in 20 cc. of ethanol for 9.3 hours. After aqueous extraction of the sulfonic acid produced, 0.11 g. (0.0005 mole) of the primary sulfonic ester and 0.20 g. (0.0009 mole) of the secondary one were recovered, thus indicating that solvolysis had proceeded 90% ($k = 0.004$ mins. $^{-1}$) and 82% ($k = 0.003$ mins. $^{-1}$) respectively.

Saponification of the sulfonyl chlorides. To 0.21 g. (1.0 mg.-mole) of sulfonyl chloride in a covered 10-cc. beaker was added 0.15 g. (1.1 mg.-mole) of potassium carbonate as a 10% aqueous solution. After the mixture had been heated momentarily to boiling, the covered beaker was placed on a steam-bath which maintained the reaction mass at about 75° . After approximately an hour the primary sulfonyl chloride had been completely saponified as judged by its disappearance as a separate phase. A trace of the secondary chloride remained as a separate phase after about eight hours.

Alkaline ethanolysis of the sulfonyl chlorides. The sulfonyl chloride (2.13 g., 0.0100 mole), followed by a 10-cc. ethanol rinse, was added rapidly to a stirred solution of 1.0 g. (0.043 g.-atom) of sodium in 40 cc. of dry ethanol at 19° . Aliquots were periodically removed from the charge, which was maintained at 20 – 25° by cooling, and were analyzed for sulfonyl chloride and ester in the manner described under the earlier section on ethanolysis of the sulfonyl chlorides. The sulfonyl chloride which had reacted also was determined by mercuric nitrate titration of the chloride ion produced. The amount of sulfonic acid was estimated by stoichiometric difference. The results are shown in parts E and F of Table I.

Solid derivatives from the sulfonyl chlorides. Numerous sulfonamides were prepared in the conventional manner from octane-1-sulfonyl chloride; heating the amine-sulfonyl chloride mixture with pyridine as a catalyst was necessary in the case of aromatic amines while aliphatic amines reacted quite vigorously in ether solution. "Isooctane" (2,2,4-trimethylpentane) was a most satisfactory solvent for recrystallization of the amides. In Table II are shown the various derivatives prepared.

Preparation of a solid derivative from octane-2-sulfonyl chloride was difficult. Neither the amide, the benzylamide, nor the *p*-chloroanilide could be induced to crystallize. The sulfonyl chloride did not react when heated with potassium phthalimide. The method of formation of the sulfonphthalimide recommended by Evans (12), wherein the sulfonamide is reacted with phthalyl chloride in boiling toluene, failed to force a reaction. However, when an equimolar mixture of the crude liquid sulfonamide (0.82 g., 0.0042 mole) and phthalyl chloride (symmetrical, 0.86 g.) was heated, hydrogen chloride began to be evolved at 130 – 140° . Heat was increased until no more gas was given off at 225° . After the residue had been dissolved in benzene and clarified with charcoal, the sulfonphthalimide was repeatedly crystallized from "isooctane" containing 5% (by volume) of benzene or 8% of chloroform until there was no increase in melting point (95.5 – 96.5°). The yield of such recrystallized product was 9% (0.12 g., 0.0004 mole).

Anal. Calc'd for $C_{16}H_{21}NO_4S$: C, 59.42; H, 6.55.

Found: C, 59.47; H, 6.13.

TABLE I
ATTACK ON OCTANESULFONYL COMPOUNDS BY ETHANOL, BY HYDROGEN
CHLORIDE, AND BY SODIUM ETHOXIDE

EXPERIMENT ^a	TIME, MINS.	RSO ₂ Cl MG.-MOLES	RSO ₂ OC ₂ H ₅ MG.-MOLES	RSO ₂ OH MG.-MOLES		k ₁ , MINS. ⁻¹	k ₂ , MINS. ⁻¹
				Obt'd ^b	Calc'd ^c		
A	8.5 ^d	4.7	4.7	0.3	0.6	0.090	
	13.5 ^d	3.0	5.8	1.1	1.2	.089	0.01 ^e
	18.5 ^d	1.9	5.8	2.2	2.3	.090	.03 ^e
	28.5 ^d	0.8	5.1	4.1	4.1	.089	.04 ^e
					Average ^f	.089	
B	30	6.5	1.2	0.4	2.3	.014	
	49	5.5	1.7	0.9	2.8	.012	.04 ^e
	60	4.6	1.5	0.9	3.9	.013	.05 ^e
	82	3.0	1.2	3.0	5.8	.015	.06 ^e
					Average ^f	.014	
C	11		6.2	3.0	3.8	.043	
	33		1.6	7.3	8.4	.056	
	53.5		0.6	8.9	9.4	.053	
					Average ^f	.051	
D	12		5.7	2.6	4.3	.047	
	25		3.7	4.3	6.3	.040	
	45		1.7	6.7	8.3	.039	
	60.5		0.9	7.0	9.1	.040	
					Average ^f	.041	
E	3	0.0	5.3		4.7	>1.	
	10	0.0	5.2		4.8		.004 ^e
	50	0.0	4.4		3.6		
F	3	0.0	8.2		1.8	>1.	
	14	0.0	7.5		2.5		.008 ^h

A. *Ethanolysis of octane-1-sulfonyl chloride.* Mixture of 2.13 g. of sulfonyl chloride, 0.50 g. of hydrogen chloride, and 11.2 g. of dry ethanol refluxed different times and analyzed. B. *Ethanolysis of octane-2-sulfonyl chloride.* Treated as A. C. *Alkylation of hydrogen chloride with ethyl octane-1-sulfonate in ethanol.* A mixture of 2.22 g. of ethyl octanesulfonate, 0.83 g. of hydrogen chloride, and 11.0 g. of dry ethanol refluxed different times and analyzed. D. *Alkylation of hydrogen chloride with ethyl octane-2-sulfonate in ethanol.* Treated as C. E. *Alkaline ethanolysis of octane-1-sulfonyl chloride.* Mixture of 1.0 g. of sodium in 50 cc. of dry ethanol reacted with 2.13 g. of sulfonyl chloride at 20-25° for different times and analyzed. F. *Alkaline ethanolysis of octane-2-sulfonyl chloride.* Treated as E.

^a Each experiment is based on 10.0 mg.-moles of starting sulfonyl compound. ^b Calculated from weight of isolated barium salt. ^c Calculated by stoichiometric difference from the determined combined yields of sulfonyl chloride and ester. ^d Actual time measured was 1.5 mins. longer in each case. The following constants were obtained based on time other than zero (min.⁻¹): 0.090 (10 and 15 mins.), 0.092 (15 and 20 mins.), 0.086 (20 and 30 mins.), 0.091 (10 and 20 mins.), 0.089 (10 and 30 mins.), 0.088 (15 and 30 mins.); mean value of 0.089 was used then for calculation of time zero. When 1.5 mins. is deducted from the observed times all points including calculated time zero fall on a straight line in a log conc'n vs time plot. The accuracy of the data may not warrant such a correction; however, the mean rate constant calculated from the observed time ($k = 0.082 \text{ mins.}^{-1}$) also is significantly different from that of the secondary sulfonyl chloride. ^e Calculated from $B = \frac{k^1 A_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$

in which B = conc'n of ester at time t; k_1 = rate constant for disappearance of RSO₂Cl; A_0 = init. conc'n of RSO₂Cl; k_2 = rate constant for disappearance of ester. ^f Average values determined graphically. ^g Assuming first order and calculations based on data for 3 and 50 mins. and for 10 and 50 mins. Second order constant similarly determined is 0.15 moles⁻¹ mins.⁻¹. ^h Assuming first order and calculations based on data for 3 and 14 mins. Second order constant similarly determined is 0.26 moles⁻¹ mins.⁻¹.

TABLE II
 AMIDE DERIVATIVES OF OCTANE-1-SULFONIC ACID

DERIVATIVE	M.P., °C.	ANALYSES					
		Calc'd			Found		
		C	H	N	C	H	N
Dimethylamide ^a	23.5-24.5			6.33			5.63
Piperidide.....	33-34			5.36			5.28
Dibenzylamide.....	35.5-36.5	70.73	8.37		70.46	8.42	
Anilide.....	41.5-42.5			5.20			5.37
Morpholide.....	47-48			5.32			5.23
Methylamide.....	47.5-48	52.13	10.21		52.00	10.06	
<i>p</i> -Toluidide.....	54.5-55.5			4.94			4.94
Cyclohexylamide.....	63.5-64.5			5.09			5.30
<i>p</i> -Chloroanilide.....	64-65			4.61			4.48
Amide.....	70.5-71.5	49.71	9.91	7.25	49.70	9.90	7.28
Benzylanilide.....	74-75	70.15	8.13		69.90	8.18	
β -Naphthylamide.....	75.5-76.5			4.38			4.45
Benzylamide.....	77.5-79	63.56	8.88		63.82	8.70	
<i>n</i> -Octylamide.....	87.5-88.5			4.59			4.47
<i>p</i> -Nitroanilide.....	92.5-94			8.91			9.17
Phenylhydrazide.....	126-127.5	Decomposed before analysis					

^a Not analytically pure.

Like the secondary sulfonyl chloride, the primary one would not react with potassium phthalimide, nor would it react with phthalimide alone. The sulfonphthalimide was prepared from the primary sulfonamide (0.70 g., 0.0036 mole) by heating with an equimolar quantity of symmetrical phthalyl chloride (0.73 g.) as in the case of the secondary except that hydrogen chloride did not commence to be evolved until the charge had been heated to 175°. A 60% yield (0.69 g., 0.0021 mole) of analytically pure sulfonphthalimide (m.p. 120.5-122°) was obtained.

Anal. Calc'd for C₁₆H₂₁NO₄S: C, 59.42; H, 6.55.

Found: C, 59.33; H, 6.61.

DISCUSSION OF KINETIC RESULTS

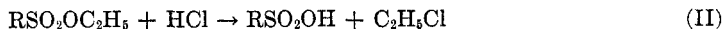
In determining the rate of ethanolysis of these sulfonyl chlorides, a relatively large volume of ethanol was used to reduce to first order the kinetics of the reaction I.



Because hydrogen halide is a product of alcoholysis of sulfonyl halide, ethanolic hydrogen chloride was used in order to minimize any effects on rates of attack on sulfonyl chloride or sulfonic ester caused by variations in its concentrations.³

³ Goubau (1) considered that an apparent drift from first order ethanolysis of aromatic sulfonyl chlorides was due to autocatalysis by hydrogen chloride. If allowance is made in the total acidity on which he based his calculations for an increase due to slow solvolytic attack on the sulfonic ester (concurrent with the more rapid attack by hydrogen chloride which results in no change in total acidity), the apparent drift disappears. Although Goubau observed an increased rate of ethanolysis when alcoholic hydrogen chloride was used, this

Competing reactions consecutive to reaction I are represented as II and III.



In parts A and B of Table I are shown the amounts of sulfonyl chloride, sulfonic ester, and sulfonic acid present at different times during alcoholysis of these sulfonyl chlorides with boiling ethanolic hydrogen chloride. Graphic representations of these data in Figures 1 and 2 illustrate the first order attack on sulfonyl chlorides and consecutive conversion of the resultant sulfonic ester into sulfonic acid.

Only differences in steric requirements of the two sulfonyl chlorides seem to be consistent with the significantly greater rate of ethanolysis determined for octane-1-sulfonyl chloride ($k = 0.089 \text{ mins.}^{-1}$), as compared with that found for octane-2-sulfonyl chloride ($k = 0.014 \text{ mins.}^{-1}$); and the assumption that the alcoholysis of aliphatic sulfonyl halides proceeds by a mechanism similar to that for primary alkyl halides rather than for acyl halides seems well justified. The relative rates of 6.4 to 1 are about what would be expected on the basis of the relative rates of $\text{S}_{\text{N}}2$ reaction of similarly hindered alkyl bromides with potassium iodide in acetone (13), assuming that the sulfo group is the equivalent of a methylene group except about a third larger.⁴

Apparently uncatalyzed alcoholysis to produce sulfonic esters is less practicable for sulfonyl halides having large steric requirements than for straight chain ones. Figure 2 demonstrates that the secondary sulfonic ester is more rapidly attacked than its sulfonyl chloride while Figure 1 shows that the primary one is less rapidly attacked than its sulfonyl chloride.

Although rate constants calculated for the consecutive attack on the sulfonic esters are too erratic to be much more than qualitative (see parts A and B of Table I) they are of the same order as the more accurate constants resulting from data obtained when the pure sulfonic esters were reacted with boiling ethanolic hydrogen chloride (see parts C and D of Table I). The amount of hydrogen chloride necessarily varies during ethanolysis of sulfonyl chlorides, consequently the maximum amount that could be present was used in determining the rate of attack on the pure esters. Therefore the resulting constants represent the maximum rates for the consecutive reaction during ethanolysis of the sulfonyl chloride.

In Figure 3 the rates of attack on the sulfonic esters are graphically compared with those for the sulfonyl chlorides. The primary sulfonic ester reacts ($k = 0.051$

would not be expected to affect a comparison of isomeric sulfonyl chlorides. Recent work with another aliphatic sulfonyl chloride by John B. Gayle at the University of Alabama indicates that there is no change in rate occasioned by the added hydrogen chloride.

⁴ Since *n*-butyl bromide is attacked by potassium iodide in acetone sixteen times as fast as β -methylbutyl bromide, the primary sulfonyl chloride should react $16 \left(\frac{0.77}{1.04} \right)^3 = 6.5$ times as fast as the secondary one assuming that the hindrance varies inversely as the surface exposed of the attacked atoms.

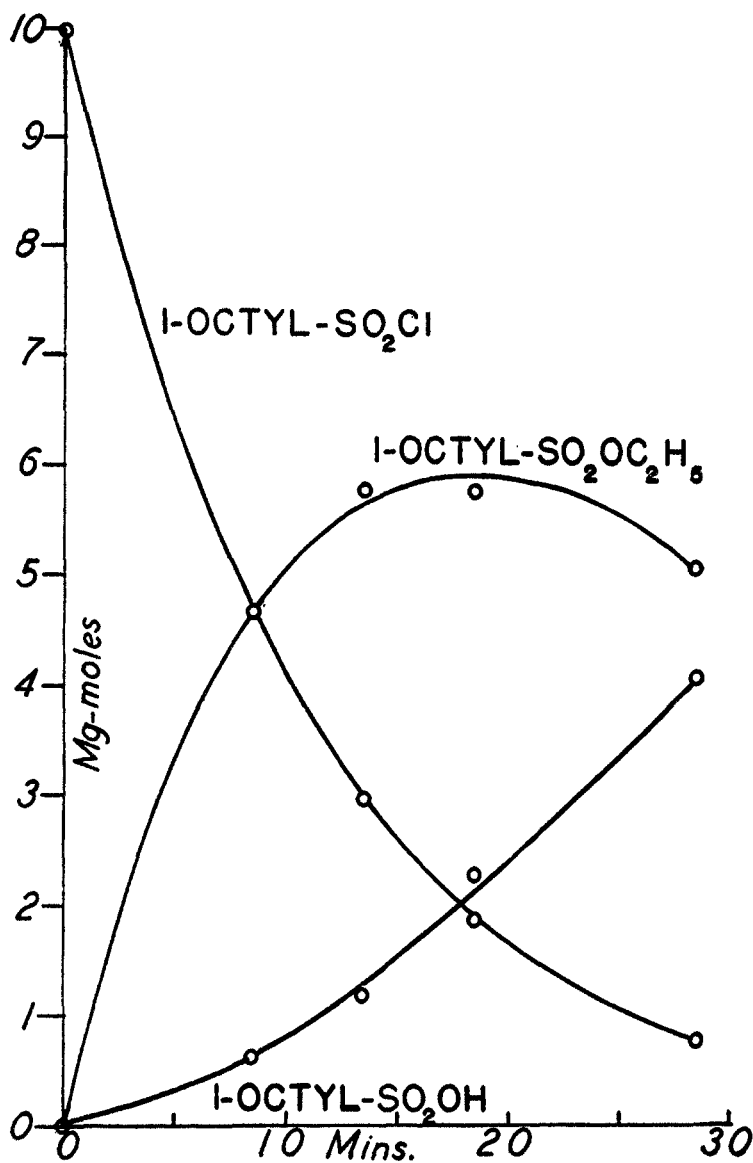


FIGURE 1. ETHANOLYSIS OF OCTANE-1-SULFONYL CHLORIDE IN BOILING ETHANOLIC HYDROGEN CHLORIDE⁵.

⁵ Sulfonyl chloride and ester concentrations were estimated from refractive indices of isolated mixtures of the two components freed of other materials. Sulfonic acid concentrations were estimated by stoichiometric difference and, in the case of the 1-sulfonyl chloride, they agree well with values calculated stoichiometrically from the weight of barium salt isolated.

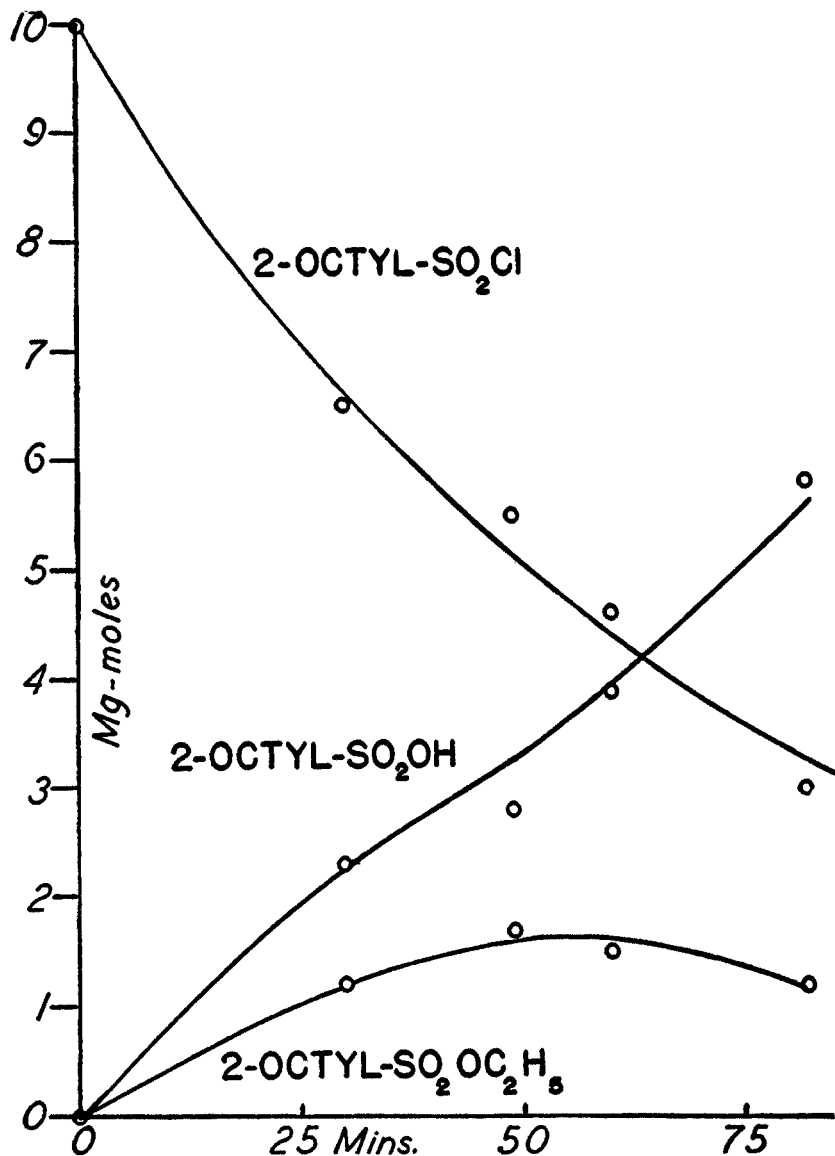


FIGURE 2. ETHANOLYSIS OF OCTANE-2-SULFONYL CHLORIDE IN BOILING ETHANOLIC HYDROGEN CHLORIDE⁵.

mins.⁻¹) about 1.2 times as fast as the secondary one ($k = 0.041$ mins.⁻¹), thereby suggesting that the steric requirements of the latter may be significantly greater. Although these esters alkylate the solvent as well as react with the hydrogen chloride, the reaction with boiling ethanol alone is only about 7% as fast as with the alcoholic hydrogen chloride. Again the steric requirements of the secondary sulfonic ester ($k = 0.003$ mins.⁻¹) are shown to be greater than those of the primary one ($k = 0.004$ mins.⁻¹).

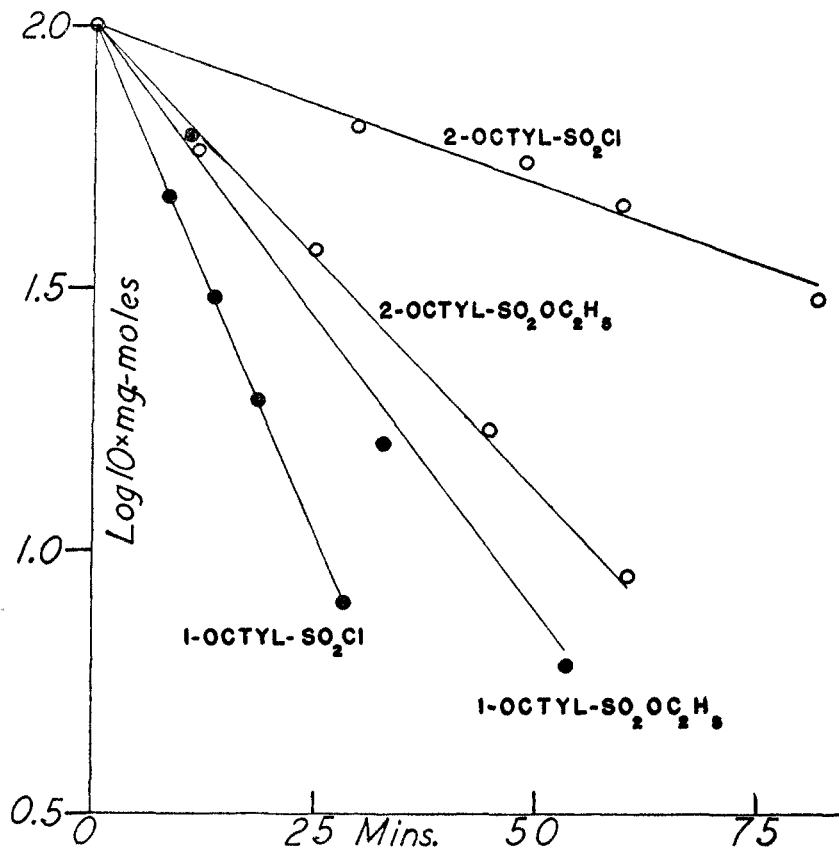


FIG. 3. COMPARISON OF RATES OF REACTION OF OCTANE-1- AND -2-SULFONYL CHLORIDES AND ETHYL OCTANE-1- AND -2-SULFONATES WITH BOILING ETHANOLIC HYDROGEN CHLORIDE

Since bases increase the rate of alcoholysis of sulfonyl halides, the alkaline ethanolsis of the sulfonyl chlorides was carried out at 25°. Even so the reaction is so rapid that no sulfonyl chloride remains in either case after three minutes, while the resultant esters then are more slowly attacked; this supports Hirsjärvi's conclusion (14) that shorter than conventional reaction periods would be better when preparing sulfonic esters in this manner. As a three-fold excess of ethoxide was present after the sulfonyl chlorides had been reacted, the base attack on the resultant esters can be considered as partially reduced toward first order for comparative purposes. At least these rough values ($k_1 = 0.004$ mins.⁻¹, $k_2 = 0.15$ moles⁻¹ mins.⁻¹ for the primary and $k_1 = 0.008$ mins.⁻¹, $k_2 = 0.26$ moles⁻¹ mins.⁻¹ for the secondary) serve to fix the order of magnitude and indicate that base attack is much more prominent at this temperature and concentration than solvolysis (see parts E and F of Table I).

As further evidence of the greater steric requirements of the secondary sulfonyl chloride, saponification with hot aqueous potassium carbonate solution proceeds

roughly eight times as fast with the primary as with the secondary sulfonyl chloride.

SUMMARY

Octane-1- and -2-sulfonyl chlorides and the ethyl esters of the corresponding sulfonic acids can be distilled *in vacuo* without decomposition through an unpacked column provided the distilland is stabilized with potassium carbonate.

Useful physical constants have been determined for octane-1- and -2-sulfonyl chlorides and for the ethyl esters of the corresponding sulfonic acids.

A number of solid derivatives of octane-1-sulfonyl chloride and one solid derivative of octane-2-sulfonyl chloride have been prepared.

Steric hindrance to ethanolysis by octane-2-sulfonyl chloride has been demonstrated by kinetic studies.

CHARLOTTESVILLE, VIRGINIA
UNIVERSITY, ALABAMA

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