mercury thermostat regulator. The reaction tubes were inserted in the bath and removed at intervals for measurement in the colorimeter. The intermittent withdrawal of the tubes introduced no detectable error since the interval between measurements was of long duration compared with the ten seconds required to obtain the color measurement.

For elevated temperatures the runs were made in cells immersed in solvent boilers. Acetone and benzene were used to give temperatures of 57 and 80°, respectively, in the boilers.

Because of the presence of the alcohol in enormous excess over the carbonium ion the rates were generally susceptible to treatment as first-order reactions. The specific rate constants were evaluated from the equation

$$2.303 \log_{10} \frac{A_{si} - A_{s\infty}}{A_s - A_{s\infty}} = k_1 t$$

where A_{si} represents initial absorbancy; A_s, the absorbancy at time t; $A_{s\infty}$, the absorbancy at infinite time; t, the time in seconds; and k_1, the specific rate in sec.$^{-1}$. The slope of a plot of log $(A_{si} - A_{s\infty})/(A_s - A_{s\infty})$ against t was used to determine k_1.

Table III gives a set of representative data for the reduction of dianisylcarbinol by isopropyl alcohol.

Acknowledgment.—The expenses of this research were met by a grant from the Mallinckrodt Chemical Works.

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[CONTRIBUTION FROM THE TEXTILE FIBERS DEPARTMENT, PIONEERING RESEARCH DIVISION, E. I. DU PONT DE NEMOURS AND CO., INC.]

Kinetics of Reactions of Acyl Chlorides. II. Mechanisms of Hydrolysis of Sulfonyl Chlorides

BY H. K. HALL, JR.

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The hydrolysis and amidation rates of a series of sulfonyl chlorides, ZSO_2Cl, [Z = CH_3–, C_6H_5–, CH_3O–, C_2H_5O– and $(CH_3)_2N$–] were determined. Methane- and benzenesulfonyl chlorides hydrolyzed by an SN2 mechanism, whereas dimethylsulfamyl chloride underwent ionization (SN1). The alkoxysulfonyl chlorides underwent ionization at the S–Cl bond, followed by rapid nucleophilic attack on carbon, but some contribution of bimolecular reactions could be detected.

The kinetics of hydrolysis of sulfonyl chlorides, ZSO_2Cl, where Z may be CH_3–, C_6H_5–, CH_3O– or $(CH_3)_2N$–, has been studied by relatively few investigators. The classical investigation of Berger and Olivier,[1] relating to the hydrolysis of aromatic sulfonyl chlorides in aqueous acetone, was extended by the very careful measurements of Hedlund[2] to pure water solutions. The latter investigator also studied alkanesulfonyl chlorides, showing that these compounds hydrolyze much more slowly than the aromatic derivatives. More recently Swain and Scott[3] have shown that benzenesulfonyl chloride in aqueous acetone is highly susceptible to nucleophilic attack by hydroxyl ion or aniline. Linetskaya and Sapoznikhova have supplied additional data on hydrolysis rates of aromatic sulfonyl chlorides.[4] Böhme and Schürhoff,[5] working in aqueous solutions of water-soluble ethers, confirmed that methanesulfonyl chloride hydrolyzes very slowly, but noted that it was very reactive toward methoxide ion.

No kinetics studies have yet been made of the hydrolysis of an alkoxysulfonyl chloride (alkyl chlorosulfonate) or of a sulfamyl chloride. As a continuation of our studies of displacement reactions on carbonyl chlorides,[6] it was of interest to investigate the mechanisms of reaction available to these two types of sulfonyl halide.

Experimental

Materials.—The following compounds were purchased from Eastman Kodak and were redistilled: methanesulfonyl chloride, b.p. 31° (1 mm.), $n^{20}D$ 1.4509; benzenesulfonyl chloride, b.p. 117.5° (12 mm.); ethyl chlorosulfonate, b.p. 30° (1 mm.), $n^{20}D$ 1.4155. Dimethylsulfamyl chloride was prepared by refluxing 100 g. of dimethylamine hydrochloride (Eastman Kodak Co.) with 512 g. of sulfuryl chloride (Hooker Electrochemical Co.) overnight and distilling the reaction mixture directly.[7] There was obtained 120.4 g. of product, b.p. 67° (8 mm.) (lit.[13] b.p. 66° (10 mm.)), $n^{20}D$ 1.4524 (lit.[13] $n^{20}D$ 1.4526). Methyl chlorosulfonate, b.p. 36° (12 mm.) (lit.[8] b.p. 48.1° (29 mm.)), $n^{20}D$ 1.4128–38 (lit.[8] $n^{20}D$ 1.414), was prepared by the reaction of methanol with sulfuryl chloride.[8]

Solvents.—It was noted that solutions of ethyl chlorosulfonate in reagent grade acetone rapidly turned a deep red color. Accordingly, the kinetic runs were made in aqueous dioxane instead of aqueous acetone. Dioxane was purified by the method of Fieser.[9] The mixed solvents were made up by volume at 25.0°.

Kinetics Methods.—The methods of following the rates already have been described.[6] It was found for ethyl chlorosulfonate and dimethylsulfamyl chloride that the rate constants in pure water lacked precision and gave unsatisfactory Arrhenius plots. Subsequent measurements were made in 86.1% water-13.9% dioxane. Under these conditions dimethylsulfamyl chloride behaved satisfactorily, but the data for ethyl chlorosulfonate were still unsatisfactory. Attention was diverted to the more hydrophilic methyl chlorosulfonate, and this chloride in the mixed solvent gave better data. Representative rate plots are given in Fig. 1 and the Arrhenius plots are shown in Fig. 2.

One additional kinetics method was devised in order to obtain data for alkaline and aminiacal solutions in which the silver-silver chloride electrodes did not behave satisfactorily. This consisted of hydrolyzing the acid chloride in the presence of one-half an equivalent of alkali or amine. The *p*H of the reaction solution was noted as a function of time. The time at which the solution changed from alkaline to acidic was sharply defined and was taken as the half-life of the reaction, from which k_1 could be calculated. By this "half-life" method, it was confirmed that the rate of hydrolysis of dimethylcarbamyl chloride, which was studied earlier,[6] was unaffected by added amines or alkali.

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(1) G. Berger and S. C. J. Olivier, *Rec. trav. chim.*, **46**, 516 (1927).

(2) I. Hedlund, *Arkiv Kemi*, **14A**, 1 (1940).

(3) C. G. Swain and C. B. Scott, THIS JOURNAL, **75**, **141**, 247 (1953).

(4) Z. G. Linetskaya and N. V. Sapoznikhova, *J. Appl. Chem. (USSR)*, **21**, 876 (1948); *C. A.*, **43**, 926 (1949); *Doklady Akad. Nauk. S.S.S.R.*, **86**, 753 (1952); *C. A.*, **47**, 955 (1953).

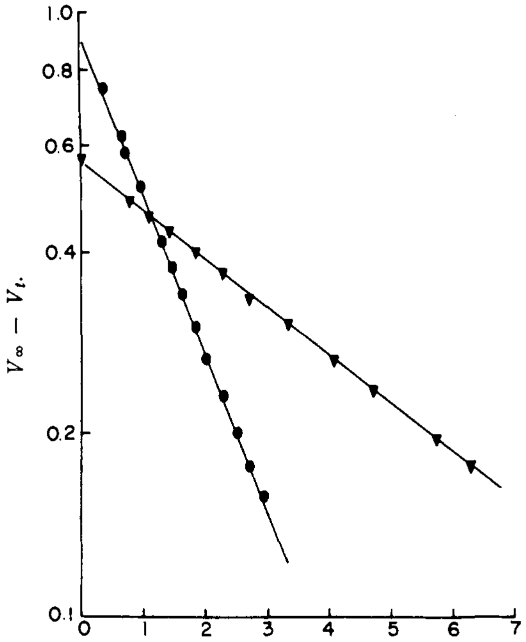
(5) H. Böhme and W. Schürhoff, *Chem. Ber.*, **84**, 28 (1951).

(6) H. K. Hall, Jr., THIS JOURNAL, **77**, 5993 (1955).

(7) (a) K. W. Wbeeler and E. F. Degering, *ibid.*, **66**, 1242 (1944); (b) R. Behrend, *Ann.*, **222**, 116 (1884).

(8) W. W. Binkley and E. F. Degering, THIS JOURNAL, **60**, 2810 (1938).

(9) L. F. Fieser, "Experiments in Organic Chemistry," 2nd Ed., D. C. Heath and Co., New York, N. Y., 1941, p. 369.



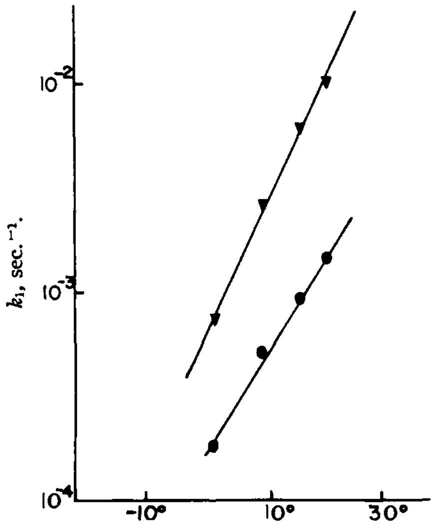
Time, minutes.

Fig. 1.—Representative first order hydrolysis rate plots for 20.0°: circles, methyl chlorosulfonate; triangles, dimethylsulfamyl chloride.

Reaction Products: Methyl Chlorosulfonate-Pyrrolidine.—A solution of 29.7 g. (0.418 mole) of pyrrolidine in 3.0 liters of water and 450 ml. of dioxane was cooled to 8.5°. To it was added with stirring a solution of 15.0 g. (0.115 mole) of methyl chlorosulfonate in 30 ml. of dioxane. After 1 hour the solution was allowed to warm to room temperature and to stand for several days. To it was added with stirring over 20 minutes a solution of 50 ml. of benzoyl chloride in 200 ml. of acetone. The solution was maintained alkaline to brom thymol blue through the progressive addition of 175 ml. of 5 *N* sodium hydroxide solution. Excess pyrrolidine was destroyed by this treatment. After the addition was completed the solution was basified with an additional 100 ml. of alkali and was steam distilled. After 690 ml. had distilled, no further odor of amine was detected. A 310-ml. portion of the distillate was distilled in a spinning band column. The first fraction, 50.78 g., boiled sharply at 56°. Treatment with 450 ml. of a saturated solution of picric acid in ether gave 3.71 g. of picrate, m.p. 222–230°. Digestion with 30 ml. of boiling ethyl acetate gave 3.19 g. (19.6%) of 1-methylpyrrolidine picrate, m.p. 226–230° (lit.[10] m.p. 218°). The second fraction, b.p. 86–87°, gave no picrate on similar treatment and was not further investigated.

Ethyl Chlorosulfonate-Pyrrolidine.—The reaction was performed essentially as above except that 18.0 g. (0.253 mole) of pyrrolidine was used. Fractionation of the final solution gave fractions, b.p. 100–101°, whose picrates melted from 146–147° to 182.0–182.5°. The picrates, 3.76 g., were crystallized from ethyl acetate to provide 2.78 g. (20.0%) of 1-ethylpyrrolidine picrate, m.p. 184–184.5° (lit.[11] m.p. 185°).

Methyl Chlorosulfonate-*m*-Cresoxide Ion.—The reaction was performed as above, except that the pyrrolidine was replaced by 30.0 g. (0.278 mole) of purified *m*-cresol, 53.6 ml. of 5.2 *N* sodium hydroxide solution, and 6 ml. of dioxane. After completion of the reaction the solution was extracted twice with 1-liter portions of methylene chloride, and the aqueous layers were continuously extracted overnight with this solvent. The combined organic layers were dried over magnesium sulfate and the solvent was distilled. The residue, on distillation from a small Claisen flask, gave 6.96 g. of material, b.p. 173–181°. Redistillation gave 4.40 g. (31.4%) of *m*-methylanisole, b.p. 170–184°, $n^{20}\text{D}$ 1.5127. Authentic material, obtained from Eastman Kodak Co., had $n^{20}\text{D}$ 1.5126 (lit.[12] b.p. 177°).



Temperature, °C.

Fig. 2.—Arrhenius plots for the hydrolysis of methyl chlorosulfonate (triangles) and dimethylsulfamyl chloride (circles).

Dimethylsulfamyl Chloride-Piperidine.—Water, 2.7 liters, 400 ml. of dioxane and 20.0 g. (0.235 mole) of piperidine were cooled to 8.5° and to the solution was added with stirring a solution of 15.0 g. (0.104 mole) of dimethylsulfamyl chloride in 30 ml. of dioxane. The solution was held at 8.5° for 1 hour and was allowed to warm to room temperature. It was acidified with 7 ml. of concentrated sulfuric acid dissolved in 100 ml. of water and was extracted twice with 1.5-liter portions of methylene chloride. The aqueous layer was extracted continuously overnight with methylene chloride. The combined organic layers were dried with magnesium sulfate and the solvents were distilled. The dioxane was removed under aspirator vacuum. The oily residue crystallized on standing. It was taken up in ether, treated with Norite, filtered and evaporated. There was obtained 13.1 g. (65.2%) of slightly yellow crystals of 1,1-dimethyl-3,3-pentamethylenesulfamide, m.p. 55–56° (lit.[13] m.p. 55.5–56.2°).

An authentic sample was prepared in 98.5% yield by the reaction of dimethylsulfamyl chloride with piperidine in benzene solution, m.p. 56–57°, mixed melting point 55–56°.

Results

The results of the rate measurements are given in Table I. The rate sequence was: $CH_3SO_2Cl < C_6H_5SO_2Cl \sim (CH_3)_2NSO_2Cl < CH_3^-, C_2H_5OSO_2Cl$ in agreement, for the first two chlorides, with the results of Hedlund.[2]

In the presence of hydroxyl ion (0.0237 *M*) or pyrrolidine (0.0527 *M*), methanesulfonyl chloride reacted too rapidly to measure. Benzenesulfonyl chloride is known to be highly reactive toward nucleophilic reagents.[3] Therefore, these halides are assumed to be undergoing SN2 reactions. This may be a direct displacement

$$H_2O + YSO_2Cl \longrightarrow H^+ + HO_3S^-Y + Cl^-$$
$$Y = CH_3^-, C_6H_5^-$$

Alternatively the reaction may involve nucleophilic attack by water to form the sulfonyl chloride hydrate, which can then ionize

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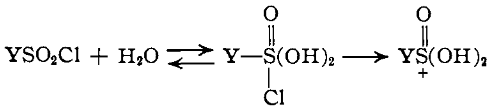
[10] G. Ciamician and A. Piccinini, *Ber.*, **30**, 1791 (1897).

[11] J. von Braun, *ibid.*, **44**, 1256 (1911).

[12] J. Pinette, *Ann.*, **243**, 32 (1888).

[13] W. W. Binkley and E. F. Degering, THIS JOURNAL, **61**, 3250 (1939).



$$\mathrm{YSO_2Cl} + \mathrm{H_2O} \rightleftarrows \mathrm{Y{-}}\underset{\mathrm{Cl}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{S}}}\mathrm{(OH)_2} \longrightarrow \mathrm{Y}\overset{\overset{\mathrm{O}}{\|}}{\underset{+}{\mathrm{S}}}\mathrm{(OH)_2}$$

A mechanism of the latter type was postulated for the hydrolysis of benzoyl chloride.[6]

TABLE I

KINETICS OF HYDROLYSIS OF SULFONYL CHLORIDES

Halide	Concn. × 10^3, M	Temp., °C.	Added reagents, M	$k_1 \times 10^4$, sec.$^{-1}$
		Solvent, water		
CH_3SO_2Cl	2.12	15.0	Na_2SO_4, 0.25	0.847
CH_3SO_2Cl	1.6	8.5	NaOH, 0.0237 Na_2SO_4, 0.25	280<
CH_3SO_2Cl	32.7	8.5	Pyrrolidine, 0.0527	860<
		Solvent, 86.1% water–13.9% dioxane		
$(CH_3)_2NSO_2Cl$	1.11	0.5	$NaClO_4$, 0.0544	1.83
	0.70	8.5	$NaClO_4$, 0.0068	5.09
	3.74	8.5	NaOH, 0.0138	4.91
	11.4	8.5	Piperidine, 0.0231	4.60
	0.48	15.0	None	9.31
	0.78	20.1	$NaClO_4$, 0.0068	14.3
	1.50	20.1	*m*-Cresol, 0.0617 NaOH, 0.0621	44.9
CH_3OSO_2Cl	2.01	0.4	$NaClO_4$, 0.0544	7.13
CH_3OSO_2Cl	3.60	0.7	Pyrrolidine, 0.00530	38.5
CH_3OSO_2Cl	2.99	8.5	$NaClO_4$, 0.0027	31.3
CH_3OSO_2Cl	2.89	8.5	NaOH, 0.0206	50.2
CH_3OSO_2Cl	17.8	8.5	Pyrrolidine, 0.0218	29.9
CH_3OSO_2Cl	1.47	8.5	*m*-Cresol, 0.0618 NaOH, 0.0618	210
CH_3OSO_2Cl	1.42	15.0	$NaClO_4$, 0.0545	59.2[a]
CH_3OSO_2Cl	1.56	15.0	$NaClO_4$, 0.0545	58.9[b]
CH_3OSO_2Cl	1.72	20.0	$NaClO_4$, 0.0545	105
$C_2H_5OSO_2Cl$	2.54	8.5	$NaClO_4$, 0.0068	18.8
$C_2H_5OSO_2Cl$	12.3	8.5	Pyrrolidine, 0.0277	19.6
$C_2H_5OSO_2Cl$	3.08	8.5	NaOH, 0.0138	26.6
		Solvent, water		
$C_6H_5SO_2Cl$	4.24	8.5	$NaClO_4$, 0.0467	5.32
$C_6H_5SO_2Cl$	4.24	30.0	$NaClO_4$, 0.0467	50.0
$C_6H_5SO_2Cl$	4.70	39.7	$NaClO_4$, 0.0467	115.6

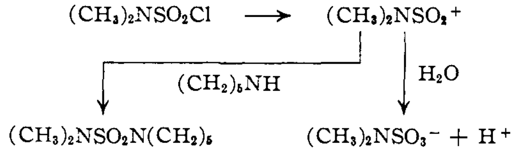
[a] Obtained by alkalimetric intermittent titration. [b] Obtained by following the rate of appearance of chloride ion.

TABLE II

THERMODYNAMIC QUANTITIES OF ACTIVATION FOR HYDROLYSIS OF SULFONYL CHLORIDES

Halide	$\Delta E^{\ddagger}$, kcal. per mole	$\Delta S^{\ddagger}$, e.u.	Reference
CH_3SO_2Cl	20.7	− 8.2	2
$C_6H_5SO_2Cl$	17.5	−13.4	2
CH_3OSO_2Cl	22.3	+ 7.0	This work
$(CH_3)_2NSO_2Cl$	17.0	−15.0	This work

The reactivity of dimethylsulfamyl chloride was unaffected by added hydroxyl ion or pyrrolidine. These facts pointed toward an SN1 mechanism for the hydrolysis of this halide. Proof of such a mechanism was obtained by conducting the reaction in the presence of piperidine. Although the rate was unaffected by the presence of this amine, the product was 1,1-dimethyl-3,3-pentamethylenesulfamide, resulting from attack by the amine on an intermediate dimethylsulfamylium ion



It was of interest that chloride ion was unable to reverse the initial step. The first-order plots for dimethylsulfamyl chloride were strictly linear throughout the reaction, no downward drift with time being observed. This result contrasts with that obtained for dimethylcarbamyl chloride.[6]

It was possible to bring about SN2 reactions of this halide in water solution through the use of more strongly nucleophilic reagents. Thus *m*-cresoxide ion, 0.0617 M, accelerated the rate of reaction of dimethylsulfamyl chloride, pointing to a very high nucleophilic reactivity for this anion.

The reactions of methyl and ethyl chlorosulfonates presented a more complex and interesting pattern. The hydrolysis of these chlorides proceeded directly to the corresponding alcohols without intervention of the alkyl hydrogen sulfate

$$2H_2O + ROSO_2Cl \longrightarrow ROH + 3H^+ + SO_4^= + Cl^-$$

This was shown by the excellent agreement of the rate constant obtained by alkalimetric intermittent titration with that obtained by following the rate of appearance of chloride ion, three hydrogen ions being formed for each chloride ion. The rate of hydrolysis of methyl hydrogen sulfate is far too slow to account for these results.[14]

The reactions of *methyl* chlorosulfonate were accelerated appreciably by added nucleophilic reagents. Thus, in the presence of 0.0618 M *m*-cresoxide ion, the rate constant at 8.5° was increased from 27.8×10^{-4} to 210×10^{-4} sec.$^{-1}$. A major product was found to be *m*-methylanisole, isolated in 31.4% yield. No methyl *m*-methylphenyl sulfate was found. This reaction is probably a direct SN2 attack on carbon, as

$$m\text{-}CH_3C_6H_4O^- + CH_3OSO_2Cl \longrightarrow m\text{-}CH_3C_6H_4OCH_3$$

Pyrrolidine and hydroxyl ion also accelerated the rate of disappearance of methyl chlorosulfonate in water. 1-Methylpyrrolidine was isolated from the former reaction in 19.6% yield. This alkylation reaction probably proceeds by a direct displacement on carbon. Methyl chlorosulfonate behaves similarly in these reactions to methyl *p*-toluenesulfonate. The reactions could not be followed by the concentration cell method because of the unsatisfactory behavior of silver–silver chloride electrodes in strongly alkaline or aminiacal solutions. The rates could be determined by the less accurate conductivity and "half-life" methods, however, and were appreciably higher in the presence of these nucleophilic reagents.

Ethyl chlorosulfonate hydrolyzed at approximately the same rate as the methyl derivative. An inspection of the literature showed a number of reactions of ethyl chlorosulfonate in aqueous media which might be bimolecular attacks on carbon.

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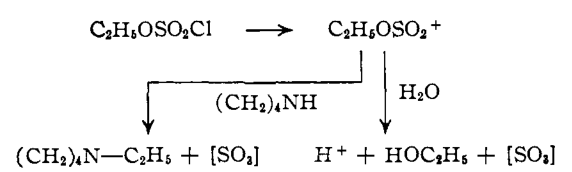
[14] J. Zawidski and J. Zaykowski, *Anzeiger Wiss. Akad. Krakau*, 75 (1916); *C. A.*, **11**, 2294 (1917).

The reagents included concentrated hydrochloric acid, disodium cyanamide, the tripotassium salt of hydroxylamine disulfonic acid and phenoxide ion.[15] In the present study, pyrrolidine and hydroxyl ion were studied. The experimental difficulties noted above prevented precise determination of the rates. The half-life in the presence of 0.0138 *M* hydroxyl ion was significantly different from that observed in the absence of the nucleophiles. Pyrrolidine, however, was without detectable effect. The latter experiment was performed at low concentration, so that a bimolecular reaction is not excluded for higher initial concentrations. When ethyl chlorosulfonate was hydrolyzed in the presence of a concentration of pyrrolidine which was too low to affect the rate significantly, the product was found to contain 1-ethylpyrrolidine, isolated in 20.0% yield as the picrate. The low yield is at least partly due to the difficulty of separating the amine from unreacted pyrrolidine. We believe that this is strong evidence for the occurrence of an ethoxysulfonylium ion as an intermediate

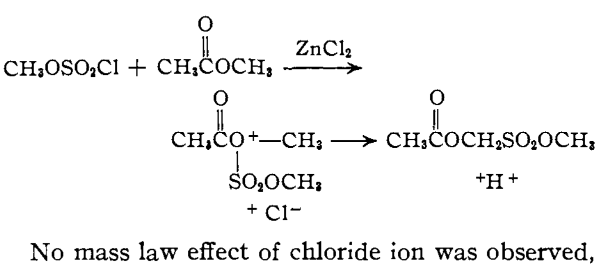


$$C_2H_5OSO_2Cl \longrightarrow C_2H_5OSO_2^+$$

$$\xrightarrow{(CH_2)_4NH} (CH_2)_4N{-}C_2H_5 + [SO_3] \qquad \xrightarrow{H_2O} H^+ + HOC_2H_5 + [SO_3]$$

The extreme affinity of sulfur trioxide for water makes its role as a leaving group a reasonable one. The same mechanism probably partly applies to methyl chlorosulfonate, but some direct displacement on carbon also occurs.

Indirect evidence also points to ionization as the rate-controlling step in the reactions of both methyl and ethyl chlorosulfonates. First, if nucleophilic attack on carbon by the solvent were the slow step, the methyl derivative should be appreciably more reactive than the ethyl. This is not observed. Secondly, nucleophilic attack on carbon would imply the separation of $-OSO_2Cl$ as an entity. If this were the case, alkyl fluorosulfonates should be equally reactive. They are known, however, to be much less prone to solvolyze.[16] Finally, other reactions are known in which alkoxysulfonylium may exist and there seems no reason that they should not be reasonably stable intermediates. For example[17]



$$CH_3OSO_2Cl + CH_3\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow{ZnCl_2}$$

$$CH_3\overset{O}{\overset{\|}{C}}O^+{-}CH_3 \ (SO_2OCH_3) + Cl^- \longrightarrow CH_3\overset{O}{\overset{\|}{C}}CH_2SO_2OCH_3 + H^+$$

No mass law effect of chloride ion was observed, the first-order rate plots remaining linear throughout each run.

Sulfuryl chloride (Z = Cl) hydrolyzed with a half-life of less than one second at 8.5° ($k_1 > 0.6$ sec.$^{-1}$).

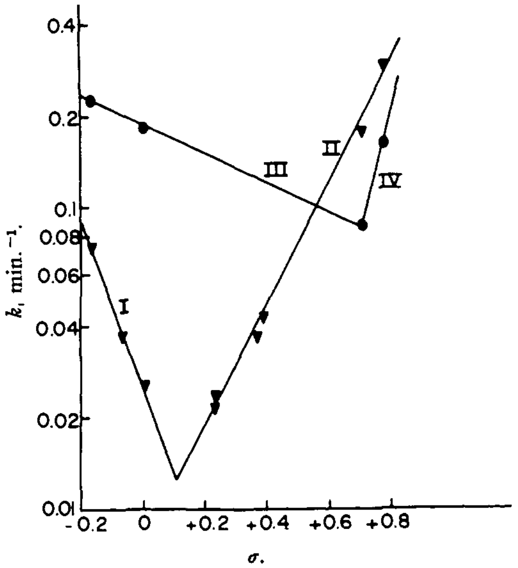
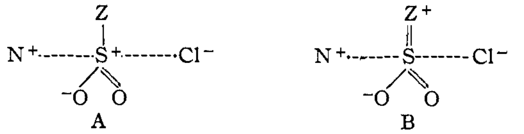


Fig. 3.—Hammett plots for the hydrolysis of substituted benzenesulfonyl chlorides in water at 20.0° (Ref. 2) (circles), and of substituted benzoyl chlorides in 50% aqueous acetone at 0° (Ref. 1).

Discussion

A point of mechanistic change in the ZSO_2Cl series has been shown to occur between benzenesulfonyl chloride and ethyl chlorosulfonate. (We have given the reasons for believing that the latter compound undergoes ionization, and therefore can be compared to the other halides of the series.) The fact that such a point exists is explicable on the same general basis as in the ZCOCl series, namely, the occurrence of steeply increasing electron donation by resonance as one proceeds from CH_3- to $(CH_3)_2N-$. The precise rate sequences are unusual, however, and require further discussion.

Neutral Nucleophiles.—The reason for the inversion in the rate sequence for neutral hydrolysis from that observed in the hydrolysis of carbonyl chlorides appears to be the high positive charge on sulfur. For *neutral* nucleophiles, a strong coulombic repulsion will arise in the transition state between N and S (A). If the group Z can supply electrons to minimize this repulsion, as in B, reaction will be facilitated. Since, on the other hand, electron supply by Z will diminish the electrophilic reactivity of sulfur, it is necessary to postulate further that the former of these two opposing effects is dominant. If this viewpoint is correct, then other neutral nucleophiles should react more rapidly with benzenesulfonyl chloride than with methanesulfonyl chloride. Data are not available to test this prediction.



A B

The data of Hedlund[2] on the hydrolysis rates of a variety of sulfonyl chlorides are consistent with this hypothesis. He observed the following rate sequences: $C_2H_5SO_2Cl > CH_3SO_2Cl \sim ClCH_2CH_2SO_2Cl >> CH_3CHClSO_2Cl$ and: p-$CH_3C_6H_4$-

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[15] W. Traube, *et al.*, *Z. angew. Chem.*, **38**, 441 (1925).

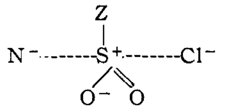
[16] J. Meyer and G. Schramm, *Z. anorg. allgem. Chem.*, **206**, 24 (1932).

[17] R. Levaillant, *Compt. rend.*, **200**, 1053 (1935).

$SO_2Cl > C_6H_5SO_2Cl > m\text{-}NO_2C_6H_4SO_2Cl$. In each case electron supply assists the reaction. The slow rate for 1-chloroethanesulfonyl chloride cannot be attributed to a steric effect, because in the carbonyl chloride series the following SN2 solvolytic rate sequence is observed[18]: $Cl_2CHCOCl > ClCH_2COCl > CH_3COCl$.

As noted above, the reactions of methanesulfonyl and benzenesulfonyl chlorides may proceed by a hydration mechanism. An intimation that this may be the case for the latter is obtained by plotting Hedlund's rate data[2] for substituted benzenesulfonyl chlorides against the Hammett σ-constants of the substituents (Fig. 3). The data for substituted benzoyl chlorides[1] are included for comparison. It can be seen that both plots fall into two parts. This behavior can be interpreted in terms of a duality of mechanisms.[6] Lines II and IV are considered to describe a region of reaction by direct displacement, while lines I and III describe a region where the hydration mechanism is dominant.

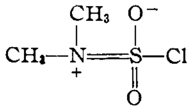
Negative Nucleophiles.—Here the reaction will be facilitated by strong coulombic attraction between N and S, as



Therefore, it is predicted that toward negative nucleophiles (hydroxide, phenoxide), methanesulfonyl chloride should be more reactive than benzenesulfonyl chloride. Again no data are available to test this prediction.

A similar point of view has been taken by Swain and Scott[3] in explaining the high reactivity of hydroxyl ion toward aromatic acid chlorides.

Ionization.—The high positive charge on sulfur may also be responsible for the SN1 sequence, $(CH_3)_2NSO_2Cl < CH_3OSO_2Cl$. Since dimethylamino is much more effective than methoxyl at stabilizing a carbonylium ion, the observed sequence must mean that much of the stabilization by the former is already provided in the initial state by the resonance form:



$$CH_3\text{—}\overset{CH_3}{\underset{+}{N}}\text{=}\overset{O^-}{\underset{O}{S}}\text{—}Cl$$

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WILMINGTON, DELAWARE

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Solvolysis and Base-catalyzed Dehydrohalogenation of 1,1- and 1,2-Dihalocyclohexanes[1]

BY HARLAN L. GOERING AND HERBERT H. ESPY[2]

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The relative rates of second-order dehydrohalogenation of 1,1- and *cis*- and *trans*-1,2-dihalocyclohexanes (dibromo-, dichloro- and bromochloro-) and cyclohexyl bromide and chloride in "80%" ethanol containing 0.1 *M* sodium hydroxide have been determined. Under the conditions of the kinetic experiments the reactions are second-order and E_2 elimination is not accompanied by SN2 substitution. The solvolytic reactivities of a number of the compounds in "80%" ethanol were determined and show that under the conditions of the dehydrohalogenations, the E_2 reactions are essentially completely isolated from competing solvolysis except for the 1,1-dihalocyclohexanes. The order of reactivity for the E_2 dehydrohalogenation of the isomeric dihalides is: *cis*-1,2- $\gg$ 1,1- $>$ *trans*-1,2-. Under the conditions of the present experiments the 1,1- and *cis*-1,2-dihalocyclohexanes eliminate one molecule of hydrogen halide. The *trans*-1,2-dihalocyclohexanes give two molecules of hydrogen halide. The stoichiometry and relative reactivities indicate that a *trans*-elimination is involved. The relative reactivities, together with conformational considerations, provide information concerning the effects of α- and β-halogen atoms on the rate of dehydrohalogenation.

Introduction

In connection with other work[3] in this Laboratory pure samples of 1,1- and *cis*- and *trans*-1,2-dihalocyclohexanes (dibromo-, dichloro- and bromochloro-) were obtained. These compounds are suitable simple models for studying the stereochemistry of dehydrohalogenation and the effect of α- and β-halogen atoms on the rate of dehydrohalogenation. This paper describes the stoichiometry and relative rates of base-catalyzed dehydrohalogenation of these compounds and of cyclohexyl chloride and bromide in "80%" ethanol containing 0.1 *M* sodium hydroxide. With the isomeric 1,2-dihalocyclohexanes the orientation, and thus the stereochemistry, of the dehydrohalogenation can be determined readily from the stoichiometry, *i.e.*, the number of molecules of hydrogen halide eliminated. If the elimination product is 1-halocyclohexene only one molecule of hydrogen halide is eliminated. The initial formation of 3-halocyclohexene leads to the formation of two molecules of hydrogen halide since the allylic halide is rapidly dehydrohalogenated (or solvolyzed) under the conditions of the reaction.

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(2) Du Pont Summer Research Assistant, 1953, 1954.

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