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# SYNTHESIS AND SOLVOLYSIS OF ARYLSULFONYLMETHYL ARENESULFONATES

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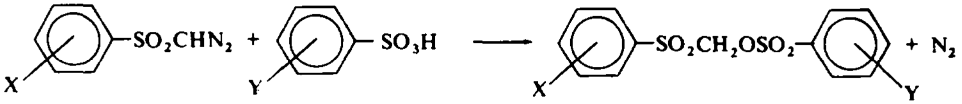
**Abstract**—Nine arylsulfonylmethyl arenesulfonates were prepared by reaction of the corresponding α-diazosulfones and arenesulfonic acids in an aprotic solvent. Hydrolysis of these sulfonates in alkaline media gives formaldehyde and the parent sulfinic and sulfonic acids. The hydrolysis reaction shows specific base catalysis as indicated by the solvent deuterium isotope effect, rapid CH/CD exchange during solvolysis, kinetic data with bases other than hydroxide ions and the effect of nucleophiles on the product formation and the rate of hydrolysis. The substituent effects on the rates of CH/CD exchange, on the solvent induced chemical shift of the methylene group and on the rates of hydrolysis are discussed in terms of the proposed mechanism.

## INTRODUCTION

IN PREVIOUS studies[1-3] we demonstrated that the reaction of α-diazosulfones with perchloric acid in an aprotic solvent produces the covalent sulfonylmethylperchlorates, $RSO_2CH_2OClO_3$, which are thermally fairly stable. The hydrolysis of these perchloric esters is a general base-catalysed reaction involving a redox reaction during the fast product determining steps.[2,3]

$$RSO_2CH_2OClO_3 + H_2O \xrightarrow{\text{base}} RSO_2H + HCOOH + HClO_3$$

In view of these results it became of interest to investigate the hydrolysis of similar esters of other strong oxygen acids. In this paper we report the synthesis of arylsulfonylmethyl arenesulfonates and a study of their mechanism of hydrolysis. These previously unreported types of sulfonates (Ia-Ii) are readily accessible from the reaction of an α-diazosulfone[4] and the appropriate arenesulfonic acid in ethyl acetate.*



## SYNTHESIS

The arylsulfonylmethyl arenesulfonates (Ia-Ii) were prepared by reaction of the α-diazosulfone dissolved in ethyl acetate with 1·5–2·0 equivalents of arenesulfonic acid. The formation of the sulfonates is proposed to proceed *via* initial protonation of the α-diazosulfone to give the corresponding diazonium ion and subsequent nucleophilic displacement of the $-^{\oplus}N{\equiv}N$ group by the sulfonate anion.[1]

The structures of the arylsulfonymethyl arenesulfonates are based on correct

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* The first representative of this type of compounds (Ib, $X{=}Y{=}p\text{-}CH_3$) was reported in a preliminary communication[1].

elemental analyses and spectral data. The IR spectra show the expected strong sulfonyl stretching vibrations around 1280 and 1150cm$^{-1}$. The PMR spectra exhibit characteristic singlets due to the methylene protons in the $SO_2CH_2OSO_2$ moiety (Table 4). The sulfonates can be stored at room temperature for at least two years without noticeable decomposition.

In 1951 Field and Settlage isolated an unstable compound (m.p. 84–86°) in a 3% yield from the reaction of hydroxymethyl *p*-tolysulfone with *p*-toluenesulfonylchloride. They claimed this compound to be *p*-tosylmethyl tosylate (Ib)[5] but in view of our findings their structural assignment is questionable.

## SOLVOLYSIS: RESULTS AND DISCUSSION

*Reaction products.* Hydrolysis of Ib in 80% (v/v) dioxan-water containing 0·45N NaOH gave *p*-toluenesulfinic acid (66%)* and sodium *p*-toluenesulfonate (89%). The reaction of Ib with sodium methoxide in methanol gave *p*-toluenesulfinic acid (60%)* and sodium *p*-toluenesulfonate (91%), while Ig ($X = p\text{-}CH_3$; $Y = H$) under the latter condition afforded *p*-toluenesulfinic acid (81%) and sodium benzenesulfonate (89%).

The formation of formaldehyde in the base catalysed reaction of Ib in water or methanol was confirmed by positive tests with Schiff's reagent and *p*-phenylenediamine after acidification with dilute aqueous sulfuric acid.[7]

The UV spectra recorded after the kinetic measurements were in excellent agreement with those expected for equimolar amounts of sulfinic and sulfonic acid. This indicates that the reactions go to completion under kinetic conditions.

*Kinetic measurements.* The rates of hydrolysis of Ia-Ii could be determined conveniently by following the change in absorbance at a suitable wavelength in the UV spectra (Table 2). Measurable rates of hydrolysis were found only in the presence of hydroxide ions. Pseudo first order kinetics were found for at least three half lives. Because of the limited solubility of the substrates in water most of the rate measurements were performed at 32° rather than 25°.

*Base catalysis* vs *nucleophilic displacement.* Initially the possibility of a nucleophilic displacement reaction was considered. Three possible sites for such a reaction can be envisaged, i.e. the methylene C atom[8] as well as the S atoms[9] of the sulfonyl and the sulfonate groups. Accordingly experiments were performed with Ib in the presence of a variety of hard and soft nucleophiles,[10] e.g. NaBr and NaF (in 0·1N NaOH) and NaF, NaI, $NaNO_2$ and $NaN_3$ (in MeOH). In 0·1N NaOH the rate of hydrolysis of Ib was not affected by added bromide or fluoride ions (Table 2). The UV spectra of the reaction mixtures show that equimolar amounts of *p*-toluenesulfinic acid and *p*-toluenesulfonic acid are formed and the complete absence of *p*-tolylsulfonylmethyl halides. Attempted reactions of Ib with NaF, NaI, $NaNO_2$ and $NaN_3$ in methanol at reflux temperature for three days resulted in all cases in a quantitative recovery of starting material. All these observations exclude nucleophilic displacement reactions either at C or at S.

Rate measurements in dilute aqueous NaOH showed that the hydrolysis reaction is catalyzed by hydroxide ions; acid catalysis was not observed. In order to decide

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* Part of the sulfinic acid is lost during the work-up procedure.[3] Addition of sodium nitrilte to the reaction mixture of Ib and subsequent acidification afforded 92% $(p\text{-}CH_3C_6H_4SO_2)_2NOH$.[6]

between specific and general base catalysis the following criteria were applied: contribution of other bases than hydroxide ions, solvent deuterium isotope effect and CH/CD exchange at the methylene C atom.

*Contribution of bases.* The rate of hydrolysis of Ib could be measured conveniently only at a rather high pH(>12). Since no adequate buffers are available in this pH region the contribution of acetate ions was determined in the presence of 0·1N NaOH. The rate constants presented in Table 2 indicate that the addition of substantial amounts of sodium acetate did not increase the rate of hydrolysis of Ib (for comparison rate measurements for Ib were performed in the presence of $NaClO_4$). Accordingly the rates of hydrolysis in these alkaline media are indicative for *specific base catalysis.*

$$\text{rate} = k_{\psi} \cdot c_{Ib} = (k_{OH^{\ominus}} \cdot c_{OH^{\ominus}})c_{Ib}$$

From a plot of $k_{\psi}$ *vs* $c_{OH^{\ominus}}$ the second order rate constant $k_{OH^{\ominus}}$ is obtained (36 . $10^{-4}$ L. $\text{mole}^{-1}$ . $\text{sec}^{-1}$). (Fig. 1) The rate of hydrolysis is reduced to zero at $c_{OH^{\ominus}} = 0$ as shown by extrapolation indicating that the contribution of water as a base to the rate of hydrolysis is negligible.

*Solvent deuterium isotope effect.* The solvent deuterium isotope effect $k_{OD^{\ominus}}k_{OH^{\ominus}}$ was determined for Ib, Ie and Ii in dilute aqueous NaOH. The observed $k_{OD^{\ominus}}/k_{OH^{\ominus}}$ value which is larger than unity (about 1·4; see Table 2) is in accordance with specific base catalysis.[11,12]

CH/CD *exchange.* The occurrence of specific base catalysis is supported by the observation of fast CH/CD exchange at the methylene group of Ib by PMR spectroscopy. Upon addition of a few drops of 0·1N NaOD in $D_2O$ to a solution of Ib in dioxan the methylene signal disappeared quickly and completely while no additional

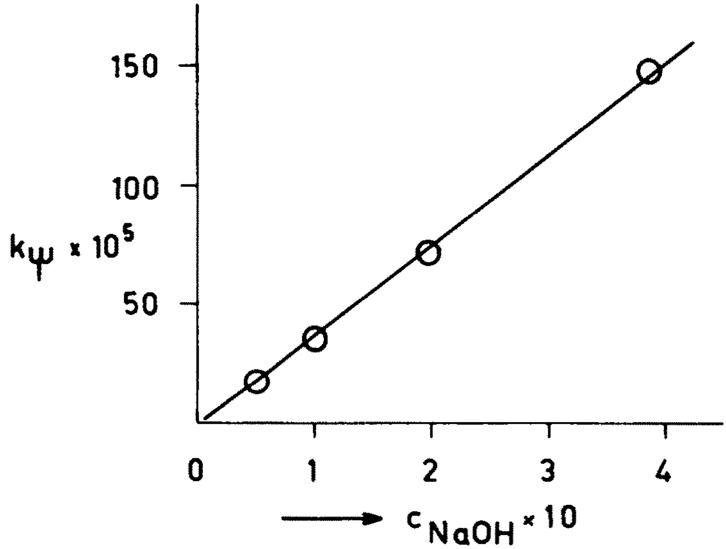

FIG. 1 Pseudo first order rate constants for the hydrolysis of Ib in dilute aqueous NaOH at 25°.

changes in the PMR spectrum were observed. Subsequent addition of $H_2O$ resulted in a partial reappearance of the methylene absorption. Ib was recovered from this reaction mixture in 80% yield.

The rates of exchange for Ia-Ii could not be measured in solutions containing strong bases such as hydroxide or methoxide ions. Even in solutions containing 0·003N NaOD (in 70% (v/v) dioxan-$D_2O$ or in 70% (v/v) 1,2-dimethoxyethane-$D_2O$) or 0·002N NaOMe (in MeOD) a very fast CH/CD exchange occurred. However with the weaker base triethylamine in MeOD the rate of exchange of Ib, Ic, Id, Ig and Ih was easily measured by following the integration of the PMR methylene signal ($S_t$) as a function of time. Pseudo first order rate constants of exchange, $k_{ex}$, were obtained by plotting log $S_t$ *vs* time and are given in Table 3. The $k_{ex}$ values are proportional to the rate constants can be correlated by Hammett's $\sigma$ constants[13,14] (Fig 2) giving $\rho_X = 3{\cdot}0$ and $\rho_Y = 1{\cdot}5$. Comparison of the $\rho_X$ with the $\rho_Y$ value indicates that the substituents X have a larger effect on the carbanion formation that the substituents Y.

An indication for the acidity of the methylene protons of the sulfonates (I) can also be obtained from their ability to H-bond with an acceptor solvent molecule.[15] The relative strength of the H-bond will be reflected in the solvent shift of the methylene proton absorption. Therefore accurate chemical shifts of the methylene group of

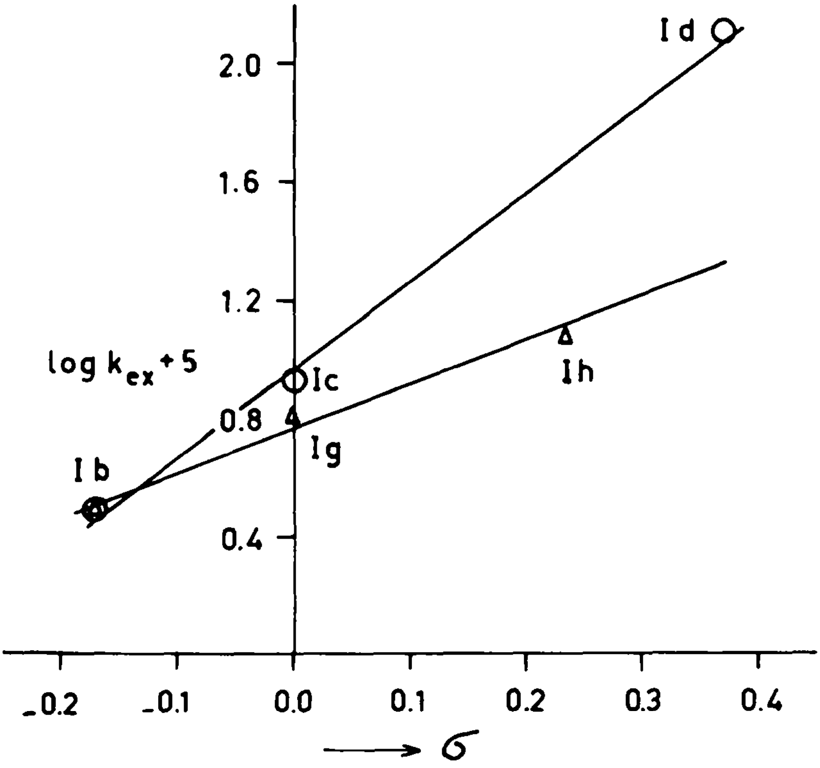

Fig. 2 Relation between log $k_{ex}$ and Hammett $\sigma$ for the CH/CD exchange of arylsulfonylmethyl arenesulfonates in $CH_3OD$ with triethylamine at 40°.

Ia-Ii were determined in DMSO-$d_6$ and $CDCl_3$* (Table 4). Reasonable straight lines are obtained when the solvent shifts ($\Delta\delta$) are plotted *vs* Hammett's $\sigma$ constants (Fig 3) giving $\rho_X = 0{\cdot}2$ and $\rho_Y = 0{\cdot}1$. These rather small $\rho$ values reflect an only slight bond weakening upon H-bonding. Again the substituents X have the largest influence on the acidity of the C—H bonds. It is noteworthy that the ratio $\rho_X/\rho_Y$ is approximately the same for the rates of exchange and the solvent induced chemical shifts.

*Activation parameters.* The rates of hydrolysis of Ib were measured at four different temperatures. The activation parameters $\Delta G^‡$(20·9 Kcal mole$^{-1}$), $\Delta H^‡$(15·8 Kcal mole$^{-1}$) and $\Delta S^‡$(− 17 e.u.) were obtained from the plot of log $k_\psi$ *vs* $^1/T$. (Fig 4).

*Substituent effects.* The rates of hydrolysis $k_\psi$ of Ia-Ii in 0·1N NaOH (Table 2) can be correlated by Hammett's $\sigma$ constants[13, 14] (Fig 5), giving $\rho_X = 0{\cdot}49$ and $\rho_Y = 2{\cdot}12$. Taking into account the substituent effects on the preequilibrium step, these $\rho$ values for the hydrolysis reaction point to a transition state for the rate determining step in which the negative charge is accommodated mainly by the arenesulfonate group.

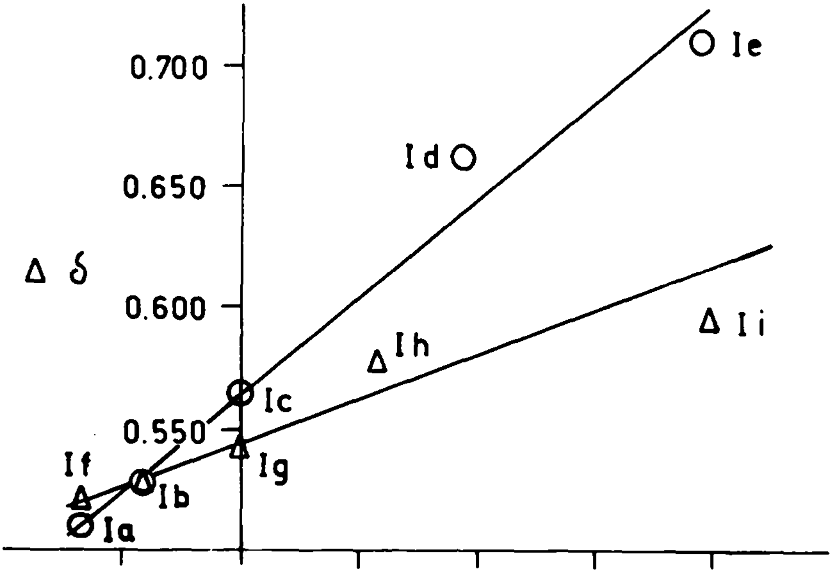

FIG. 3 Correlation between the solvent induced chemical shifts of the methylene protons of Ia-Ii and Hammett $\sigma$.

*Discussion of the mechanism.* In the foregoing sections it was shown that the hydrolysis of the arysulfonylmethyl arenesulfonates is specifically base catalysed implying a rapid proton exchange at the methylene group prior to the rate determining step. The $\rho_X$ value for the reversible $\alpha$-sulfonylcarbanion formation is in the same range as that found for the proton exchange of some 3-arylsulfonyl bicyclo[2.2.1]

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* Unfortunately the more inert $CCl_4$ or n-hexane could not be employed due to the limited solubility of the sulfonates.

hept-5-ene 2-carboxylic acids.[16] From the much smaller $\rho_X$ value for the hydrolysis reaction it may be concluded that the C atom $\alpha$ to the sulfonyl group is electron deficient (as compared to the carbanion intermediate) in the transition state of the rate determining step. Support for this conclusion is found in the effect of the substituents Y on the hydrolysis reaction since the large $\rho_Y$ value is indicative for a transition state of the rate controlling step in which the negative charge is situated mainly on the arenesulfonate part.

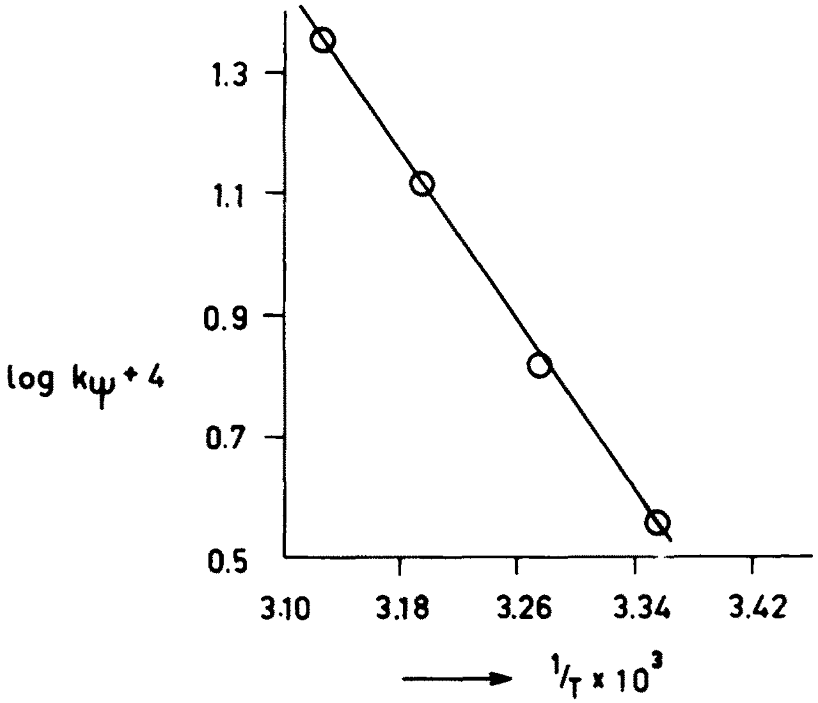

Fig. 4 Plot of log $k_\psi$ vs $^1/T$ for the hydrolysis of Ib in 0·100N NaOH.

The kinetic evidence presented thusfar may be reconciled with an $\alpha$-elimination of arenesulfonate anion from the $\alpha$-sulfonyl carbanion to give an $\alpha$-sulfonylcarbene. The elimination of sulfonate rather than sulfinate anion is in accordance with their known difference in leaving abilities (in nucleophilic displacement reactions).[17] Subsequent reaction of the $\alpha$-sulfonylcarbene with water will give an hydroxymethyl arylsulfone, which is known to hydrolyse rapidly to arenesulfinic acid and formaldehyde in neutral or alkaline media (Scheme 1).[18, 19] On basis of this mechanism one would expect that in *methanol* the $\alpha$-sulfonylcarbene will be trapped to give arylsulfonylmethyl methyl ether,[20] which was shown to be relatively stable towards sodium methoxide in methanol.* However, the actual product obtained upon reaction of Ib with sodium methoxide in methanol is sodium $p$-toluenesulfinate. Assuming similar mechanistic pathways in water and methanol this would indicate that the

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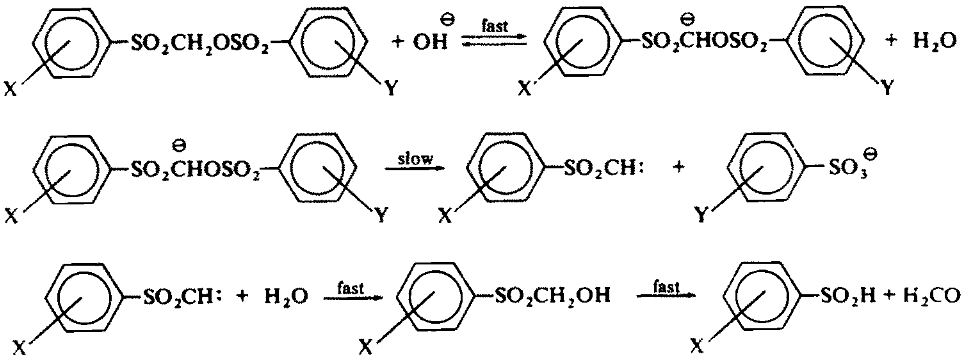
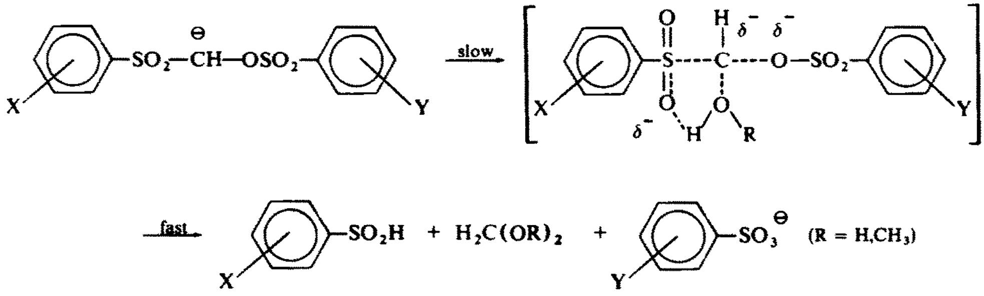
* After refluxing $p$-$CH_3C_6H_4SO_2CH_2OCH_3$ with sodium methoxide in methanol for three days 70% starting material was obtained together with 14% $p$-toluenesulfinic acid.

SCHEME 1:



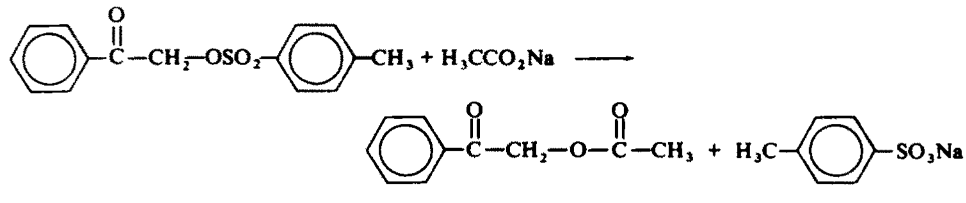
α-sulfonylcarbene stage has been bypassed. Apparently a transition state is involved in which the S—C bond is also weakened although to a much lesser extent than the O—C bond (cf $\rho_X$ *vs* $\rho_Y$ for the hydrolysis reaction). The weakening of these two bonds will induce a relative electron deficiency on the central C atom facilitating participation of the solvent (water or methanol) in the transition state. In this manner the formation of the observed reaction products can be visualized as shown in Scheme 2.

SCHEME 2:



The negative entropy of activation ($-1.7$ e.u.) supports the involvement of the solvent in the transition state.

In view of the difference in rates of nucleophilic displacement reactions at C atoms adjacent to a sulfonyl or carbonyl group,[3, 21] we carried out some solvolysis experiments with benzoylmethyl tosylate. The latter compound was prepared from benzoyldiazomethane and *p*-toluenesulfonic acid.[22] Treatment of benzoylmethyl tosylate with excess sodium acetate in refluxing methanol afforded benzoylmethyl



acetate in 85% yield. This result can be best interpreted by assuming a bimolecular nucleophilic displacement reaction at the C atom α to the carbonyl group.

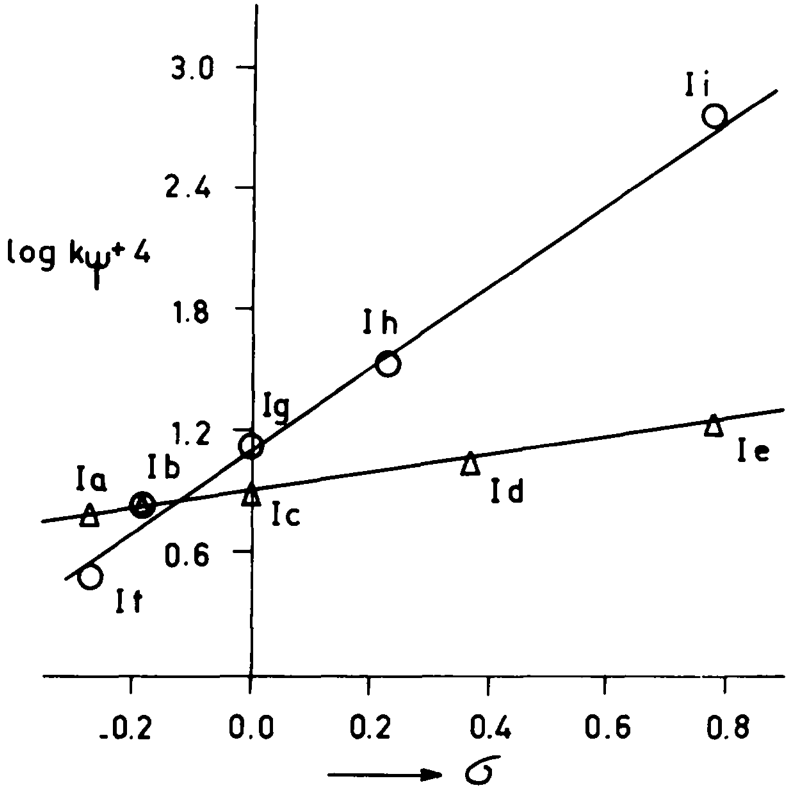


Fig. 5 Relation between log $k_\psi$ and Hammett σ for the hydrolysis of arylsulfonylmethyl arenesulfonates in 0·100N NaOH at 32°.

## EXPERIMENTAL

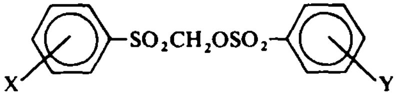
*Starting materials, solvents, reagents.* The α-diazosulfones, $ArSO_2CHN_2$, were prepared by the method of van Leusen and Strating.[4,23] The arenesulfonic acids were obtained upon hydrolysis of the parent arenesulfonyl chlorides in water. The reagent grade solvents $CH_2Cl_2$, EtOAc and MeOH were distilled before use. The water, used in the kinetic measurements, was demineralized and distilled twice in an all-quartz distillation unit. $D_2O$ (99·75% $D_2O$) was purchased from E. Merck A.G. Darmstadt and was used as such. Analytically pure materials were employed for the preparation of the solns used in the kinetic measurements.

M.ps were recorded with an electrically heated oil bath and are uncorrected. The combustion analyses were carried out in the micro-analytical department of this laboratory under the supervision of Mr. W. M. Hazenberg.

### *Synthesis of the arylsulfonylmethyl arenesulfonates* (Ia-Ii)

*General procedure.* The α-diazosulfone (5 mmole) dissolved in 25 ml EtOAc was placed in a 50 ml 3-necked flask fitted with a gas burette. At room temp hydrated arenesulfonic acid (1·5–2·0 equivs) was added to the magnetically stirred soln. A brisk evolution of $N_2$ occurred and the yellow colour of the soln vanished. After 3–5 min a nearly quantitative amount of $N_2$ had been evolved. Stirring was continued for 10 min. Subsequently $CH_2Cl_2$ (20 ml) and water (10–15 ml) were added and the resulting mixture was neutralized

TABLE 1. THE ARYLSULFONYLMETHYL ARENESULFONATES.



| | X | Y | % Yield | m.p.(°C) | C Calc. | C Found | H Calc. | H Found | S Calc. | S Found | Cl or N Calc. | Cl or N Found |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ia | p-$CH_3O$ | p-$CH_3$ | 70 | 129·5–131·5 | 50·54 | 50·8<br>50·6 | 4·53 | 4·6<br>4·6 | 17·99 | 18·1<br>18·0 | | |
| Ib | p-$CH_3$ | p-$CH_3$ | 63 | 109–112 | 52·93 | 52·3<br>52·5 | 4·74 | 4·8<br>4·2 | 18·84 | 18·3<br>18·3 | | |
| Ic* | H | p-$CH_3$ | 66 | 73–75 | 51·52 | 51·6<br>51·7 | 4·33 | 4·3<br>4·3 | 19·65 | 19·7<br>19·7 | | |
| Id* | m-Cl | p-$CH_3$ | 60 | 110–112 | 46·61 | 46·3<br>46·5 | 3·63 | 3·5<br>3·6 | 17·78 | 17·5<br>17.8 | 9·83 | 10·0<br>10·1 |
| Ie | p-$NO_2$ | p-$CH_3$ | 73 | 174·5–177 | 45·27 | 45·0<br>45·1 | 3·53 | 3·5<br>3·5 | 17·27 | 17·2<br>17·1 | 3·78 | 3·7<br>3·7 |
| If | p-$CH_3$ | p-$CH_3O$ | 64 | 93–95 | 50·54 | 50·1<br>50·2 | 4·53 | 4·6<br>4·4 | 17·99 | 18·3<br>18·1 | | |
| Ig | p-$CH_3$ | H | 64 | 100 102 | 51·52 | 51·4<br>51·5 | 4·33 | 4·2<br>4·2 | 19·65 | 19·5<br>19·5 | | |
| Ih | p-$CH_3$ | p-Cl | 66 | 132–134 | 46·61 | 46·6<br>47·0 | 3·63 | 3·8<br>3·7 | 17·78 | 18·1<br>18·0 | 9·83 | 9·9<br>9·9 |
| Ii | p-$CH_3$ | p-$NO_2$ | 73 | 153–155 | 45·27 | 45·3<br>45·5 | 3·53 | 3·8<br>3·7 | 17·27 | 17·2<br>17·1 | 3·78 | 3·8<br>3·9 |

* Prepared from the α-diazosulfone and *anhydrous* p-toluenesulfonic acid in $CH_2Cl_2$.

Table 2. Pseudo first order rate constants for the hydrolysis of Ia-Ii in aqueous NaOH

| Compound (solvent) | UV* (mμ) | $c_{NaOH} \cdot 10^4$ (mole, $l^{-1}$) | c added salt · $10^4$ (mole . $l^{-1}$) | Temp (°C) | $k_\psi \cdot 10^5$ ($sec^{-1}$) | $k_{OD^\ominus}/k_{OH^\ominus}$ |
|---|---|---|---|---|---|---|
| Ia in $H_2O$ | 250 | 1001 | | 32·2 | 60·4 | |
| Ib in $H_2O$ | 235 | 508 | | 25·0 | 18·0 | |
| Ib in $H_2O$ | | 1017 | | 25·0 | 36·3 | |
| Ib in $H_2O$ | | 1985 | | 25·0 | 73·2 | |
| Ib in $H_2O$ | | 3880 | | 25·0 | 147 | |
| Ib in $H_2O$ | | 1017 | 1000 NaBr | 25·0 | 35·7 | |
| Ib in $H_2O$ | | 1017 | 1000 NaOAc | 25·0 | 36·4 | |
| Ib in $H_2O$ | | 1017 | 5000 NaOAc | 25·0 | 35·5 | |
| Ib in $H_2O$ | | 1017 | 10000 NaOAc | 25·0 | 34·4 | |
| Ib in $H_2O$ | | 1017 | 1000 $NaClO_4$ | 25·0 | 35·3 | |
| Ib in $H_2O$ | | 1017 | 5000 $NaClO_4$ | 25·0 | 34·4 | |
| Ib in $H_2O$ | | 1017 | 10000 $NaClO_4$ | 25·0 | 34·2 | |
| Ib in $H_2O$ | | 1003 | 1000 NaF | 25·0 | 35·6 | |
| Ib in $H_2O$ | | 1017 | | 32·2 | 64·9 | |
| Ib in $H_2O$ | | 1017 | | 39·8 | 133 | |
| Ib in $H_2O$ | | 1017 | | 46·6 | 228 | |
| Ib in $D_2O$ | | 2102 | | 25·0 | 104 | 1·37 |
| Ic in $H_2O$ | 235 | 1003 | | 32·2 | 81·3 | |
| Id in $H_2O$ | 233 | 1001 | | 32·2 | 124 | |
| Ie in $H_2O$ | 235 | 1001 | | 32·2 | 191 | |
| Ie in $D_2O$ | | 998 | | 32·2 | 266 | 1·40 |
| If in $H_2O$ | 250 | 1003 | | 32·2 | 29·5 | |
| Ig in $H_2O$ | 235 | 1003 | | 32·2 | 145 | |
| Ih in $H_2O$ | 235 | 1003 | | 32·2 | 340 | |
| Ii in $H_2O$ | 235 | 100 | | 32·1 | 590 | |
| Ii in $D_2O$ | | 100 | | 32·1 | 851 | 1·44 |

* Wavelength used for rate measurements.

Table 3. Rate constants for CH/CD exchange of Ib, Ic, Id, Ig and Ih in $CH_3OD$ in the presence of $Et_3N$* at 40·0 ± 0·8°

| | $k_{ex} . 10^5(sec^{-1})$ | | $k_{ex} . 10^5(sec^{-1})$ |
|---|---|---|---|
| Ib | 3·4 | Ig | 6·5 |
| Ic | 8·5 | Ih | 12·5 |
| Id | 135 | | |

* Concentration: $33 . 10^{-5}$ mole . $l^{-1}$.

with $NaHCO_3$ to pH 6–7. The aqueous layer was extracted 3 times with $CH_2Cl_2$ (25 ml). The combined organic layers were washed with water (10 ml) and dried over $MgSO_4$ or $CaCl_2$. The solvent was removed *in vacuo* at 20°. The crude crystalline product was purified by crystallization from $CHCl_3$ or MeOH.

The sulfonates Ic and Id were prepared using anhydrous *p*-toluenesulfonic acid in $CH_2Cl_2$.

*Reaction products.* To a soln of Ib (1·020 g; 3·0 mmole) in dioxan (80 ml) and 0·5 N NaOH (20 ml) were added. After stirring the somewhat opalescent soln for 6 days at room temp the water and dioxan were distilled off *in vacuo*. The resulting pale yellow solid was treated with water (25 ml) whereupon the solid dissolved partly and afforded upon filtration starting material (0·22 g, 22%), m.p. 107–109°. The aqueous

TABLE 4. SOLVENT EFFECT ON THE CHEMICAL SHIFTS OF THE METHYLENE PROTONS OF Ia-Ii.*

| | $\delta_{CH_2}$(CDCl$_3$) (ppm) | $\delta_{CH_2}$(DMSO-d$_6$) (ppm) | $\Delta\delta$ (ppm) |
|---|---|---|---|
| Ia | 4·867 | 5·375 | 0·508 |
| Ib | 4·879 | 5·410 | 0·531 |
| Ic | 4·898 | 5·462 | 0·564 |
| Id | 4·939 | 5·602 | 0·663 |
| Ie | 4·982 | 5·689 | 0·707 |
| If | 4·870 | 5·388 | 0·518 |
| Ig | 4·913 | 5·457 | 0·544 |
| Ih | 4·932 | 5·512 | 0·580 |
| Ii | 5·015 | 5·611 | 0·596 |

* Recorded on Varian A-60D using an audio oscillator side band technique. Estimated accuracy: ±0·004 ppm. Mole. fraction: 0·0024.

filtrate was acidified with 2N $H_2SO_4$ (15 ml) and extracted with four 10 ml portions of ether. The combined ethereal solns were washed with 2N$H_2SO_4$ (10 ml) and dried over $MgSO_4$. The solvent was removed *in vacuo* at 20° affording a white solid (0·270 g), m.p. 72–79°. After one crystallization from ether/hexane, pure *p*-toluenesulfinic acid (0·240 g; 51% or 66%, calc. on converted Ib), m.p. 83–87° was isolated. The aqueous layer was made alkaline with conc NaOHaq and evaporated to dryness. The resulting white solid was extracted with 3 portions of boiling ethanol (25 ml). Removal of ethanol *in vacuo* and drying at 100° gave sodium *p*-toluenesulfonate (0·420 g; 69% or 89%, calc. on converted Ib).

The reaction of Ib (1·020 g; 3·0 mmole) with NaOMe (0·470 g; 8·7 mmole) in MeOH (30 ml) was carried out at a room temp. After stirring for 3 days the MeOH was removed *in vacuo*. To the resulting white solid water (25 ml) was added. The solid dissolved partly and upon filtration di *p*-tolyl sulfone (5 mg; 0·7%) was obtained (m.p. 151–154°, IR and PMR spectrum and comparison with an authentic sample. No sulfones could be detected upon the reaction of Ig or Ii with NaOMe in MeOH. The aqueous filtrate was acidified with 4N $H_2SO_4$ to pH 0–1 and extracted with four 15 ml portions ether. The combined ethereal extracts were washed with 2N $H_2SO_4$ (10 ml) and dried over $MgSO_4$. The solvent was removed *in vacuo* at 20° yielding a pale yellow solid (0·380 g; 81%), m.p. 67–73°. After two crystallizations from ether/pentane pure *p*-toluenesulfinic acid (0·280 g; 60%), m.p. 82–86° was isolated. Sodium *p*-toluenesulfonate (0·526 g; 91%) was isolated from the aqueous layer as described above.

The reaction of Ig (0·810 g; 2·5 mmole) with NaOMe (0·300 g; 5·5 mmole) was performed in MeOH (30 ml). After stirring for 3 days at room temp the MeOH was distilled off *in vacuo*. The remaining white solid was dissolved in water (25 ml). As described above for Ib, pure *p*-toluenesulfinic acid (0·318 g; 81%), m.p. 83–87° and sodium benzenesulfonate (0·400 g; 89%) were isolated.

Solvolysis of benzoylmethyl tosylate (2·00 g, 6·9 mmole) was carried out in MeOH containing NaOAc (2·0 g; 24 mmole). After refluxing for 12 hr the MeOH was removed *in vacuo*. The resulting white solid was treated with water (25 ml) and $CH_2Cl_2$ (25 ml). The aqueous layer was extracted with 3 portions of $CH_2Cl_2$ (15 ml). The combined organic layers were washed with water (15 ml) and dried over $MgSO_4$. Removal of the solvent *in vacuo* afforded, after cooling at −40° and washing with pentane, crude benzoylmethyl acetate (1·10 g; 90%), m.p. 44–47°. After one crystallization from ether/pentane, a pure product (1·04 g; 85%), m.p. 48·5–49·5° was obtained.

*Kinetic measurements.* The hydrolysis reactions were carried out in 2·0 cm quartz cells, equipped with a magnetic stirring device. The cells were placed in the adequately thermostated (± 0·04°) cell compartment of a Zeiss PMQ II spectrophotometer. About 1 mg of the sulfonate was dissolved in dry MeOH (0·1 ml); 2 or 3 drops of this soln were added to the content of the cell with a glass capillary. Care should be excercised that no precipitation of the sulfonate occurs; the absorbance (E) of the soln must be kept below 0·5. At appropriate intervals the absorbance was measured for about 3 half-life times. After 10 half-lives $E_\infty$ was determined. Pseudo first order rate constants, $k_\psi$, were obtained by plotting log($E_t$–$E_\infty$) *vs* time. Pseudo first order kinetics were found for at least 3 half lives. Rate constants were averaged over 2 measurements and were reproducible to within 3%. After each kinetic experiment the UV spectrum of the hydrolysis mixture was recorded.

The CH/CD rates of exchange were measured using a Varian A-60D instrument. The sulfonates ($3 \cdot 10^{-5}$ mole) were dissolved (with warming) as fast as possible (2–3 min) in 0·6 ml of a previously prepared soln of triethylamine (0·003 g) in MeOD (9 ml). The soln was placed in the probe (40·0 ± 0·8°) of the PMR instrument and the integration of the $CH_2$ signal ($S_t$) was recorded at intervals, during 2–3 half lives. Pseudo first order rate constants, $k_{ex}$, were obtained by plotting log $S_t$ *vs* time. Apart from CH/CD exchange at the methylene group no spectral changes were observed. Addition of MeOH resulted in a partial re-appearance of the $CH_2$ signal.

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