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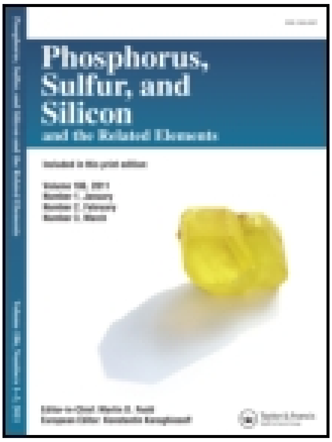

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ADDITION OF SULFINIC ACIDS TO METHACRYLIC DERIVATIVES

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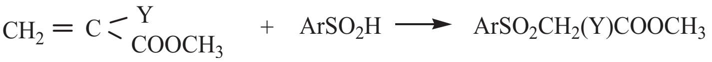
GRAPHICAL ABSTRACT



$$\underset{1}{CH_2=C\begin{matrix}\diagup Y\\ \diagdown COOCH_3\end{matrix}} + \underset{2}{ArSO_2H} \longrightarrow \underset{3}{ArSO_2CH_2(Y)COOCH_3}$$

Abstract *The kinetics of the addition of arenesulfinic acids to methacrylic derivatives were studied. The reactions were found to be second order over a range of concentrations from 0.01 to 0.10 M. For pH values ranging from 4 to 8, the following rate constants were obtained pH the methylacrylate, chloromethylacrylate, and bromomethylacrylate with benzenesulfinic acids (278 K) were investigated:* $2.37\ (\pm 0.2).10^{-4}\ M^{-1}s^{-1}$, $2.60\ (\pm 0.1).10^{-4}\ M^{-1}s^{-1}$, $3.15\ (\pm 0.3).10^{-4}\ M^{-1}s^{-1}$.

Keywords Methacrylic derivatives; nucleophilic addition; sulfinic acids

INTRODUCTION

The salts of sulfinic acids and sulfinic acids themselves, when reacting with α,β-unsaturated compounds, behave like typical nucleophilic compounds.[1,2] No matter what the pH of the medium is, sulfinic acids and α,β-unsaturated compounds react in equimolar quantities, with the corresponding sulfones being obtained. When there is a halogen at the double bond, the reaction depends on the pH of the medium: additive compounds are obtained in acidic medium, and unsaturated sulfones are obtained in alkaline medium. The interaction of the sodium salts of sulfinic acids with acrylonitrile, α-chloroacrylonitrile, methyl-, ethyl-, and butyl-esters of acrylic acids was studied.[3,4] Achmatowicz and Michalski studied the addition of sulfinic acids to acrylic compounds such as acrylonitrile, methylacrylate, ethylacrylate, amide of acrylonitrile, and vinilpyridine.[5,6]

The aim of the present study is to obtain some new sulfones by a nucleophilic addition of benzene-, toluene-, and 4-chlorobenzenesulfinic acids to methylacrylate, α-chloro-, and α-bromomethylacrylate, as well as to determine the kinetic parameters of these reactions.

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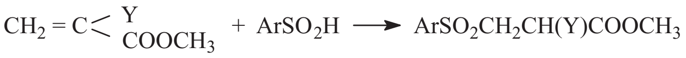
RESULTS AND DISCUSSION

Synthesis and Structure

A series of aryl–β-carbomethoxyethyl sulfones and aryl–β-halogenocarbomethoxyethyl sulfones were obtained by the reaction shown in Scheme 1.



$$CH_2=C\begin{matrix}Y\\COOCH_3\end{matrix} + ArSO_2H \longrightarrow ArSO_2CH_2CH(Y)COOCH_3$$

1a - c 2a - c 3a - i

Y = H (1a); Y = Cl (1b); Y= Br (1c); Ar = Ph (2a); Ar = 4-MeC$_6$H$_4$ (2b);
Ar = 4-ClC$_6$H$_4$ (2c); Y = H, Ar = Ph (3a); Ar = H , Ar = 4-MeC$_6$H$_4$ (3b);
Y = H, Ar = 4-ClC$_6$H$_4$ (3c); Y =Cl, Ar = Ph (3d); Y =Cl, Ar = 4-MeC$_6$H$_4$ (3e)
Y =Cl, Ar = 4-ClC$_6$H$_4$ (3f); Y =Br, Ar = Ph (3g); Y =Br, Ar = 4-MeC$_6$H$_4$ (3h)
Y =Br, Ar = 4-ClC$_6$H$_4$ (3i)

Scheme 1

These are available concerning some of these compounds, namely **3a**, **3c**, **3e**, and **3f**.[3] The synthesized aryl β-carbomethoxyethyl sulfones and aryl β-halogenocarbomethoxyethyl sulfones are white crystalline substances, stable at long storage. All newly formed compounds were analyzed by analytical and instrumental methods (Tables 1 and 2).

The IR-spectra of aryl β-carbomethoxyethyl sulfones and aryl β-halogenocarbomethoxyethyl sulfones contain intense bands of asymmetric and symmetric valence vibration due to the sulfonyl groups at 1315–1305 cm^{-1} and 1145–1130 cm^{-1}. There are absorption maxima characteristic of the valence vibrations of C—O at 1300–1100 cm^{-1}. The valence vibrations at 1740–1725 cm^{-1} prove the presence of C=O groups. The characteristic bands at 3100–3000 cm^{-1} correspond to valence C—H aryl vibrations. Skeleton vibrations of the arene nucleus can be seen at 1640–1600 cm^{-1} and 1480–1450 cm^{-1}. The absorption bands due to the monosubstituted benzene nucleus are at 700 cm^{-1}, and those for the *p*-disubstituted benzene nucleus are at 810–800 cm^{-1}. The presence of a methylene group is proven by the absorption maximum for the valence asymmetric and symmetric vibrations at 2900–2840 cm^{-1}, and the deformation vibrations at 1470–1450 cm^{-1}.

The ^{1}H NMR spectra of the synthesized compounds contain shifts corresponding to aromatic multiplets at 7.27–7.82 ppm. The doublets that prove the presence of methine protons are centered at 2.72–2.85 ppm, and the chemical shift corresponding to methylene protons (a triplet) is at 3.38–3.47 ppm. Shifts due to the methyl protons of the methoxygroup can be seen at 3.65 ppm.

Kinetic Study

The main kinetic parameters of the nucleophilic addition of sulfinic acids to methylacrylate and its halogenoderivatives were determined by UV spectroscopy. The absorption maxima of sulfinic acids and the final aryl halogenocarbomethoxyethyl sulfones overlap, so the change in their concentration is difficult to estimate. That is why a method suggested by Ogata et al.[7] modified by the present authors was used to determine the kinetic parameters of the reaction. In the course of the interaction, the change in the concentration of sulfinic

Table 1 Characterization data of the newly synthesized compounds

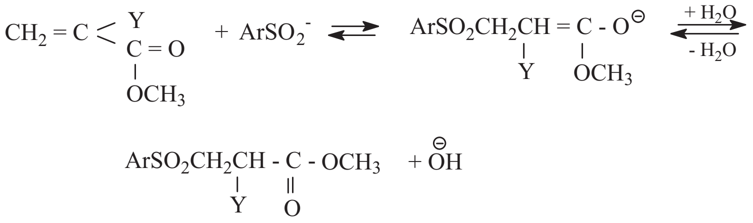
Compound No.	Mp °C (solvent)	Yield (%) color	Mol. formula (m.w.)	% Analyses calcd./found		
				C	H	S
3b	70–71 (EtOH)	67 White	$C_{11}H_{14}O_4S$ (242.76)	54.42 (54.38)	5.77 (5.72)	13.21 (13.18)
3g	82–83 (Toluene)	63 White	$C_{10}H_{11}BrO_4S$ (307.11)	39.10 (39.08)	5.58 (5.55)	10.44 (10.40)
3h	80–81 (EtOH)	71 White	$C_{10}H_{13}BrO_4S$ (321.18)	41.14 (41.10)	4.05 (4.00)	9.98 (9.92)
3e	82–83 (EtOH/toluene)	62 White	$C_{10}H_{10}BrO_4S$ (306.17)	39.23 (39.19)	3.27 (3.22)	10.47 (10.44)

Table 2 Spectra of the newly synthesized compounds

Compound no.	Spectral data
3b	IR (υ, cm^{-1}, KBr): 1310, 1145 (SO_2); 1110, 1725 ($-COOCH_3$) ^{1}H NMR (δ, ppm, $CDCl_3$): 2.72 (t, 2H, CH_2), 3.38 (t, 2H, CH_2), 3.65 (s, 3H, OCH_3), 2.46 (S, 3H, CH_3), 7.72–7.82 (m, 4H, C_6H_4), $J_{(CH-CH)}$7.2 Hz.
3g	IR (υ, cm^{-1}, KBr): 1300, 1135 (SO_2); 1115, 1730 ($-COOCH_3$) ^{1}H NMR (δ, ppm, $CDCl_3$): 2.75 (d, 2H, CH_2), 3.38 (t, 1H, CH), 3.62 (s, 3H, OCH_3), 2.46 (S, 3H, OCH_3), 7.30–7.77(m, 5H, C_6H_5), $J_{(CH-CH)}$7.4 Hz.
3h	IR (υ, cm^{-1}, KBr): 1300, 1140 (SO_2); 1125, 1730 ($-COOCH_3$) ^{1}H NMR (δ, ppm, $CDCl_3$): 2.78 (d, 2H, CH_2), 3.47 (t, 1H, CH), 3.65(s, 3H, OCH_3), 2.45 (S, 3H, CH_3), 7.26–7.820 (m, 4H, C_6H_4), $J_{(CH-CH)}$7.3 Hz.
3e	IR: (υ, cm^{-1}, KBr): 1310, 1140 (SO_2); 1130, 1740 ($-COOCH_3$) ^{1}H NMR (δ, ppm, $CDCl_3$): 2.81 (d, 2H, CH_2), 3.45 (t, 1H, CH), 3.60 (s, 3H, OCH_3), 7.28–7.84 (m, 4H, C_6H_4), $J_{(CH-CH)}$7.4 Hz.

acid was studied, making use of the fact that the acid turns into dihydroxybenzosulfone when a standard solution of benzoquinone is added to it.

The concentration of dihydroxybenzosulfones (and therefore the concentration of sulfinic acid) was determined at 324 nm. The data concerning the reaction order of the addition of benzenesulfinic acid to methylacrylate, chloro-, and bromomethylacrylate are presented in Table 4. Using straight lines for the reactions under study it is possible to calculate the bimolecular rate constants. Having in mind that the nucleophilic addition of sulfinic acids corresponds to a second order kinetic reaction, the most probable reaction scheme can be suggested, as shown in Scheme 2.



$$CH_2=C\begin{matrix}Y\\C=O\\|\\OCH_3\end{matrix} + ArSO_2^- \rightleftarrows \underset{\quad\;\; Y \qquad\;\; OCH_3}{ArSO_2CH_2CH=C-O^{\ominus}} \underset{-H_2O}{\overset{+H_2O}{\rightleftarrows}}$$

$$\underset{\qquad\quad Y \quad\;\; O}{ArSO_2CH_2CH-\overset{}{C}-OCH_3} + \overset{\ominus}{O}H$$

Scheme 2

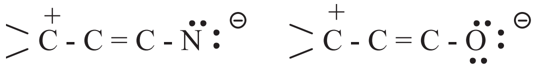
Table 3 Experimental values of the benzenesulfinic acid addition order to methacrylate, chloro-, and bromomethacrylate by methods of Van’t Hoff and half-time at 298 K

Concentration range C, M	0.01–0.025	0.025–0.05	0.05–0.075	0.075–0.1
Order value by Van’t Hoff method 1a and 2a	1.63	1.60	1.66	1.68
Order value by half- time method 1a and 2a	1.65	1.64	1.67	1.65
Order value by Van’t Hoff method 1b and 2a	1.70	1.68	1.73	1.70
Order value by half- time method 1b and 2a	1.72	1.70	1.72	1.72
Order value by Van’t Hoff method 1c and 2a	1.68	1.66	1.60	1.64
Order value by half- time method 1c and 2a	1.69	1.71	1.66	1.66

Table 4 Rate coefficient and activation parameters for the reaction of methacrylic derivatives with sulfinic acids

Methacrylic derivatives	Sulfinic acids	T, K	k .10^4 M^{-1}, s^{-1}	Ea (kJ/mol)	Δ $H^{\neq}$ (kJ/mol)
1a	**2a**	278	2.37 ± 0.2	65.02	63.25
		288	2.45 ± 0.2		
		298	2.59 ± 0.2		
1a	**2b**	278	2.51 ± 0.1	60.75	58.50
		288	2.70 ± 0.09		
		298	2.89 ± 0.1		
1a	**2c**	278	1.80 ± 0.25	73.83	71.25
		288	1.95 ± 0.1		
		298	2.12 ± 0.2		
1b	**2d**	278	2.60 ± 0.1	62.30	60.55
		288	2.75 ± 0.2		
		298	2.90 ± 0.2		
1b	**2b**	278	2.93 ± 0.3	58.25	55.70
		288	3.15 ± 0.25		
		298	3.30 ± 0.35		
1b	**2c**	278	2.12 ± 0.2	66.80	64.75
		288	2.56 ± 0.2		
		298	2.85 ± 0.3		
1c	**2a**	278	3.15 ± 0.3	60.80	58.35
		288	3.30 ± 0.25		
		298	3.52 ± 0.3		
1c	**2b**	278	3.27 ± 0.25	55.70	52.65
		288	3.47 ± 0.3		
		298	3.60 ± 0.3		
1c	**2c**	278	2.80 ± 0.25	62.45	60.15
		288	3.10 ± 0.3		
		298	3.20 ± 0.3		

Our studies on the reactivity of α,β-unsaturated compounds regarding sulfinic acids show that the activity of the double carbon–carbon bond changes depending on the activity of the electron-acceptor substituent at the α-position. The interaction between nitroethene and sulfinic acids takes place at a high rate and very low temperatures,[8] while acrylonitrile is less active regarding nucleophilic reagents. According to their reactivity, the unsaturated substrates can be divided into three groups: nitroethene is the most active of all, and acrylonitrile is the least reactive. The nitrile group has a stronger induction effect and gives off fewer electrons than the electronegative carbomethoxy group. However, the resonance effect prevails in these α,β-unsaturated systems, which is confirmed by the polarized forms:



$$>\overset{+}{C}-C=C-\ddot{N}\colon^{\ominus} \qquad >\overset{+}{C}-C=C-\underset{\cdot\cdot}{\ddot{O}}\colon^{\ominus}$$

Hence it might be expected that the resonance polarization would be more powerful for the acrylate due to the greater electronegative character of the oxygen as compared to the nitrogen atom.

CONCLUSION

1. The reaction of nitroolefins with sulfinic acids takes place at a higher rate than the one with methacrylic derevatives.

2. The interaction of a halogen atom at the α-position regarding the cyano group results in an increase in the activity of the ethylene system in the nucleophilic addition reaction.
3. The nucleophilic activity of sulfinic acids increases with the introduction of electron-donor substituents and degreases in the presence of an electron-withdrawing group.

EXPERIMENTAL

Methods

Melting points were determined on a Melt-Temp apparatus and are uncorrected. Microanalyses were obtained using an Elemental Analyser (Carlo-Erba), and IR and UV spectra were obtained using a Bruker and Specord UV-Vis. ^{1}H NMR (chemical shifts measured in solvents are given in ppm from TMS) spectra were recorded on a Bruker 250 MHz spectrometer, using $CDCl_3$ solution.

General Procedure for Compounds 1–6

Sulfinic acids, methylacrylate, chloro-, and bromomethylacrylate were obtained and purified by known methods.[3,9]

Sulfinic acids (0.01 mol) were dissolved in water (10 mL). Acetic acid (0.1 mol) and halogenoacrylate (0.15 mol), which were initially dissolved in ethanol (10 mL), were added to that solution, and the new mixture was stabilized by a catalytic quantity of hydroquinone. The flask containing the reaction mixture was sealed and allowed to stand for 24 h, and then recrystallized.

Rate Measurement

Purified sulfinic acid (0.01 mol) was added to an acetate buffer containing methacrylic derivatives (0.01 mol). Aliquots were taken out at regular intervals of time and diluted with ethanol. Then excess aqueous *p*-benzoquinone was added to the solvent to convert the remaining sulfinic acids to dihydroxyphenylsulfone, which were determined by means of UV spectroscopy. Since a large excess of methacrylic derivatives was used, the rate is pseudo–first order with respect to arylsulfinic acids, the rate is estimated as dihydroxyphenylsulfone. The second order rate constants were calculated by (pseudo–first order rate constants)/methacrylic derivatives.

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