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ARYLSULFONYLMETHYLNITRATES
SYNTHESIS AND MECHANISM OF SOLVOLYSIS

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Abstract—Five arylsulfonylmethylnitrates (Ia–Ie) were prepared from the reaction of an arylsulfonyldiazomethane with nitric acid. These esters hydrolyse in a general base-catalyzed reaction to formic acid, nitrous acid and the parent sulfinic acid. The solvent and the kinetic deuterium isotope effects for this reaction have been measured. The Brønsted coefficient for Ie, the activation parameters and the substituent effects on the rates of hydrolysis and on the solvent induced chemical shift of the methylene protons are discussed. Most likely an $E_{CO}2$ mechanism is operative involving an intermediate α-oxosulfone.

INTRODUCTION

In previous papers[1–3] we described the synthesis and solvolysis of the aryl- and alkylsulfonylmethylperchlorates, $RSO_2CH_2OClO_3$, and the arylsulfonylmethyl arenesulfonates, $ArSO_2CH_2OSO_2Ar'$. These esters are readily accessible *via* the reaction of an arylsulfonyldiazomethane and the appropriate acid in an aprotic solvent.[2–4] The hydrolysis of the covalent perchloric esters was shown to be a general base-catalyzed reaction involving a redox reaction in the fast product determining steps.[2]

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

Hydrolysis of the arylsulfonylmethyl arenesulfonates however, leads in a specific base-catalyzed reaction to the formation of formaldehyde and the parent sulfinic and sulfonic acids.[3]

$$ArSO_2CH_2OSO_2Ar' + H_2O \xrightarrow{OH^\ominus} ArSO_2H + H_2CO + Ar'SO_3H$$

In view of these interesting differences in reaction mechanisms our studies on sulfonyl substituted methyl esters of strong oxygen acids have now been extended to similar esters of nitric acid.

SYNTHESIS

Five representatives of a new class of nitrates i.e. arylsulfonylmethylnitrates (Ia–Ie) were prepared by a procedure similar to that reported previously for the corresponding perchlorates.[2] The formation of the nitrates is proposed to proceed *via* protonation of the arylsulfonyldiazomethane to give the diazonium ion which then undergoes nucleophilic displacement of the $-\overset{\oplus}{N}{\equiv}N$ group by the nitrate anion.[4]

$$ArSO_2CHN_2 + HNO_3 \rightarrow \underset{\text{Ia–Ie}}{ArSO_2CH_2ONO_2} + N_2$$

TABLE 1. THE ARYLSULFONYLMETHYLNITRATES, $ArSO_2CH_2ONO_2$

Compound	Yield %	m.p.	C		H		S		N	
			Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
Ia Ar = p-$CH_3OC_6H_4$	59	28–30	38·87	39·0 38·9	3·67	3·7 3·7	12·97	13·0 13·2	5·67	5·6 5·7
Ib Ar = p-$CH_3C_6H_4$	75	50·5–52	41·55	41·7 41·7	3·93	4·0 4·0	13·87	13·9 13·9	6·06	5·6 5·6
Ic Ar = m-ClC_6H_4	72	40–42	33·40	33·8 33·5	2·40	2·5 2·5	12·74	12·7 12·8	5·57	5·3 5·2
Id Ar = m-$NO_2C_6H_4$	77	62·5–63·5	32·07	32·5 32·2	2·31	2·3 2·4	12·23	12·5 12·3	10·68	10·5 10·5
Ie Ar = p-$NO_2C_6H_4$	85	84–85	32·07	32·2 32·1	2·31	2·3 2·3	12·23	12·2 12·2	10·68	10·4 10·3

The structures of the arylsulfonylmethylnitrates are based on correct elemental analyses (Table 1) and spectral data. The IR spectra show strong sulfonyl stretching vibrations around 1160 and 1350 cm^{-1} together with absorptions around 1280 and 1680 cm^{-1} characteristic for the O—NO_2 moiety. The low field NMR signals at about $\delta = 5{\cdot}5$ ppm in $CDCl_3$ (Table 7) are typical for methylene protons flanked by two electron withdrawing groups.

The arylsulfonylmethylnitrates are crystalline compounds that can be stored at − 20° for extended periods. These nitrates show no explosive properties upon mechanical impact in contrast to the sulfonylmethylperchlorates.

SOLVOLYSIS: RESULTS AND DISCUSSION

Reaction products. Hydrolysis of Ib in 50% (v/v) dioxan-H_2O containing 0·4 N NaOH followed by acidification afforded di-(N-*p*-tolylsulfonyl)hydroxylamine (92%). This product arises from the reaction of *p*-toluenesulfinic acid with HNO_2 in an acidic medium as was shown in a separate experiment.[5] When the hydrolysis of Ib was performed in the presence of one equivalent of sodium *p*-toluenesulfinate the yield of di-(N-*p*-tolylsulfonyl)hydroxylamine rose to 192% corresponding to 96% HNO_2.

NMR spectra of the reaction mixtures obtained after complete hydrolysis of Ib in 50% (v/v) dioxan-D_2O containing 2N NaOD revealed the quantitative formation of formate anion ($\delta_{HOO^\ominus} = 8{\cdot}15$ ppm).

The UV spectra of the reaction mixtures recorded after hydrolysis of Ia–Ie in buffers of pH 5–8 were identical within 4% with those of an equimolar mixture of $NaNO_2$ and the appropriate sodium sulfinate in the same media. This indicates the quantitative formation of sulfinate and nitrite.

Kinetic measurements. The rates of hydrolysis of Ia–Ie could be measured conveniently by following the change in absorbance at a suitable wavelength in the UV spectra (Table 2). Pseudo first order kinetics were found for at least three half lives. Easily measurable rates of hydrolysis were found at pH's around 7 at 25°.

TABLE 2. SECOND ORDER RATE CONSTANTS[a] FOR THE HYDROLYSIS OF IA–IE IN AQUEOUS PHOSPHATE BUFFERS ($\mu = 0{\cdot}10$ N)

Compound	λ^b (nm)	Buffer ratio[c]	Temp.	pH	$k_{HPO_4^{\ominus -}} \cdot 10^3$ (1 $mole^{-1}$ sec^{-1})	$k_{OH^\ominus} \cdot 10^{-2}$ (1 $mole^{-1}$ sec^{-1})
Ia	255	4·000	25·0	7·48	14·5	47
Ib	235	0·324	25·0	6·36	20	61
Ib		1·500	25·0	7·06	21	62
Ib		4·000	25·0	7·47	21	62
Ib		0·324	39·9	6·30	102	390
Ic	255	0·324	25·0	6·34	94	160
Id	275	0·324	25·0	6·34	268	356
Ie	245	0·324	25·0	6·36	370	404
Ie		0·324	39·9	6·28	1850	2540

[a] Obtained from the plots of k_ψ *vs.* $c_{Na_2HPO_4}$

[b] Wavelength used for rate measurements.

[c] $c_{Na_2HPO_4}/c_{KH_2PO_4}$.

Base catalysis. Rate measurements were carried out for Ia–Ie in aqueous KH_2PO_4 – Na_2HPO_4 buffer solutions with different total concentrations but a constant acid/base ratio and a constant ionic strength μ. Reaction rates varied linearly with the concentration of HPO_4^{2-} and are expressed by equation 1.

$$\text{rate} = k_\psi \cdot c_I = (k_{OH^\ominus} \cdot c_{OH^\ominus} + k_{HPO_4{}^{2}_{\ominus}} + k_{HPO_4^\ominus} \cdot c_{HPO_4^\ominus} + k_{H_2O} \cdot c_{H_2O})c_I \qquad (1)$$

From plots* of k_ψ *vs.* $c_{HPO_4}{}^{2-}$ values for $k_{HPO_4}{}^{2\ominus-}$and $k_{OH^\ominus}$ (the term $k_{H_2O} \cdot c_{H_2O}$ is within the experimental error of k_ψ in the pH region used) were obtained (Table 2).

Brønsted equation. The buffer contribution to the rate of hydrolysis of Ie has been determined in phosphate. acetate and formate buffer solutions giving the catalytic constants for $OH^\ominus$, $HPO_4^{\ominus}$ (Table 2), $H_3COO^\ominus$ and $HCOO^\ominus$ (Table 3). In addition the value of k_{H_2O} could be estimated using $c_{H_2O} = 55{\cdot}5$ mole^{-1}. Although a wide range of basicity constants is spanned, a straight line is obtained by plotting log k_B *vs.* log K_B (Fig. 1). The β value of the Brønsted relation[6] amounts to 0·65.

TABLE 3. SECOND ORDER RATE CONSTANTS[a] FOR THE HYDROLYSIS OF IE IN AQUEOUS ACETATE AND FORMATE BUFFERS (μ = 0·10 N) AT 25°

Buffer ratio[b]	pH	$k_{AcO^\ominus} \cdot 10^5$ (1 mole^{-1} sec^{-1})	$k_{HCOO^\ominus} \cdot 10^5$ (1 mole^{-1} sec^{-1})	$k_{OH^\ominus} \cdot 10^{-2}$ (1 mole^{-1} sec^{-1})	$k_{H_2O} \cdot 10^7$ (1 mole^{-1} sec^{-1})
4·000	5·28	487		404	8
8·000	4·54		105	404	3

[a] Obtained from plots of k_ψ *vs.* c_{NaOAc} resp. c_{HCOON}.

[b] c_{NaOAc}/c_{HOAc} resp. c_{HCOONa}/c_{HCOOH}

Solvent deuterium isotope effect. The catalytic constants of $OD^\ominus$ and $DPO_4^{\ominus}$ have been determined for the hydrolysis of Ib and Ie in buffer solutions in D_2O (Table 4). For the hydrolysis of Ie the catalytic constant of $AcO^\ominus$ in D_2O has also been measured.

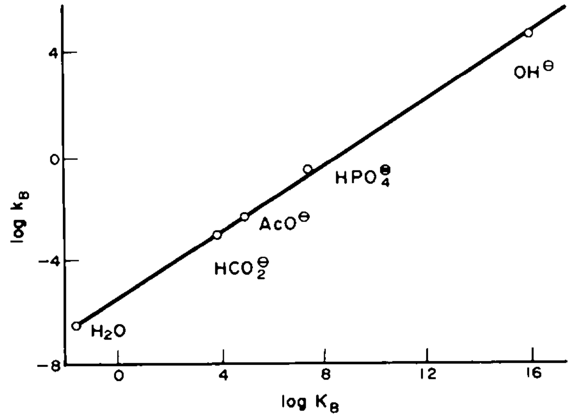

FIG 1. Brønsted plot for the hydrolysis of Ie

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* For each plot at least four k_ψ values at constant pH were determined. Full details will be published in the Ph.D. thesis of A. Bruggink.

TABLE 4. SECOND ORDER RATE CONSTANTS[a] FOR THE HYDROLYSIS OF IB AND IE IN AQUEOUS (D_2O) PHOSPHATE AND ACETATE BUFFERS ($\mu = 0{\cdot}10$ N) AT 25°

Compound	Buffer ratio[b]	pD	$k_{DPO_4^{\ominus 2-}} \cdot 10^4$	$k_{AcO^\ominus} \cdot 10^4$	$k_{OD^\ominus} \cdot 10^{-2}$	$k_{D_2O} \cdot 10^7$	$\frac{k_{HPO_4^\ominus}}{k_{DPO_4^\ominus}}$	$\frac{k_{AcO^\ominus}(H_2O)}{k_{AcO^\ominus}(D_2O)}$	$\frac{k_{OH^\ominus}}{k_{OD^\ominus}}$	$\frac{k_{H_2O}}{k_{D_2O}}$
				(1 mole^{-1} sec^{-1})						
Ib	2·120	7·57	185		14		1·1		4·4	
Ie	0·480	6·94	3450		86		1·1		4·7	
Ie	4·000	5·78		51	86	3		1·0	4·7	1·8

[a] Obtained from plots of k_ψ *vs.* $c_{Na_2PO_4}$ resp. c_{NaOAc}.

[b] $c_{Na_2PO_4}/c_{KD_2PO_4}$ resp. c_{NaOAc}/c_{DOAc}.

The ratio $k_{OH^{\ominus}}/k_{OD^{\ominus}}$ for Ib and Ie amounts to 4·4 and 4·7, respectively, suggesting general base catalysis.[7, 8] No significant isotope effects were found on the buffer contribution of phosphate and acetate anions. This result is expected since no O—D or O—H bonds are affected in the transition state of the reactions brought about by these bases. The ratio k_{H_2O}/k_{D_2O} was estimated to be 1·8.

Table 5. Activation parameters for the hydrolysis of Ib and Ie in aqueous phosphate buffers ($\mu = 0{\cdot}10$ N)

	$\Delta G^{\ddagger}(OH^{\ominus})$ Kcal mole^{-1}	$\Delta G^{\ddagger}(HPO_4^{\boldsymbol{\ominus}})$ Kcal mole^{-1}	$\Delta H^{\ddagger}(OH^{\ominus})$ Kcal mole^{-1}	$\Delta H^{\ddagger}(HPO_4^{\boldsymbol{\ominus}})$ Kcal mole^{-1}	$\Delta S^{\ddagger}(OH^{\ominus})$ e.u.	$\Delta S^{\ddagger}(HPO_4^{\boldsymbol{\ominus}})$ e.u.
Ib	12·1	19·8	22·3	19·4	34	−1·3
Ie	11·1	18·0	22·2	19·4	37	4·6

The possitility of H—D exchange in the $SO_2CH_2ONO_2$ moiety of the substrate was checked by means of NMR. Spectra of the reaction mixtures obtained after hydrolysis of Ib in 50% (v/v) D_2O-dioxan or 50% (v/v) D_2O-acetone-d_6 containing 0·1N NaOD revealed the formation of sulfinate and formate anions. Careful integration of the signals of substrate and products showed the absence of H—D exchange of the methylene protons in the substrate.

Kinetic deuterium isotope effects. A useful tool to test the occurrence of proton (or deuterium) transfer in the transition state of the rate determining step is the kinetic deuterium isotope effect.[9] Therefore we synthesized the CD_2 analogue of Ib from the reaction of p-$CH_3C_6H_4SO_2CDN_2$ (obtained upon H–D exchange of p-$CH_3C_6H_4SO_2CHN_2$ in excess MeOD) with DNO_3 in CH_2Cl_2. Comparison of the rates of hydrolysis of p-$CH_3C_6H_4SO_2CD_2ONO_2$ (If) with those of Ib in phosphate buffer solutions gave $k_H/k_D = 5{\cdot}9$ for $OH^{\ominus}$ as a base and $k_H/k_D = 2{\cdot}6$ for $HPO_4^{\boldsymbol{\ominus}}$ as a base (Table 6). These values are indicative for proton transfer in the transition state of the rate determining step. From the CH and CD frequencies in the IR spectra of Ib and If (see experimental) the maximal value of k_H/k_D was calculated to be 6·4.[9]

Table 6. Second order rate constants[a] for the hydrolysis of p-$CH_3C_6H_4SO_2CD_2ONO_2$ in aqueous phosphate buffers ($\mu = 0{\cdot}10$ N) at 25°

Buffer ratio[b]	pH	$k_{HPO_4^{\boldsymbol{\ominus}}} \cdot 10^4$ (1 mole^{-1} sec^{-1})	$k_{OH^{\ominus}} \cdot 10^{-2}$ (1 mole^{-1} sec^{-1})	$\frac{k_H}{k_D}(HPO_4^{\boldsymbol{\ominus}})$	$\frac{k_H}{k_D}(OH^{\ominus})$
4000	7·46	79	10·3	2·6	5·9

[a] Obtained from the plot of k_{ψ} vs. $c_{Na_2HPO_4}$.

[b] $c_{Na_2HPO_4}/c_{KH_2PO_4}$

Activation parameters. The rates of hydrolysis of Ib and Ie in aqueous phosphate buffer solutions were determined at two different temperatures. The activation parameters are compiled in Table 5.

Substituent effects. The catalytic constants of $OH^{\ominus}$ and $HPO_4^{\ominus}$ for the hydrolysis of Ia–Ie in aqueous phosphate buffer solutions (Table 2) are correlated by Hammett's σ constants[10, 11] (Fig 2). The ρ values, $\rho_{OH^{\ominus}} = 0{\cdot}87$ and $\rho_{HPO_4^{\ominus}} = 1{\cdot}33$, are in accordance with a partial proton transfer in the transition state of the rate determining step.

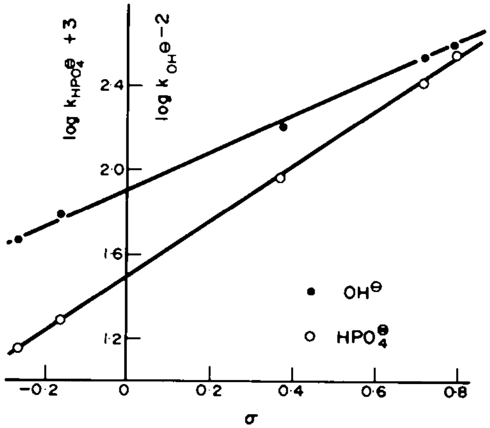

FIG 2. Relation between Hammett σ and log $k_{HPO_4^{\ominus}}$ — and log $k_{OH^{\ominus}}$ for the hydrolysis of Ia–Ie

In order to gain some insight into the ground state acidities of the methylene protons of Ia–Ie the substituent effects on the chemical shift of these protons were measured in $CDCl_3$* and CD_3COCD_3. A straight line is obtained when δ_{CH_2} (Table 7) is plotted *vs.* Hammett's σ constants giving $\rho(CDCl_3) = 0{\cdot}10$ and $\rho(CD_3COCD_3) = 0{\cdot}28$ (Fig 3). For the arylsulfonylmethylperchlorates these values were found to be 0·10 ($CDCl_3$) and 0·34 (CD_3COCD_3).† The relatively small solvent induced shift of the methylene protons of the *p*-nitro derivatives in CD_3COCD_3 may be the result of a specific interaction of the strongly electron deficient aromatic ring with this solvent.

TABLE 7. SOLVENT EFFECT ON THE CHEMICAL SHIFTS[a] OF THE METHYLENE PROTONS OF IA–IE

	δ_{CH_2} ($CDCl_3$) (ppm)	δ_{CH_2} (CD_3COCD_3) (ppm)	$\Delta\delta$ (ppm)
Ia	5·391	5·766	0·375
Ib	5·414	5·809	0·395
Ic	5·453	5·946	0·493
Id	5·515	6·055	0·540
Ie	5·493	6·010	0·517

[a] Varian A-60D, audio oscillator side band technique. Estimated accuracy: ±0·004 ppm. Mole fraction: 0·0024.

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* The more inert solvents CCl_4 or *n*-hexane could not be used because of limited solubility of the nitrates.

† Although larger solvent shifts would be expected when DMSO was employed, this solvent could not be used because the perchlorates *explode violently* upon contact with DMSO.

The solvent induced shifts of 0·4–0·5 ppm on going from $CDCl_3$ to CD_3COCD_3 for Ia–Ie as compared to a shift of 0·6–0·8 ppm for the arylsulfonylmethylperchlorates are suggestive for a lower acidity of the CH_2 protons in the nitrates.[3, 12] Also the substituent effects on the solvent induced shifts are somewhat smaller for the nitrates ($\rho = 0{\cdot}17$) than for the perchlorates ($\rho = 0{\cdot}22$).

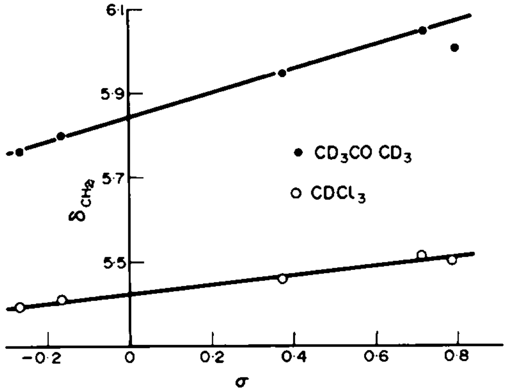
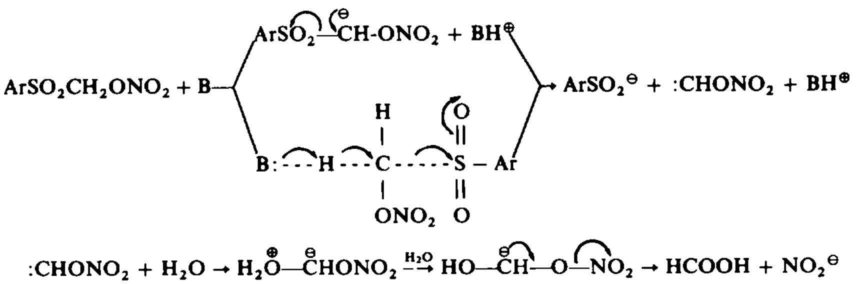


FIG 3. Correlation between Hammett σ and the chemical shift of the methylene protons of Ia–Ie in $CDCl_3$ and CD_3COCD_3

Discussion of the mechanism. On the basis of the products formed. nucleophilic substitution[14–21] either at carbon* or at nitrogen can be definitely excluded during the hydrolysis of the arylsulfonylmethylnitrates. The observed kinetic pattern. the solvent and kinetic deuterium isotope effects and the absence of H–D exchange in the $SO_2CH_2ONO_2$ moiety are indicative of slow proton transfer in the rate determining step. Hence, the hydrolysis of these nitrates is subjected to general base catalysis. The proton transfer either leads to the formation of an α-sulfonylcarbanion or the existence of the carbanion is bypassed by a concerted pathway. Two possibilities for subsequent bond cleavage can be envisaged. An α-elimination of sulfinate anion would give the carbene:$CHONO_2$ which on further hydrolysis should give HCOOH and HNO_2 (Scheme 1). Alternatively elimination of nitrite anion in a carbonyl forming reaction (E_{CO}) gives an α-oxosulfone that is expected to hydrolyse rapidly to formic acid and sulfinic acid (Scheme 2).

SCHEME 1



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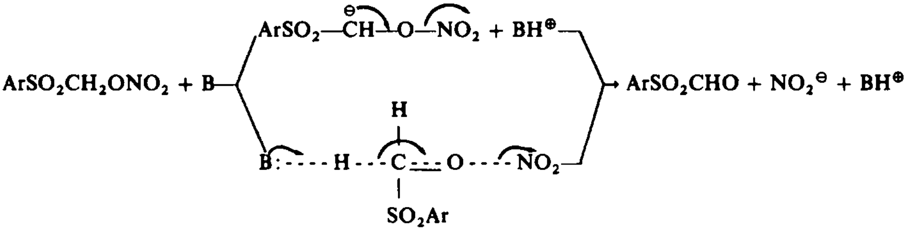
* It is known that nucleophilic displacement reactions at the carbon atom adjacent to a sulfonyl group are strongly hampered[22, 23] even in the presence of very good leaving groups such as perchlorate anion.[2]

SCHEME 2



$$ArSO_2CHO + H_2O \rightarrow ArSO_2CH(OH)_2 \rightarrow ArSO_2H + HCOOH$$

Experimental evidence in favour of one of the two schemes presented above could not be obtained. However, the sequence of reactions depicted in Scheme 2 is preferred, based on the following reasoning. α-Elimination of the sulfinate anion (Scheme 1) would imply in terms of the observed general base catalysis either of the two possibilities: (i) elimination of sulfinate anion from the deprotonated substrate is faster than protonation of this intermediate, (ii) elimination of sulfinate anion is concerted with deprotonation of the substrate. There is abundant evidence that α-elimination of sulfinate anions is generally an energetically unfavourable process.[24–26] The only known example is the base catalyzed decomposition of difluoromethyl phenyl sulfone, $C_6H_5SO_2CHF_2$(II), to give a benzenesulfinate anion and the rather stable carbene:CF_2.[27] In this case an intermediate α-sulfonyl carbanion is formed, protonation of this intermediate being much faster than elimination of benzenesulfinate anion (specific base catalysis). Since the hydrolysis of Ia–Ie shows general base catalysis with rate constants for deprotonation about 10^6 times larger than for deprotonation of II, the very high rate constants for α-elimination of sulfinate anion which must then be assumed in processes (i) and (ii) seems highly unlikely.

Moreover, the proposed hydrolysis of the carbene:$CHONO_2$ as included in Scheme 1 is doubtful. The redox reaction starting from $HO\text{—}\overset{\ominus}{C}HONO_2$ may well be offset by protonation of this carbanion to give $HOCH_2ONO_2$. Nitrate esters of this type prefer to undergo a nucleophilic displacement reaction of the nitrate group[14–18] which in the present case cannot be reconciled with the observed products.

Carbonyl forming elimination reactions of organic nitrates as proposed in Scheme 2 find ample precedent in the literature.[14–21, 28, 29] Buncel and Bourns[28] have shown that the formation of benzaldehyde and nitrite anion from benzylnitrate occurs in a general base catalyzed reaction with a concerted reaction pathway. The reaction has found synthetic application for the preparation of glyoxals, glyoxalate esters and α-diketones from α-carbonyl nitrate esters and NaOAc.[29]

In the reaction path for the hydrolysis of the sulfonyl substituted methylnitrates an α-oxosulfone, $ArSO_2CHO$, will be involved as an intermediate (Scheme 2). These types of compounds have not been isolated so far, but by analogy with α-oxosulfoxides[30] it might be assumed that α-oxosulfones will be very sensitive to nucleophilic reagents. Accordingly the reaction of the α-oxosulfone with H_2O to give sulfinic acid and HCOOH can be regarded as an addition-elimination reaction (Scheme 2).

It is of interest to compare the relative extents of proton transfer in the transition state of the general base catalyzed hydrolysis of the sulfonylmethylnitrates and—perchlorates. The difference in the Brønsted β-values for the hydrolysis of the nitrates ($\beta = 0{\cdot}65$) and the perchlorates ($\beta = 0{\cdot}51$) may be interpreted in terms of a more complete proton transfer in the transition state of the nitrate hydrolysis.[31, 32] This is supported by the observed substituent effects on the rates of hydrolysis of the nitrates and the perchlorates showing that a larger amount of negative charge has developed on the α-sulfonyl carbon atom in the transition state of the hydrolysis of the nitrates. Moreover the magnitudes of the solvent and kinetic deuterium isotope effects are probably also a measure for the extent of proton transfer.[33] However, it is not very fruitful to compare the isotope effects on the rates of hydrolysis for the perchlorates* and the nitrates since they have been measured for different bases. The variation of the kinetic isotope effects with the strength of the base may be the result of changes in transition state symmetry.[33, 34] The more symmetrical the transition state the larger the isotope effect will be. On the other hand the variation of the isotope effects with base strengths has been discussed by Bell in terms of transition states in which the proton transfer is concerted with the making or breaking of other bonds in the substrate.[33] A concerted reaction pathway (Scheme 2, bottom line) for the hydrolysis of the sulfonylmethylnitrates (and also for the perchlorates) is eminently reasonable since a two step mechanism involving an α-sulfonyl carbanion is unlikely in view of the generally high rates of protonation of these types of carbanions.[24, 25]

The differences in the mechanisms of hydrolysis of sulfonylmethyl substituted esters of the three oxygen acids studied so far (i.e. perchlorates, sulfonates and nitrates) deserve some comment. Perchlorates and nitrates react by very similar mechanisms involving a rate determining proton transfer that is probably concerted with a subsequent redox reaction. Contrastingly, the sulfonates show a reversible deprotonation step followed by a slow α-elimination without reduction of the ester function. These differences in the propensities for reduction of the oxygen acid part of the molecule are in accord with the known contrast in oxidizing properties of perchloric and nitric acid compared with sulfonic acids.

EXPERIMENTAL

Pro analyse grade HNO_3 (65% soln in H_2O) was used for the preparation of Ia–Ie. The DNO_3, used for the preparation of If was a 50% soln in D_2O with an isotopic purity over 99% D (Ciba, Switzerland). See also refs. 2 and 3.

Synthesis of the arylsulfonylmethylnitrates Ia–Ie

General procedure. The α-diazosulfone (3–5 mmole) dissolved in 25 ml CH_2Cl_2 was placed in a 50 ml 3-necked flask fitted with a gasburette. With cooling in an icebath 1·5–2·0 equivs. of HNO_3 (65% soln in H_2O) were added to the magnetically stirred soln. A brisk evolution of N_2 occurred and the yellow colour of the soln vanished. After 5–10 min an equimolar volume of N_2 had been evolved. H_2O (20–30 ml) was added and the mixture carefully neutralized with $NaHCO_3$ to pH 6–7. The water was extracted 3 times with 20 ml CH_2Cl_2. The combined organic layers were washed with 10 ml H_2O and dried over $MgSO_4$. The solvent was removed *in vacuo* at 5–15°. The crude product (usually a clear viscous oil, which solidified upon cooling at − 30°) was purified by crystallization from $CHCl_3$/pentane or CCl_4/pentane at 20° or lower.

p-Tolylsulfonyldideuteromethylnitrate, $p\text{-}CH_3C_6H_4SO_2CD_2ONO_2$ (If). *p*-Tolylsulfonyldiazomethane (1·0 g, 5·1 mmole) was dissolved in 10 ml CH_3OD. H–D exchange appeared to be complete after 45 min. The solvent was removed *in vacuo* at 0°. The resulting yellow oil was washed with *n*-hexane and dissolved

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* The kinetic isotope effects for *p*-tolylsulfonyldideuteromethylperchlorate are $k_H/k_D = 5{\cdot}5$ for H_2O as a base and $k_H/k_D = 7{\cdot}2$ for acetate as a base.

in 20 ml CH_2Cl_2. With cooling in ice 1 ml 50% DNO_3 in D_2O was added. After 10 min 10 ml D_2O was added and the mixture neutralized with anhyd. Na_2CO_3 to pH 6–7. The aqueous layer was extracted 3 times with 10 ml CH_2Cl_2. The organic layers were washed with 10 ml D_2O and dried over $CaCl_2$. The solvent was removed *in vacuo* at 0°. The resulting oil was dissolved in CCl_4/hexane and upon cooling at $-20°$ 0·77 g (3·3 mmole, 65%) white crystalline product was obtained, m.p. 49–51°. From CCl_4/*n*-hexane m.p. 50–52°. NMR ($CDCl_3$) showed no CH_2 signal at $\delta = 5{\cdot}5$ ppm indicating the incorporation of more than 95% D at the methylene group. The IR (in CCl_4) showed characteristic CD absorptions at 2259 and 2172 cm^{-1}. The CH frequencies of Ib (in CCl_4) at 3001 and 2941 cm^{-1} are absent.

Reaction products. To a mixture of 25 ml 0·4 N NaOH and 25 ml dioxan 0·50 g (2·16 mmole) Ib was added under N_2. The slightly yellow solution was stirred for 4 hr at 0°. With cooling in ice the reaction mixture was acidified with 10 ml 4N H_2SO_4. The white precipitate formed, was filtered and dried *in vacuo*. From ether/pentane 0·22 g (0·65 mmole, 60%) di-(N-*p*-tolylsulfonyl)hydroxylamine, m.p. 124–126° (litt.[5] 125°). After extraction of H_2O layer with three portions of 15 ml CH_2Cl_2 an additional 0·12 g (0·35 mmole, 32%) di-(N-*p*-tolylsulfonyl)hydroxylamine was isolated, m.p. 124–126° (total yield 92%).

Kinetic measurements. The kinetic technique and the apparatus employed have been described previously.[2]

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