Hammett and Taft Substituent Constants for the Mesylate, Tosylate, and Triflate Groups

Peter J. Stang* and Albert G. Anderson

Chemistry Department, The University of Utah, Salt Lake City, Utah 84112

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The Hammett σ_p values for the mesylate (1), tosylate (2), and triflate groups (3) were determined by titration of the appropriate benzoic acids and found to be +0.33, +0.29, and +0.47, respectively. Taft σ_I values were determined by ^{19}F NMR of the appropriately substituted 3-fluorophenylsulfonate esters and found to be 1, +0.61; 2, +0.54, 3, +0.84. By interpolation using pK_a data for a number of substituted acetic acids, the value of σ^* for the $CF_3SO_2OCH_2$– group was found to be +1.98. The possible nature and origin of these values are discussed and applied to the relative leaving group ability of the various sulfonate esters in SN1 reactions.

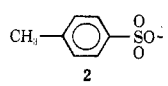
Sulfonate esters are often used in synthetic reaction schemes and mechanistic studies because of their superior leaving ability and ease of displacement by a wide variety of nucleophiles. Despite their widespread use, little is known about the electronic effects of the most important groups, namely, methanesulfonate (mesylate, 1), *p*-toluenesulfonate (tosylate, 2), and the recently developed trifluoromethanesulfonate (triflate,[1] 3), which give rise to their superior leaving ability and ease of displacement. The electronic effects of a substituent group can be conveniently divided into those of electron donation and withdrawal and are commonly expressed in terms of the Hammett σ_p and Taft σ_I and σ_R parameters.[2] Although a few σ values for some sulfonate esters have appeared in widely scattered reports,[3-5] no systematic data exist on the substituent constants of sulfonate groups. We have, therefore, determined σ_p, σ_I, and σ_R for the groups 1–3 and have also employed a number of chemical probes in order to elucidate the possible origin and nature of the electronic effects of these groups and thereby possess some basis for comparison not only of sulfonate esters among themselves but also among other sulfur containing groups such as the sulfones and thioethers.

Results and Discussion

Hammett σ_p constants were obtained by the standard technique[6] of titration of appropriately para-substituted benzoic acids in 50% (v/v) aqueous ethanol. A least-squares plot of the pK_a' vs. σ_p for a series of standard compounds is shown in Figure 1. Measurement[7] of pK_a' for the desired sulfonyloxy-substituted benzoic acids and interpolation using Figure 1 resulted in the σ_p values shown in Table I. Taft σ_I values were also obtained by standard techniques[8] using the ^{19}F NMR shift of appropriately substituted *m*-fluorobenzenes. These results are also shown in Table I. The values of σ_p obtained in this study are in good agreement with the values in the literature for 1[5] and for 3,[4] as is the value of σ_I for 2.[2,3] However, our value of σ_I = 0.84 for 3 determined by ^{19}F NMR differs substantially from the value of 0.58 given by Yagupol'skii.[4,9] Because of this discrepancy and because of some questions regarding the theoretical validity[13] of ^{19}F NMR as a tool for determining σ_I, we determined σ_I for 3 by a second independent means. This involved measurement of the pK_a's of appropriately substituted acetic acids by nonaqueous titration in 2-propanol, correlation of the pK_a's with known σ^* values,[14] and interpolation of the pK_a of $CF_3SO_2OCH_2COOH$. The results are given in Figure 2 and Table II. The Taft σ_I value can be computed from the experimentally observed σ^* value by means of the well-known relationship[2] $\sigma_{I(x)} = 0.450\ \sigma^*_{(xCH_2)}$ to be $\sigma_{I(3)} = 0.89$, which is in substantial agreement with the value found by ^{19}F NMR in Table I.

The substituent constants and the nature of sulfonate esters can best be discussed by division of their properties into those of electron-withdrawing and donating ability and comparison with sulfone and alkoxy substituents. The relevant data are assembled and summarized in Table III. As seen by examination of the data in Table III, the positive sign of the Hammett σ_p constants for the mesylate, tosylate, and triflate groups indicates that the sulfonate esters are deactivating toward electrophilic aromatic substitution, but ortho–para directing because of the negative sign of σ_R. Indeed, this observation is in accord with experimental evidence that phenyl tosylate is nitrated simply with concentrated nitric acid,[15] whereas phenyl mesylate requires treatment with a mixture of KNO_3 and H_2SO_4 for 24 h;[16] by varying the ratio of KNO_3/H_2SO_4, either a 4-nitro or a 2,4-dinitrophenyl mesylate could be obtained.

Table I. Hammett σ_p and Taft σ_I Values for the Mesylate, Tosylate, and Triflate Groups

Substituent	pK_a of p-XC_6H_4COOH[c]	σ_p	$\delta_{m\text{-}XC_6H_4F}$,[a,d] ppm	σ_I
CH_3SO_2– (1)	5.18	+0.328	181.3	+0.61
 (2)	5.25	+0.280	155.5	+0.54
CF_3SO_2– (3)	4.97	+0.473	259.0	+0.84[e] +0.89[b]

[a] In 5% CCl_4 at 25° downfield from internal C_6H_5F. [b] Calculated from σ^*; see text. [c] Registry no. are, respectively, 28547-25-3, 51804-15-0, 32578-34-0. [d] Registry no. are, respectively, 57606-63-0, 57606-64-1, 57606-65-2. [e] This value of σ_I is further confirmed by a least-squares plot of $\pi_{I(CH_2X)}$ vs. $\sigma_{I(X)}$.[14]

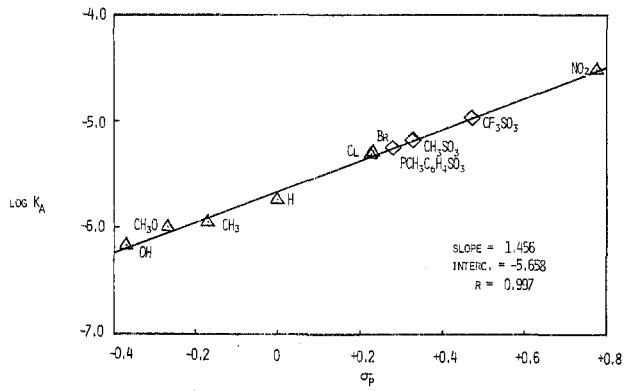


Figure 1. Log K_a vs. σ_p for p-XC_6H_4COOH.

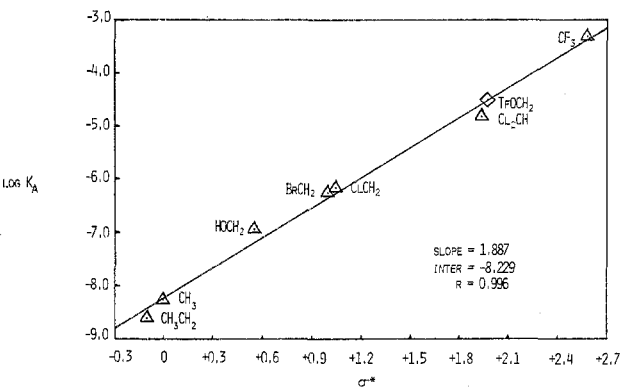
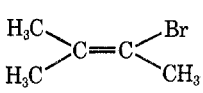


Figure 2. Log K_a vs. σ^* for XCOOH.

Phenyl triflate, possessing the most positive σ_p of the three esters, nitrates first at the 4 position and next at the 2 position, but only under forcing conditions. The strong inductive electron-attracting ability of the triflate group is also shown by the relative rate of bromination of 2-bromo-3-methyl-2-butene (**4**) and 3-methyl-2-buten-2-yl triflate (**5**), with **4** brominating three times as fast as **5** in CCl_4 at 25 °C.[17]



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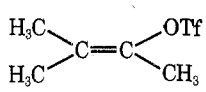

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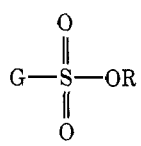
The inductive effect, arising out of differences in electronegativity of the elements, involves the σ framework of the molecule and is measured by the Taft parameter σ_I. The resonance effect operates through the π orbitals of the molecule and is a crude measure of the p_π–p_π interactions occurring within the molecule. The σ_R values for the triflate, mesylate, and tosylate groups indicate that all three groups are capable of donating electrons. What is somewhat surprising is the magnitude of the effect in the case of triflate, when contrasted to the behavior of other groups attached to a phenyl ring via an oxygen atom. It is well known that the σ_R value for the methoxy group is negative; the methoxy group interacts with the phenyl ring via $2p_\pi$–$2p_\pi$ interactions, donating electrons from the p atomic orbitals of oxygen. It is also known from photoelectron spectroscopy[20] that the two highest occupied molecular orbitals of the phenyl ring in anisole become split in energy, indicating strong interaction of the oxygen with the phenyl ring. In the case of the OCF_3 group, photoelectron spectroscopy reveals that the two highest occupied molecular orbitals are degenerate. The σ_R value (see Table III) for the CF_3 group indicates that the CF_3 group is strongly electron withdrawing by resonance. Even when present as the ether, OCF_3, its effect is dominant.[21] Sheppard has found the O=S(=O)CF_3 group to be one of the most electron-withdrawing neutral groups (σ_p = 0.93) known.[18] Thus, when substituted for the CF_3 group in a phenyl "ether", its effect should be at least as great as the CF_3 group, and no p_π–p_π interaction of the oxygen p atomic orbitals with the benzene ring should be expected. However, as shown by experiment, exactly the opposite is observed. One must then either assume that the O=S(=O)CF_3 group has no effect on the oxygen atom and that the electron donation from the triflate group is occurring solely from the p atomic orbitals of the oxygen atom or, more likely, that extensive delocalization of electrons is occurring through the sulfur atom of the triflate group out to the "sulfone" oxygen atoms. The sulfur atom of a sulfonate has no electrons to donate by resonance, since all of its electrons are used in forming the approximately tetrahedral σ framework of the sulfonate group and in double bonds to the two "sulfone" oxygen atoms. If the sulfur atom could itself donate electrons, then sulfone groups would be expected to have a negative σ_R, which they do not have (see Table III).

Table II. pK_a of Substituted Acetic Acids in *i*-PrOH at 25 °C

Registry no.	Compd	pK_a	σ^*[a]
79-09-4	CH_3CH_2COOH	8.61	−0.100
64-19-7	CH_3COOH	8.27	0.000
79-14-1	$HOCH_2COOH$	6.94	0.555
79-08-3	$BrCH_2COOH$	6.25	1.000
79-11-8	$ClCH_2COOH$	6.16	1.050
79-43-6	$Cl_2CHCOOH$	4.81	1.940
57606-66-3	$CF_3SO_2OCH_2COOH$	4.50	1.947[b]
76-05-1	CF_3COOH	3.31	2.58

[a] From ref 14. [b] This work.

Recently, Crossland[22] has presented evidence that the leaving ability of various sulfonate esters under limiting SN1 solvolysis conditions is correlated with the inductive effect of the group, G, on sulfur. However, Crossland used



σ_m to estimate the inductive effect of the group, G. If only inductive effects were operating, then σ_I would be a far better estimate of electron-withdrawing ability than σ_m, which contains about 22% resonance contribution.[23] However, inspection of the σ_I data for the group, G, on sulfur would lead one to predict that, contrary to fact, fluorosulfonates solvolyze faster than triflates.

Perhaps a better explanation of leaving ability and electronic influence of the sulfonate esters can be had by examining the effect of the group, G, on the d orbitals of sulfur, through which sulfur can interact with oxygen by virtue of $3d_\pi$–$2p_\pi$ bonding.[24] It is well known that attachment of electronegative ligands to sulfur contracts the d orbitals of sulfur.[24] In a sulfonate ester the sulfur is bonded to three oxygen atoms; the effect of the fourth group, G, as an electronegative ligand would be to further contract the d orbitals of sulfur, allowing still better overlap of the "sulfone" and "ester" oxygen 2p atomic orbitals with the sulfur 3d orbitals, and thus further enhancing the $3d_\pi$–$2p_\pi$ interactions. Indeed, the σ_R for the tosylate and mesylate groups are approximately equal, but the σ_R for the triflate group is much larger. This increase in resonance is probably due to the greater effect of the CF_3 group as an electronegative ligand on the $3d_\pi$–$2p_\pi$ interactions of the "sulfone" and "ester" oxygen atoms. In effect, a greater delocalization of

Table III. Summary of Substituent Constants for Various Sulfur and Oxygen Containing Substituents

Substituent (x)	$\sigma_{p(x)}$	$\sigma_{R(x)}$	$\sigma_{I(x)}$	$\sigma_{m(x)}$	$\sigma^*_{(xCH_2)}$	Ref
CH_3SO-	+0.33	−0.28	+0.61			This work
	+0.36			+0.39		5
C_6H_5SO-	+0.33			+0.36		5
p-$CH_3C_6H_4SO-$	+0.29	−0.21	+0.54			This work
			+0.59		+1.31	3
CF_3SO-	+0.47	−0.36	+0.84 (0.89)		+1.98	This work
	+0.53	−0.05	+0.58	+0.56		4
CH_3S-	+0.72	+0.14	+0.62	+0.65		2, 18
p-$CH_3C_6H_4S-$	+0.67	+0.12	+0.55			19
CF_3S-	+0.93	+0.22	+0.69			18
CH_3O-	−0.27	−0.47	+0.21	+0.12		2,18
CF_3O-	+0.35	−0.13	+0.51	+0.40		18
CH_3-	−0.17	−0.10	+0.06	−0.07	0.00	2
CF_3-	+0.54	+0.12	+0.39			2, 18

electrons from the R groups via the single S–OR bond through sulfur to the "sulfone" oxygens occurs in the triflate group than in the mesylate or tosylate groups.

Using a methyl sulfonate as a model, a qualitative mechanism can be inferred for the limiting SN1 solvolysis of sulfonate esters. As the O–R bond lengthens, the "ester" oxygen begins to rehybridize from sp^3 to sp^2. As the lone pair electrons on the "ester" oxygen begin to develop more p character, aided by delocalization into the lowest lying empty d orbital of sulfur, the σ framework begins to contract owing to its increase in s character. Eventually, the O–R bond is broken and the charge spread equally over the three oxygen atoms of the sulfonate anion. Internal return and scrambling of the ester oxygen can then occur depending on the nucleophilicity of the sulfonate anion and the stability of the carbonium ion generated.

Using such a mechanism, it can readily be seen why a fluorosulfonate ester solvolyzes slower under limiting SN1 conditions than a triflate ester. During the initial stage of the reaction, the developing p lobe of the "ester" oxygen must compete with back-bonding from the fluorine atom of the fluorosulfonate for the lower lying empty d orbitals of sulfur. The σ_I of a fluorine atom is +0.52 whereas that of a CF_3 group is +0.41. Thus, although the electron-withdrawing ability of a fluorine atom is much greater than that of a CF_3 group, and presumably the d orbitals of sulfur in a fluorosulfonate ester are more contracted with fluorine present, a fluorosulfonate solvolyzes slightly slower owing to $3d_\pi$–$2p_\pi$ backbonding from fluorine to sulfur.[25]

The carbon atoms of mesylate and tosylate would be expected to have less of an effect on the sulfur d orbitals and thus would be expected to have a smaller negative σ_R and solvolyze slower, as found by experiment. Since the σ_R constants for the tosylate and mesylate groups are nearly identical, this implies that the tolyl and methyl groups affect $3d_\pi$–$2p_\pi$ interactions approximately to the same extent, and leaving ability then becomes dependent on the difference in σ_I of these two substituents.

As an extension of these ideas, a tentative explanation for the electron-withdrawing effect of the CH_3SO_2 or CF_3SO_2 groups can be offered. In these groups fewer electronegative ligands are present than in the sulfonate esters. The effect on $3d_\pi$–$2p_\pi$ bonding may be to raise the energy of the lowest unoccupied d orbital on sulfur to such a level that resonance through sulfur to the sulfone oxygens is inhibited, thus making the sulfur atom which is still in a promoted hexavalent state into an electron sink via its empty d orbitals. With even fewer ligands on sulfur, as in the case of substituted sulfides, spare pairs of electrons become available for donation via $3p_\pi$–$2p_\pi$ interactions and the sign of σ_R becomes negative for most groups incapable of strong interactions with sulfur, i.e., $\sigma_{R(S-CH_3)} = -0.28$ vs. $\sigma_{R(S-CF_3)} = +0.17$, although the net flow of electrons using an spd basis set is still in the direction of sulfur,[26] i.e., $\sigma_{p(S-CH_3)} = 0.00$.[2]

Experimental Section

General. All boiling points are uncorrected. ^1H NMR spectra were recorded on a Varian Associates A-60 spectrometer and data are given in δ (parts per million) relative to internal tetramethylsilane (δ 0) as indicated. ^{19}F NMR spectra were recorded on a Varian Associates A-56/60A spectrometer operating at 56.40 Hz at 25 ± 1 °C relative to internal fluorobenzene (C_6H_5F, δ 0). All ir spectra were recorded on a Beckman IR-5A and are reported in wavenumbers (cm^{-1}) calibrated to the 1603-cm^{-1} line of polystyrene. Either a Varian Aerograph 90-P or 920 gas chromatograph using a 5 ft × 0.25 in. 10% SF-96 on 60/80 Chromosorb W was used for preparative work. A 6 ft × 0.125 in. 10% UC-W98 column was used for flame ionization GLC analysis performed on a Hewlett-Packard 700 laboratory chromatograph coupled to a Hewlett-Packard 3370B integrator. Titration curves were recorded on a Metrohm Herisau E 436 potentiograph using an E 436 D automatic pipet and EA 120X combination glass electrode.

Reagents. p-Nitrobenzoic acid, p-hydroxybenzoic acid, p-chlorobenzoic acid, p-methoxybenzoic acid, p-methylbenzoic acid, dichloroacetic acid, and bromoacetic acid were purchased from Matheson Coleman and Bell. p-Bromobenzoic acid and propanoic acid were purchased from Eastman. p-Toluenesulfonic acid was purchased from both Eastman and Matheson Coleman and Bell and was used without further purification. m-Fluorophenol was purchased from Sigma Chemical Co. and was distilled before use. Acetic acid was purchased from Allied Chemical Co. Trifluoroacetic acid, glycolic acid, glycine, and methanesulfonyl chloride were purchased from Aldrich Chemical Co. p-Toluenesulfonyl chloride was purchased from Matheson Coleman and Bell and was purified according to Pelletier.[27] Bromine, sodium nitrite, chloroacetic acid, sodium hydroxide, and potassium hydroxide were purchased from Mallinckrodt.

Purification of Benzoic Acids Used. With the exception of anisic acid, the benzoic acids were recrystallized first from ethanol and then from water, pretreating each solution with charcoal, then

sublimed at 0.01 mm. Anisic acid was purified by dissolution in water made alkaline with excess NaOH, the solution warmed to 40 °C, and $KMnO_4$ crystals added with stirring until the purple color of MnO_4^- persisted for 5 min. The solution was then cooled to 25 °C and $NaHSO_3$ crystals added until the purple color was discharged. The MnO_2 produced was filtered and the anisic acid precipitated from the colorless filtrate by addition of excess concentrated HCl. The anisic acid was then recrystallized from water to yield 3.8-cm needles which were collected by suction filtration, air dried, and sublimed in vacuo at 0.01 mm.[28] All of the benzoic acids used had melting points in good agreement with accepted literature values.

Acetic, propanoic, chloroacetic, bromoacetic, dichloroacetic, and trifluoroacetic acids were fractionally distilled either at ambient pressure or at reduced pressure through a 10-cm Vigreux column taking only a center cut whose boiling point corresponded to accepted literature values. Glycolic acid and glycine were of reagent quality and were used without further purification.

Determination of pK_a'.[29] Distilled water was treated with $KMnO_4$, refluxed for 1 h, and then twice distilled using an Ascarite tube for protection from atmospheric CO_2. Ethanol was dried according to Manske[30] and protected during distillation from atmospheric moisture and CO_2 by tubes filled with Drierite and Ascarite. The water and ethanol were thermostated to 20 °C in 1-l. volumetric flasks prior to mixing to make 50% aqueous ethanol (v/v). Approximately 0.07 g of the substituted benzoic acids were dissolved in 100 ml of the solvent and then 30-ml aliquots were titrated at 25 ± 1 °C with carbonate-free NaOH prepared in the same solvent. The midpoint of the titration curve was read graphically to determine the pK_a'. In no titration run did the resultant pK_a' differ by more than 0.01 pH unit from the average and in most runs no detectable difference was observed. Prior to each determination the glass electrode used was standardized against two known buffers, rinsed well with distilled water, gently dried with a tissue, immersed in a blank of 50% aqueous ethanol (v/v), and finally immersed in the sample to be titrated. After each titration the electrode was again checked against two known buffers. No drift was observed in the electrode.[31]

Determination of σ^* of the Trifluoromethanesulfonyloxy Group. Owing to observed leveling of dichloroacetic acid and trifluoroacetic acid in 50% aqueous ethanol (v/v) and 80% aqueous ethanol (v/v), anhydrous 2-propanol was chosen as the titration solvent. Reagent grade anhydrous isopropyl alcohol was fractionally distilled before use while protected from atmospheric CO_2 and H_2O by an Ascarite tube and Drierite tube. Potassium hydroxide from a freshly opened bottle was dissolved in anhydrous 2-propanol and was used to titrate 0.003 M samples of substituted acetic acids dissolved in 2-propanol in a manner similar to that described for the *p*-substituted benzoic acids. The $pK_{a(i\text{-PrOH})}$ was determined graphically from the midpoint of the titration curve.

Determination of Relative Bromination Rate. 2-Bromo-3-methyl-2-butene was prepared[32] and purified by GLC. 3-Methyl-2-buten-2-yl trifluoromethanesulfonate was prepared[33] and purified by GLC. Approximately equal volumes of 2-bromo-3-methyl-2-butene and 3-methyl-2-buten-2-yl trifluoromethanesulfonate were injected into a serum-capped vial at 25 °C containing 4 ml of CCl_4. Then five samples were withdrawn and analyzed on a flame ionization GLC to determine the relative ratio of the two components. A small amount of Br_2 in CCl_4 was injected into the vial and after complete discharge of the color of Br_2 (~10 min) five samples were withdrawn with a syringe and analyzed as before, resulting in an average value of $k_{Br}/k_{OTf} = 2.9$. Since the bromination products were not stable to the GLC conditions, the disappearance of the starting materials was used for the rate measurement.

Synthesis of Compounds. The phenylsulfonic esters were synthesized either by the pyridine method, A, or by a Schotten–Baumann reaction, B.

3-Fluorophenyl *p*-Toluenesulfonate. Method A. To 1.00 g of freshly distilled 3-fluorophenol was added an equal volume of pyridine, followed by 1.71 g of freshly purified *p*-toluenesulfonyl chloride. The mixture became warm and was heated on the steam bath for 10 min, cooled, and poured into 10 ml of H_2O. The ester precipitated at once and was filtered, dissolved in ethanol, and treated with charcoal, the charcoal was removed by filtration, and the filtrate was evaporated to dryness on the steam bath. The white solid was recrystallized from EtOH–H_2O to give 1.52 g (57%) of colorless needles: mp 47.5–48.5°; ir (Nujol mull) 1370, 1191, 1177 (S=O), 1242 (aromatic C–F); ^{19}F NMR δ 155.5; ^1H NMR (Me_2SO-d_6) δ 2.43 (s, 3), 7.60 (d of q, 8), 13.1 (br s, 1); mass spectrum *m/e* (rel intensity) 266 ($M\cdot^+$, 30), 202 (22), 156 (49), 155 (52), 91 (100).

Phenyl Trifluoromethanesulfonate. Method B. To 6.00 g of phenol in 60 ml of H_2O was added 6.00 g of NaOH and the mixture was shaken until dissolved. Then 20.22 g of trifluoromethanesulfonic anhydride dissolved in 20 ml of CCl_4 was added while stirring and cooling in an ice bath. The mixture was stirred for an additional 1.5 h, the CCl_4 layer separated in a separatory funnel, and the aqueous layer washed with 5 ml of CCl_4. The CCl_4 solution was dried over $MgSO_4$, the $MgSO_4$ filtered off, and the CCl_4 removed on a rotary evaporator at aspirator pressure: crude yield 11.72 g (81%), redistilled 9.10 g (63%); bp 87–88 °C (13 mm) [lit.[34] bp 99–100 °C (60 mm) and 51–53 °C (1 mm)[35]]; ir (neat) 1421, 1212 (S=O), 1248 (C–F), 1600, 1585, 1484, 1456 cm^{-1} (aromatic C=C).

3-Fluorophenyl Methanesulfonate. Method A. The product was recrystallized four times from EtOH–H_2O at −70 °C to obtain 0.41 g (21%) of colorless needles: mp 23.5–24.5°; ir (Nujol mull) 1379, 1182 (S=O), 1248 cm^{-1} (C–F); ^{19}F NMR δ 181.3; ^1H NMR (Me_2SO-d_6) δ 3.47 (s, 3), 7.83 (q, 4), 12.7 (br s, 1); mass spectrum *m/e* (rel intensity) 190 ($M\cdot^+$, 56), 126 (10), 112 (100), 96 (22).

3-Fluorophenyl Trifluoromethanesulfonate. Method B. The product was purified by distillation to obtain a colorless oil: bp 46–47 °C (3.6 mm) [lit.[4] 60 °C (20 mm)]; mp 11.5–12.4 °C; ir (neat) 1429, 1214 cm^{-1} (S=O); ^{19}F NMR δ 259; ^1H NMR (Me_2SO-d_6) δ 7.90 (q, 4), 12.87 (br s, 1); mass spectrum *m/e* (rel intensity) 244 ($M\cdot^+$, 62), 180 (50), 152 (11), 111 (100).

4-Carboxyphenyl *p*-Toluenesulfonate. Method B. The product was recrystallized from EtOH–H_2O as needles, 11.5 g (54%), sublimed at 149 °C (0.5 mm): mp 168–168.5 °C uncorrected (lit.[36] 167–169 °C uncorrected); ir (Nujol mull) 1686 (C=O), 1429, 1201, 1174 cm^{-1} (S=O).

4-Carboxyphenyl Methanesulfonate. Method B. The product was recrystallized from EtOH–H_2O, sublimed at 185 °C (0.2 mm): mp 219–220 °C (lit.[16] mp 224 °C corrected); ir (Nujol mull) 1684 (C=O), 1425, 1199, 1168 cm^{-1} (S=O).

4-Carboxyphenyl Trifluoromethanesulfonate. Method B. The product was recrystallized from EtOH–H_2O, 6.12 g (31.2%), sublimed at 140 °C (0.2 mm): mp 168–170 °C uncorrected (lit.[4] 175–177 °C corrected); ir (Nujol mull) 1686 (C=O), 1418, 1212 (S=O), 1250 cm^{-1} (CF_3).

4-Nitrophenyl Trifluoromethanesulfonate. Phenyl trifluoromethanesulfonate (1.00 ml) was added to a mixture of 6 ml of concentrated H_2SO_4 and 6 ml of concentrated HNO_3, precooled to 0–5 °C in an ice bath. The mixture was left at 0–5 °C for 14 h and ice then added to precipitate a white solid. This was recrystallized from EtOH–H_2O to give white plates, mp 54–55 °C (lit.[4] mp 51–52 °C, lit.[35] mp 53–54 °C).

2,4-Dinitrophenyl Trifluoromethanesulfonate. Phenyl trifluoromethanesulfonate (0.5 ml) was added to 6 ml of concentrated H_2SO_4 in a 25-ml Erlenmeyer flask and stirred. Very little ester appeared to dissolve in the H_2SO_4. Then 3 ml of concentrated HNO_3 was added at room temperature and the reaction mixture was heated for 2 h on the steam bath and quenched with ice, and the product was worked up in the same manner as 4-nitrophenyl trifluoromethanesulfonate to give plates, mp 52–53 °C (lit.[4] mp 51–52 °C). The plates were treated with 1 g of NaOH dissolved in 10 ml of EtOH and 10 ml of H_2O, heated for 30 min on the steam bath, made acidic with concentrated HCl, and concentrated on a rotary evaporator to 10 ml, and the faint yellow crystals were isolated and recrystallized from EtOH–H_2O (1:5 v/v) to give crystals, mp 114–115 °C. A mixture melting point with authentic 2,4-dinitrophenol was undepressed. An ir taken was identical with that of authentic 2,4-dinitrophenol.

Glycolic Acid Trifluoromethanesulfonate. Glycine benzyl ester *p*-toluenesulfonate[37] was diazotized[38] and treated with trifluoromethanesulfonic acid,[39] the benzyl ester removed by catalytic hydrogenolysis,[40] and the product recrystallized from CCl_4 to give white needles: mp 58–59 °C; ir (melt) 3000, 1750 (C=O), 1413, 1214, 1142 (S=O), 1242 (CF_3), 1032, 861, 814, 769 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.98 (s, 2), 10.52 (s, 1).

Determination of Taft σ_I and σ_R substituent Parameters. The literature[8] procedure using C_6H_5F as an internal standard in CCl_4 solution was followed; σ_I was determined from the average of six runs by the equation $\delta_m^F = 0.61\sigma_I - 0.05$. The Taft σ_R parameter was determined from the equation $\sigma_p = \sigma_I + \sigma_R$.

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Registry No.—3-Fluorophenol, 372-20-3; *p*-toluenesulfonyl-chloride, 98-59-9; phenyl trifluoromethanesulfonate, 17763-67-6; phenol, 108-95-2; trifluoromethanesulfonic anhydride, 358-23-6; glycine benzyl ester *p*-toluenesulfonate, 1738-76-7.

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Secondary Deuterium Isotope Effects in the Solvolysis of *cis*- and *trans*-2-Acetoxycyclohexyl 2,2,2-Trifluoroethanesulfonates

S. Richter, I. Bregovec, and D. E. Sunko*

Laboratory of Organic Chemistry, Faculty of Natural Sciences and Mathematics, University of Zagreb, 41000 Zagreb, Yugoslavia

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The 2,2,2-trifluoroethanesulfonates (tresylates) of specifically deuterated *cis*-2-acetoxycyclohexanol (*cis*-1βd, *cis*-1αd, *cis*-1$\beta' d_2$) and *trans*-2-acetoxycyclohexanol (*trans*-1βd, *trans*-1αd, *trans*-1$\beta' d_2$) were solvolyzed in 97 wt % trifluoroethanol at 93 and 55°C, respectively, and the secondary deuterium isotope effects were measured. The solvolysis products from the trifluoroethanolysis of the unlabeled isomeric tresylates *cis*-1 and *trans*-1 were also determined. The α effect in *trans*-1αd is similar in magnitude to the effects observed in SN2 reactions (k_H/k_D = 1.03). The β effects in *trans*-1βd and *trans*-1$\beta' d_2$ are also small (k_H/k_D = 0.98 and 1.04, respectively), reflecting the absence of significant hyperconjugative stabilization. These results are in agreement with a transition state structure closer to the oxonium ion intermediate than to the reactants. The results obtained in the solvolysis of the corresponding cis derivatives are significantly different. The α effect is large (k_H/k_D = 1.20) indicating that ionization to the solvent-separated ion pair is rate determining, while the β effects are "normal" but larger for *cis*-1βd (1.34) than for *cis*-1$\beta' d_2$ (1.23). On the basis of these results it was concluded that the cis derivative solvolyzes via a twist–boat transition state. The present work demonstrates the sensitivity of secondary deuterium isotope effects to structural changes of solvolytic transition states.

"The deuterium isotope effect has become one of the most important of the tools which physical organic chemists employ in the elucidation of the mechanisms of chemical reactions", but "a dilemma has plagued the interpretation of the experimental data". In 1961 when Westheimer wrote these lines,[1] the dilemma was associated with a spectrum of values of the ratio k_H/k_D. Regretfully, a lack of understanding of the meaning of differences in the magnitudes of observed isotope effects still pertains today.[2] In spite of a satisfactory theoretical treatment of isotope effects, primary[3] as well as secondary,[3,4] the interpretation of isotopic rate data rests mostly on the empirical comparison of these effects in systematically varied and closely related systems. The success of such an approach has been amply demonstrated by Shiner and co-workers[5] in their studies of nucleophilic substitution reactions.