

part by a research grant from the Robert A. Welch Foundation and by a fellowship for P. Y. R. from the National Aeronautics and Space Administration. The statistical calculations were performed by the Data

Processing Center, Texas Engineering Experiment Station, College Station, Texas 77843. We wish to thank a reviewer who brought to our attention the newer value of σ_p available for CHO.

The Spontaneous Hydrolysis of Sulfonyl Fluorides¹

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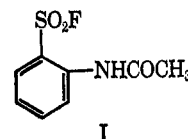
Received December 29, 1969

The rates of spontaneous hydrolyses of substituted benzenesulfonyl fluorides in dioxane-water (40:60 v/v) at 45.0 or 65.5° follow the sequence $o\text{-CH}_3\text{CONH} > p\text{-NO}_2 > m\text{-NO}_2 > o\text{-NO}_2 > p\text{-Br} > m\text{-CH}_3\text{CONH} > \text{H}$. The hydrolyses were too slow to be followed when the substituent was $p\text{-CH}_3\text{O}$, $o\text{-NH}_2$, $p\text{-NH}_2$, or $p\text{-CH}_2\text{CONH}$. The substituent effects are generally very similar to, but larger than, those found for sulfonyl chlorides and $\rho \cong 1.8$. The relatively rapid hydrolysis of o -acetamidobenzene sulfonyl fluoride is accompanied by loss of the acetyl group, suggesting that a neighboring-group participation of the acetamido group gives an unstable intermediate.

Sulfonyl fluorides are generally unreactive toward acidic and neutral water and hydroxylic solvents;³⁻⁵ for example, Swain and Scott showed that benzenesulfonyl fluoride was much less reactive (by a factor of $ca. 5 \times 10^3$) than the corresponding chloride, although it reacted readily with hydroxide ion.⁵ The results were explained in terms of the strong S-F bond and the strong electron withdrawal by fluorine. However, azo dyes derived from p -aminobenzenesulfonyl fluoride react readily with cellulose, cellulose acetate, and some synthetic fibers.⁶ In addition, Baker and his coworkers have shown that some sulfonyl fluorides are very effective enzyme inhibitors, and that the sulfonyl group is bound irreversibly near to the active site.⁷ Moreover enzymes catalyzed the hydrolysis of some sulfonyl fluorides,⁸ and Baker suggested that these nucleophilic attacks upon sulfonyl fluorides occur with assistance from a hydrogen-bonding donor which assists S-F bond breaking. This hydrogen-bonding donor could be an external water molecule or a protic group in the enzyme, and the nucleophile could be a group in the enzyme or an external water molecule. The fact that the hydrolysis of acyl fluorides, but not chlorides, is acid catalyzed⁹ suggests that a general acid or a proton assists departure of the fluoride but not the chloride ion in water.

The aim of the present work was to examine structural effects upon the rate of the spontaneous hydrolysis of arylsulfonyl fluorides because the solvolyses of the corresponding chlorides have been studied in great detail, and all the evidence points to nucleophilic attack in the rate-limiting step although there is question as to the relative importance of bond making and breaking.¹⁰⁻¹³ The unreactivity of the arylsulfonyl fluorides

prevented our studying, quantitatively, compounds containing electron-donating groups. In addition we examined the hydrolysis of o -acetamidobenzenesulfonyl fluoride (I), because a derivative of this compound has been found to be surprisingly reactive to water whereas compounds derived from m -acetamidobenzenesulfonyl fluoride showed no such reactivity.¹⁴



Experimental Section

Materials.—The following sulfonyl fluorides were obtained commercially and were recrystallized from ethanol-water: o -aminobenzene (Aldrich), mp 62–64° (lit.¹⁵ 64–65°); p -aminobenzene (Aldrich), mp 70–71° (lit.¹⁵ 70°); p -acetamidobenzene (Aldrich), mp 175–177° (lit.¹⁵ 174–176°); m -nitrobenzene (Alfred Bader), mp 46–47° (lit.¹⁵ 46–48°). The other sulfonyl fluorides were prepared by refluxing the chlorides with KF in aqueous dioxane for 0.5–1 hr or by acylating the aminosulfonyl fluoride.^{3,14} The reaction solution was poured into cold water, the liquid sulfonyl fluorides were extracted, usually into ether, the organic layer was washed with water and then dried, and the fluoride was distilled *in vacuo*. The solid fluorides were removed by filtration and recrystallized from methanol-water, ethanol-water, or benzene. The sulfonyl fluorides prepared from the chloride with fluoride ion had the following physical properties: benzenesulfonyl fluoride, bp 60–61° (1.5 mm) [lit.⁵ 83° (3 mm)]; o -nitro-, mp 52–54° (lit.¹⁵ 55–58°); p -nitro-, mp 75–78° (lit.¹¹ 77–79°); p -methoxy-, bp 103–105° (1.7 mm) [lit.¹⁶ 175° (60 mm)]; p -bromo-, mp 65–66° (lit.¹⁷ 65–66°). The infrared spectrum of the p -bromo compound was very similar to that in the literature.¹⁸ o - and m -acetamidobenzenesulfonyl fluorides were

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prepared by acetylation of the amine using acetic anhydride in chloroform.¹⁴ *o*-Acetamidobenzenesulfonyl fluoride recrystallized from benzene-methyl ethyl ketone had mp 99–101°. *Anal.* Calcd for C₈H₈FNO₂S: C, 44.2; H, 3.7; N, 6.4. Found: C, 44.3; H, 3.8; N, 6.2. *m*-Acetamidobenzene sulfonyl fluoride recrystallized from benzene had mp 114–116° (lit.¹⁴ 114–116°).

Dioxane was purified by treating it with aqueous HCl and then with KOH, refluxing it over sodium, and then redistilling it over sodium.¹⁹ It was stored under N₂ at 6°. Distilled and deionized water was used. Solutions of lanthanum nitrate (MCB) were standardized against KF.

The kinetic solvent was dioxane-water, 40:60 v/v, made up by weight from known densities, using redistilled and deionized water.

Kinetics.—The reaction was followed by determining fluoride ion by titration with lanthanum nitrate (0.03 *N*) using a specific fluoride ion electrode (Orion 94-09). Aliquots (5–10 ml) of the reaction mixture were diluted with cold ethanol²⁰ (10 ml), and the pH was brought to 6–7 with 0.022 *M* NaOAc. Polyethylene beakers and pipets were used, and the end point was taken as the point of inflection of a plot of millivolts vs. milliliters of titrant. Because the reactions were very slow, infinity titers were obtained by adding sodium hydroxide with which the fluorides rapidly react.⁵

The choice of suitable reaction vessels was a major problem. Polyethylene bottles were satisfactory for use at 45° provided that the caps were fitted with Viton O rings, but they failed at high temperatures after ca. 24 hr. Polycarbonate bottles were slightly better and lasted for ca. 36 hr, but we finally found that Teflon bottles made satisfactory containers. Generally the screw caps gave satisfactory seals, but sometimes it was necessary to use Teflon liners. Every bottle was tested for evaporation of the kinetic solvent under reaction conditions.

The hydrolyses of the more reactive sulfonyl fluorides were followed for two half-lives, but generally the reactions were so slow that we could only follow them for one half-life, and reactions of *p*-acetamidobenzene sulfonyl fluoride were followed for only ca. 30% reaction. The first-order rate constants, *k_v*, are in sec⁻¹.

Reaction Products.—Because of the possibility that hydrolysis of *o*-, *m*- and *p*-acetamidobenzenesulfonyl fluorides might be accompanied by anilide hydrolysis, we took reaction mixtures after ca. two half-lives of reaction of the *ortho* compound and treated portions of them at 0° with NaNO₂ until starch-iodide paper gave a positive test. The solution was then treated with β-naphthol in NaOH.²² The copious crop of red crystals obtained from the *ortho* compound was recrystallized from aqueous EtOH. *Anal.* Calcd for C₁₀H₁₁N₂O₄SNa·0.5H₂O: C, 53.5; H, 3.4; N, 7.8. Found: C, 53.8; H, 3.6; N, 7.6. When this test was carried out with *m*- and *p*-acetamidobenzenesulfonyl fluorides there was only a slight coloration of the solution. The results suggested that the anilide group was lost during the reaction of *o*-acetamidobenzenesulfonyl fluoride, and we examined the nmr spectrum of a 10% solution of the substrate in dioxane-D₂O, 40:60 v/v after various times at 65.5°, using 1% DSS as an internal standard. The methyl protons of the acetamido group have δ 2.20 (relative to DSS), but, as the reaction proceeds, this peak decreases and a new peak δ 2.25 appears, which is identical with that of added acetic acid.

Results

The first-order rate constants are given in Table I and the activation parameters, where available, are in Table II. These parameters are in the range expected for a bimolecular reaction for which bond making predominates in the transition state. For reactions which can be followed only to a partial extent, reaction order cannot be determined from linearity of plots based on the integrated first-order rate equation. However, the spread of independently determined values of *k_v* was generally less than 10% for twofold changes in substrate concentration, showing that first-order ki-

TABLE I
SPONTANEOUS HYDROLYSIS^a

Substituent	Registry no.	10 ² C ₀ , M	10 ⁷ <i>k_v</i> , sec ⁻¹
H	368-43-4	1.35	1.16
		2.04	1.07
<i>m</i> -CH ₃ CONH	4857-88-9	0.84	1.56
		1.11	1.57
		1.59	1.60
<i>o</i> -CH ₃ CONH	24299-90-9	0.84	6.24 ^b
		1.01	6.03 ^b
		1.69	6.10 ^b
		0.68	30.3
		1.04	33.1
		1.26	31.1
<i>p</i> -Br	498-83-9	1.07	2.45
		1.98	2.53
<i>o</i> -NO ₂	433-98-7	0.89	0.89 ^b
		1.01	4.25
		1.25	4.49
<i>m</i> -NO ₂	349-78-0	0.91	2.96 ^b
		1.15	2.71 ^b
		2.43	2.77 ^b
		0.97	12.9
		1.13	12.6
		1.55	12.4
<i>p</i> -NO ₂	349-96-2	1.14	5.05 ^b
		1.17	4.90 ^b
		2.29	5.35 ^b
		0.97	22.4
		1.29	24.8
		1.60	22.5

^a In dioxane-water, 40:60 v/v, at 65.5° unless specified.
^b 45.0°.

TABLE II
ACTIVATION PARAMETERS

Substituent	Δ <i>H</i> [‡] , kcal mol ⁻¹	Δ <i>S</i> [‡] , eu
<i>o</i> -NO ₂	16.0	-40
<i>m</i> -NO ₂	15.1	-41
<i>p</i> -NO ₂	14.8	-41
<i>o</i> -CH ₃ CONH	16.3	-36

netics are followed and confirming the earlier evidence against hydrogen ion catalysis in dilute acids.³⁻⁵ The only exception was the hydrolysis of *p*-acetamidobenzenesulfonyl fluoride where at 65.5° *k_v* ≈ 1 × 10⁻⁷ sec⁻¹ with 0.01 *M* substrate and ≈ 0.5 × 10⁻⁷ sec⁻¹ with 0.015 *M* substrate. These latter values were based on the first 10–30% of the reaction and are almost certainly unreliable because of the hydrolysis of the anilide to give the less reactive *p*-aminobenzenesulfonyl fluoride. Hydrolysis of *p*-acetamidobenzenesulfonyl fluoride was therefore not examined in detail. Hydrolysis to the amide does not appear to be a problem with the *m*-acetamido compound, and the greater electron withdrawal by a *para* compared with a *meta* sulfonyl fluoride group could be responsible for this difference. The release of fluoride from *o*-acetamidobenzene sulfonyl fluoride is much faster than anilide hydrolysis under our conditions (*cf.* ref 23).

The hydrolyses of *p*-methoxybenzene-, *p*-amino-benzene-, and *o*-aminobenzenesulfonyl fluorides were so slow that we were unable to obtain rate constants for hydrolysis of these compounds.

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Discussion

Relation between Structure and Reactivity.—The *o*-acetamido group markedly enhances the rate, but for the other compounds the rate increases with substitution of electron-attracting groups, as for hydrolysis of sulfonyl chlorides. For the sulfonyl fluorides the rate sequence (omitting the *o*-acetamido compound) is $p\text{-NO}_2 > m\text{-NO}_2 > o\text{-NO}_2 > p\text{-Br} > m\text{-CH}_3\text{CONH} > \text{H} > p\text{-CH}_3\text{CONH}$ (Table I), and for the chlorides it is $p\text{-NO}_2 > m\text{-NO}_2 > p\text{-Br} > \text{H} > o\text{-NO}_2 > p\text{-CH}_3\text{CONH}$.¹² For the hydrolyses of sulfonyl chlorides at 25° in 49.1% aqueous dioxane a plot of $\log k_{\psi}$ against σ is curved with ρ increasing from *ca.* +0.6 for σ values close to zero to *ca.* +1.2 for positive σ values.¹¹ For the fluorides at 65.5° in dioxane–water, 40:60 w/w, the corresponding plot is also concave, although a straight line of slope +1.8 can be drawn through the points by allowing a maximum deviation of 0.1 in $\log k_{\psi}$ (Figure 1). The vertical bars in Figure 1 are drawn allowing an uncertainty of $\pm 5\%$ in the values of k_{ψ} , except for k_{ψ} for *p*-acetamidobenzenesulfonyl fluoride ($\sigma = 0.00$) where we assume an uncertainty of $\pm 50\%$ (Results). The larger values of ρ suggest that electronic effects are more important for hydrolysis of the fluorides than the chlorides. Jenkins and Hambly explained the curvature in the plots of $\log k_{\psi}$ against σ for sulfonyl chloride hydrolysis in terms of a change in the relative importance of bond making and breaking with changes in substituent groups (*cf.* ref 24 and 25), and consistently they found that ρ decreased as the solvent was made more aqueous.

We could explain the curvature in the plots of $\log k_{\psi}$ against σ for sulfonyl fluorides in similar terms and assume that the larger value of $\rho \approx +1.8$ is caused by the greater importance of bond making which results from the strength of the S–F bond and the strong electron withdrawal by fluorine. However, we note that the temperature of our experiments was relatively high, and the solvent was less aqueous than that used for hydrolysis of the chlorides both of these factors tend to increase ρ .^{10–12} In addition, σ may not be the appropriate substituent parameter for these reactions.²⁶

The high relative reactivity of *o*-nitrobenzenesulfonyl fluoride, compared with the low reactivity of the corresponding chloride, also gives some support for the assumption that electronic effects are more important in the sulfonyl fluorides than in the chlorides and that the effect of the *o*-nitro group is electronic rather than steric.

Charton has shown that *ortho* substituents can exercise large electronic effects²⁷ which may be due to a resonance or to a field effect, and such electronic effects of an *o*-nitro group should be more important in hydrolysis of a sulfonyl fluoride compared with the chloride.

Effect of the *o*-Acetamido Group.—The relatively high reactivity of *o*-acetamidobenzenesulfonyl fluoride (I) cannot be caused solely by either an electronic or steric effect. For example, for *p*-acetamido $\sigma = 0.00$,

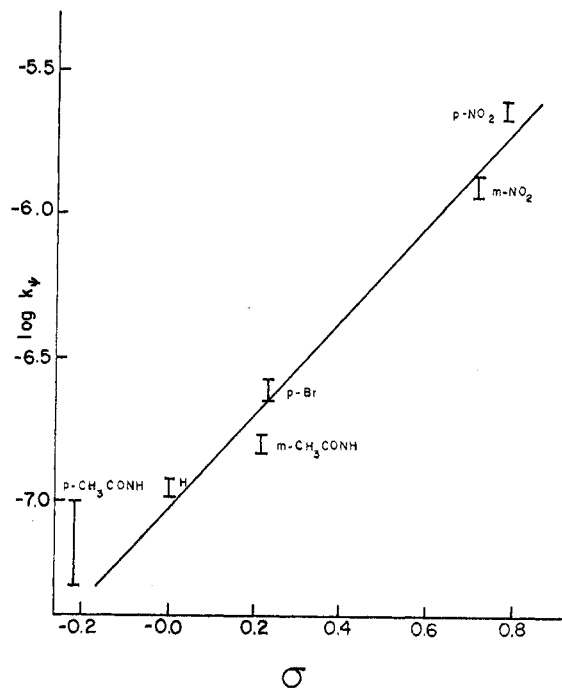
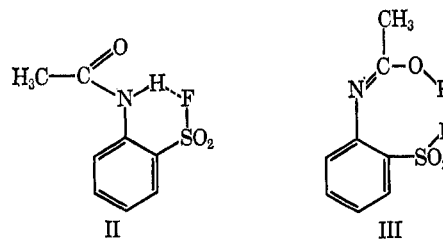


Figure 1.—Linear free energy plot for spontaneous hydrolysis.

for the *meta* substituent $\sigma = 0.21$, and $\log k_{\psi}$ for the *m*-acetamidobenzenesulfonyl fluoride fits well on a linear free energy plot, whereas the *ortho* isomer is more reactive (by *ca.* 30-fold) than expected in terms of the value of σ . In addition, comparison between *o*-, *m*-, and *p*-nitrobenzenesulfonyl fluorides suggests that a steric effect of an *ortho* group, if present, could not markedly enhance substrate reactivity.

We can eliminate hydrolysis of the acetamido residue to give *o*-aminobenzenesulfonyl fluoride, followed by its hydrolysis, as a possible mechanism. Anilides are generally unreactive except in the presence of acids or bases,²³ and neither *m*- nor *p*-acetamidobenzenesulfonyl fluoride hydrolyze rapidly to the aminobenzenesulfonyl fluoride; in addition we could detect no hydrolysis of *o*-aminobenzenesulfonyl fluoride after 2 months at +5.0° in dioxane–water 40:60 w/w.

Therefore it seems that the *o*-acetamido group provides intramolecular catalysis. One possibility is that it is acting as a general acid, as in II or III.



There is evidence for hydrogen bonding to oxygen in compounds similar to II and III, *e.g.*, in *o*-acetamidobenzene sulfones and sulfonamides.²³ However, intramolecular general acid catalysis of itself can not explain the loss of the acetyl group during hydrolysis. A reasonable mechanism involves nucleophilic attack by the acetamido group upon sulfur.

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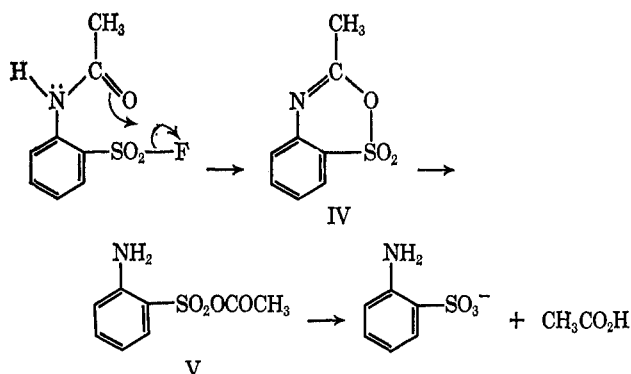
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There is no nmr evidence for the existence of the intermediates IV and V, but both of them should be

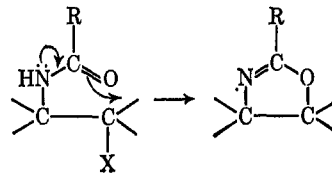


very reactive under the hydrolysis conditions. This mechanism assumes that there is no intramolecular hydrogen bonding to the leaving fluoride ion which should be solvated by solvent water, and the hydrogen on the nitrogen atom is a far way from the fluoride atom in the transition state.

In this mechanism it is assumed that water molecules will solvate the departing fluoride ion and remove the amide proton. This mechanism is very similar to that

proposed by Baker and his coworkers for the irreversible sulfonylation of a nucleophilic group of an enzyme by a sulfonyl fluoride.^{7,8}

Amido groups provide powerful anchimeric assistance to ionization at saturated carbon,²⁹ and in this system the intermediate oxazoline can be isolated. In addition



intramolecular acylation of the conjugate base of an amide occurs very readily³⁰ by a reaction which is somewhat similar to that proposed here.

Acknowledgment.—We thank Professor B. R. Baker for helpful discussions and Mr. D. Hachey for technical assistance.

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Rearrangements of Sulfones to Sulfinic Acids via Carbanion Intermediates¹

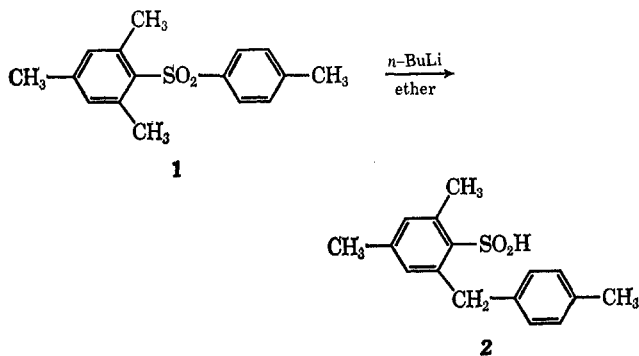
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Received January 20, 1970

Mesityl 1-naphthyl sulfone was shown to rearrange to 2-(1'-naphthylmethyl)-4,6-dimethylbenzenesulfinic acid by treatment with *n*-butyllithium in ether, or to the 2'-naphthylmethyl isomer with potassium *t*-butoxide in dimethyl sulfoxide. In contrast, mesityl *p*-tolyl sulfone, mesityl *m*-tolyl sulfone, and mesityl *o*-tolyl sulfone were shown to rearrange to the corresponding 2-(4'-methylbenzyl)-, 2-(3'-methylbenzyl)-, and 2-(2'-methylbenzyl)-4,6-dimethylbenzenesulfinic acids, respectively, with either *n*-butyllithium in ether or potassium *t*-butoxide in dimethyl sulfoxide. Mesityl *m*-tolyl sulfone, on treatment with *n*-butyllithium in ether at 0° for a short time followed by quenching with CO₂ and subsequent decarboxylation, gave 1,5,7-trimethyl-4a,9a-dihydrothioxanthene 10,10-dioxide (**8**), the product of attack *ortho* rather than *para* to the tolyl methyl. Mesityl *o*-tolyl sulfone gave, in the same reaction, or by rapid quenching with water, 2,4,9a-trimethyl-4a,9a-dihydrothioxanthene 10,10-dioxide (**12**), resulting from ionization of the tolyl methyl. When **8** was treated with either base-solvent system, it rearranged to the same acid product as did its sulfone precursor. Sodium ethoxide in hot ethanol, however, caused **8** to rearrange to 2-(2'-methylbenzyl)-4,6-dimethylbenzenesulfinic acid. These results are discussed in terms of the proton-donating ability of the solvent, the aromatic character of the rings, and relative acid-base strengths.

Aryl sulfones containing an *o*-methyl group have been shown to rearrange to *o*-benzylbenzenesulfinic acids when treated with *n*-butyllithium in ether,² or with potassium *t*-butoxide in dimethyl sulfoxide (DMSO).³ In the conversion of mesityl *p*-tolyl sulfone (**1**) to 2-(4'-methylbenzyl)-4,6-dimethylbenzenesulfinic acid (**2**),



the rearrangement was shown to proceed *via* displacement at the carbon bearing the sulfonyl group (*i.e.*, with retained orientation on the part of the migrating group).³ The reaction was also shown to proceed with various substituents other than methyl in the migrating benzene ring.⁴

Drozd and coworkers have shown that, if mesityl *p*-tolyl sulfone is treated with *n*-butyllithium for a short time, followed by rapid quenching, a 4a,9a-dihydrothioxanthene 10,10-dioxide can be isolated from the reaction mixture.⁵ Similar results were obtained with other diphenyl sulfones.^{6,7} These products must result

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