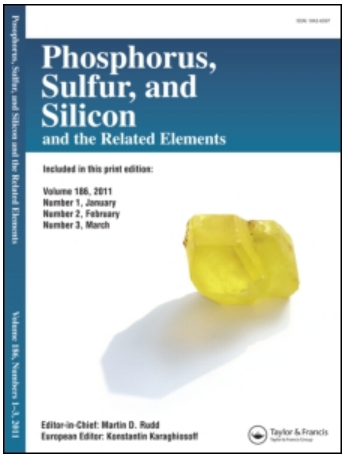

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Kinetic Studies on the Reaction of Sulfinic Acids with Conjugated Alkenes, V: Kinetics of the Addition of Arenesulfinic Acids to 1-Aryl-1-arylsulfonyl-2-nitroethenes

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The addition of unsubstituted and substituted benzenesulfinic acids to 1-aryl-1-arylsulfonyl-2-nitroethenes has been studied kinetically by means of LC. The rection follows the second-order kinetics $v = k$ [1-aryl-1-arylsulfonyl-2-nitroethene].[sulfinic acid]. The dependence of rate constants on the temperature and the influence of p-substituents on the kinetic parameters have been investigated. The activation energy and the enthalpy of the activation are calculated in the temperature range 288–308 K.

Keywords 1-Aryl-arylsulfonyl-2-nitroethenes; nucleophilic addition; sulfinic acid

INTRODUCTION

The 1-aryl-1,2-diarylsulfonyl-2-nitroethanes were obtained by the nucleophilic addition of arenesulfinic acids to 1-aryl-1-arylsulfonyl-2-nitroethenes.[1–3] These products possess pesticide, fungicide, and acaricide activity, and they are used as initial products for obtaining biologically active substances.[4–6] There are no systematic data available concerning the reactivity of 1-aryl-1-arylsulfonyl-2-nitroethenes when reacting with nucleophilic reagents.

The aim of the present work was to determine quantitative parameters of the nucleophilic addition of arenesulfinic acids to heteroconjugated alkenes, as well as to draw conclusions about the activity of the carbon–carbon double bond in the presence of different substituents.

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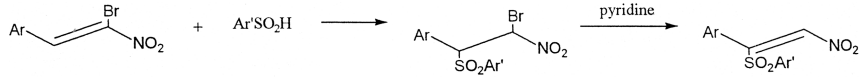
RESULTS AND DISCUSSION

1-aryl-1-arylsulfonyl-2-nitroethenes were synthesized for the first time by Scheme 1:



SCHEME 1 Ar = Ph, 4-MeC_6H_4, 4-$NO_2C_6H_4$; Ar = Ph, 4-MeC_6H_4, 4-ClC_6H_4.

Products resulting from the addition of arenesulfinic acids to 2-bromo-2-nitroethenylarenes were dehydrobromated in dioxane in the presence of pyridine at a low temperature for 8 h. The composition and structure of the compounds obtained were confirmed by elemental analysis and IR, UV, and ^1H NMR spectroscopic data (Table I).

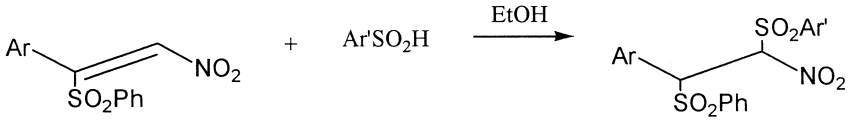
The IR spectra of 1-aryl-1-arylsulfonyl-2-nitroethenes contain intensive absorption bands of asymmetric and symmetric valence vibrations of the nitro group at 1550–1530 cm^{-1} and 1380–1320 cm^{-1}, and the sulfophenyl group at 1350–1300 cm^{-1}. The absorption maximum at 890–810 cm^{-1} confirms the presence of a triple-substituted double bond. Absorption bonds corresponding to C-H aryl valence vibrations can be seen at 3080–3000 cm^{-1} (a triplet). Skeleton vibrations of the aromatic nucleus give rise to absorption maxima at 1630–1600, 1500–1490, and 1450–1400 cm^{-1}. In some cases, the band at 1600 cm^{-1} is a doublet with a second maximum at 1580 cm^{-1} resulting from the conjugation of the benzene nucleus. The ^1H NMR spectra of 1-aryl-1-arylsulfonyl-

TABLE I Analytical Data of Compound 3

Compound no.	Yield %	M.p. °C	Formula mol. wt.	Analysis (%) found (calcd.) C	H	N	S
3a	89	189	$C_{22}H_{19}NO_6S_2$ 445.36	56.64 (56.90)	4.27 (4.07)	3.15 (3.60)	14.40 (13.95)
3b	73	177	$C_{22}H_{21}NO_6S_2$ 459.37	57.52 (56.90)	4.57 (4.76)	3.05 (2.80)	13.96 (13.35)
3c	84	174	$C_{21}H_{18}ClNO_6S_2$ 479.81	52.57 (51.80)	3.75 (3.27)	2.92 (2.55)	13.37 (12.97)
3d	89	180	$C_{20}H_{16}N_2O_8S_2$ 476.36	50.43 (49.60)	3.36 (2.75)	5.88 (5.97)	13.46 (13.83)
3e	77	183	$C_{21}H_{18}N_2O_8S_2$ 490.37	51.44 (50.80)	3.67 (3.45)	5.71 (5.50)	13.08 (13.21)
3f	85	179	$C_{20}H_{15}ClN_2O_8S_2$ 510.81	47.03 (46.85)	2.94 (2.57)	5.48 (5.50)	12.55 (12.37)

2-nitroethenes contain shifts of aromatic multiplets in a comparatively wide range of 7.16–8.04 ppm. Shifts for aromatic protons tend to shift toward a weaker field, and so does the shift for the vinyl proton since the carbon atoms are bound to acceptor substituents. The shift for the vinyl proton in the spectra of these compounds is at 8.21–8.25 ppm. The UV spectra of the synthesized compounds show that the polarization of the double bond is inessential because of the centrofugal effect of the sulfophenyl and nitro groups.

1-aryl-1,2-diarylsulfonyl-2-nitroethanes were synthesized by Scheme 2.



1 **2** **3**

SCHEME 2 Ar = 4-MeC_6H_4 (**1a**); Ar = 4-$NO_2C_6H_4$ (**1b**); Ar = Ph (**2a**); Ar = 4-MeC_6H_4 (**2b**); Ar′ = 4-ClC_6H_4 (**2c**); Ar = 4-MeC_6H_4, Ar′ = Ph (**3a**); Ar = Ar′ = 4-MeC_6H_4 (**3b**); Ar = 4-MeC_6H_4, Ar′ = 4-ClC_6H_4 (**3c**); Ar = 4-$NO_2C_6H_4$, Ar = Ph (**3d**); Ar = 4-$NO_2C_6H_4$; Ar′ = 4-MeC_6H_4 (**3e**); Ar = 4-$NO_2C_6H_4$, Ar′ = 4-ClC_6H_4 (**3f**).

The chromatographic separation of 1-aryl-1-diarylsulfonyl-2-nitroethanes shows that the amount of one of the isomeric forms was prevalent. If the type of the substituents and their position to each other are taken into consideration, it could be supposed that the percentage of isomers will be greater (Table II). Such as interpretation of data obtained is based on Newman projections of 1-aryl-1,2-diarylsulfonyl-2-nitroethanes. These formulas show that the voluminous and electronacceptor substituents (—SO_2Ar') in the

TABLE II Isomer Composition of 1-Aryl-1-Arylsulfonyl-2-Nitro-1-Phenylsulfonylethanes

	Isomer composition, %	
Product	Threo	Erythro
3a	55	45
3b	52	48
3c	53	47
3d	69	31
3e	66	34
3f	64	36

erythro-form threo-form

FIGURE 1

threo-isomers are as far from each other as possible, and, therefore, this is the most favorable structure from energy points of view. The composition and structure of synthesized substances were determined by instrumental methods (Figure 1).

The IR spectra of 1-aryl-1,2-diarylsulfonyl-2-nitroethanes contain intensive absorption bands corresponding to asymmetric and symmetric valence vibrations of nitro- and sulfogroups at 1560–1510, 1355–1340, 1340–1320, and 1145–1120 cm^{-1}. Absorption bands due to C-H aryl vibrations can be seen at 3070–3020 cm^{-1}. What is characteristic of these bands is that they are in the form of a triplet with decreasing intensity. Skeleton vibrations of the aromatic nucleus result in absorption bands at 1640–1460 cm^{-1}. p-Derivatives are characterized by higher wave frequencies, the shortest wave frequency being shifted to 1640 cm^{-1}. The off-plane C-H aryl deformation vibration at 830–800 cm^{-1} proves the presence of p-substituted benzenes. Characteristic absorption maxima can also be seen at 1360–1335 and 1170–1160 cm^{-1}, showing that there are diarylsulfonyl groups in the compounds under study. The ^1H NMR spectra contain shifts of aromatic multiplets in the interval 7.10–7.88 ppm. There are two doublets at 5.11 and 6.20 ppm, and their integrals show the presence of one proton for each doublet. The difference in the chemical shift of the two methane protons is due to the asymmetry. The resonance shift for the aromatic protons at 8.04 ppm is due to the presence of a nitro group.

Kinetic parameters of the interaction of arenesulfinic acids with 1-aryl-1-arylsulfonyl-2-nitroethenes were determined. Interactions are second order reactions, but they are first order regarding each reagent. The overall reaction order was determiend by using the van't Hoff method and the half-time method in the concentration interval 0.05–10 M. The overall reaction order for the nucleophilic addition of benzenesulfonic acid to 1-phenylsulfonyl-1-(4-tolyl)-2-nitroethene was calculated to be 1.88 (Table III). These calculations can also be proved by the line as dependence 1/[1-aryl-1-arylsulfonyl-2-nitroethene]=f(τ).

TABLE III Experimental Proof of the Benzenesulfinic Acid Addition Order to 1-Aryl-1-Arylsulfonyl-2-Nitroethenes by the Methods of Van't Hoff and Half-Time in the Concentration Range 0.005–10 M, T = 298 K

Concentration Range C, M	0.005–0.01	0.01–0.1	0.1–1	1–10
Order value by van't Hoff method	1.84	1.88	1.91	1.94
Order value by half-time method	1.85	1.88	1.87	1.90

Slopes of the straight lines for these dependencies were used to calculate rate constants for five different temperatures. The activation energy and the enthalpy of activation were determined using the Arrhenius equation.

Second rate constants for the addition of benzenesulfinic acid to 2-nitro-l(4-tolyl)-1-phenylsulfonylethene at 288, 293, 298, 303, and 308 K are $6.15.10^{-5}$, $8.30.10^{-5}$, $10.17.10^{-5}$, $13.50.10^{-5}$, and $15.65.10^{-5}$ $M^{-1}s^{-1}$. The rate constants of the reaction of 2-nitro-1(4-nitrophenyl)-1-phenylsulfonylethene with benzenesulfinic acid at 288, 293, 298, 303, and 308 K are $7.20.10^{-3}$, $11.20.10^{-3}$, $14.80.10^{-3}$, $17.35.10^{-3}$, and $20.70.10^{-3}$ $M^{-1}s^{-1}$. The activation energy and the enthalpy of activation for the reaction of 2-nitro-1(4-toeyl)-1-phenylsulfonylethene are calculated as 64.35 and 61.80 kJ/mol. The result for the reaction of 2-nitro-1(4-nitrophenyl)-1-phenylsulfonylethene were 50.75 and 40.20 kJ/mol.

The influence of various substituents in the benzene nucleus on the nucleophilic activity of sulfinic acids was studied (Table IV). As far as the activity of the double bond in 1-aryl-2-nitro-1-phenylsulfonylethene toward the nucleophilic reagents is concerned, it can be said that the presence of a nitro group in the benzene nucleus favors a faster addition reaction than in the case of 2-nitro-1-phenyl-1-phenylsulfonylethene. The introduction of a methyl group in the para-position leads to a decrease in the rate of nucleophilic addition reactions.

EXPERIMENTAL

Methods

Melting points were determined on a Melt-Temp apparatus and are uncorrected. Mcroanalyses were obtained using an elemental Analyzer −1104 (Carlo Erba). IR and UV spectra were obtained using a Bruker and Specord UV-VIS. ^{1}H NMR (chemical shifts measured in deuterated solvents are given in ppm from TMS) spectra were recorded with a Bruker 350 MHz spectrometer, using $CDCl_3$ solutions.

TABLE IV The Substituent Effect on the Rate Constants and Activation Parameters at Different Temperatures

Nucleophile	Substrate	Temp. K	$k \cdot 10^5$ $M^{-1}s^{-1}$	E, $KJ \cdot mol^{-1}$	$\Delta H\neq$ $KJ \cdot mol^{-1}$
2b	**1**	288	7.35 ± 0.7	59.20	56.60
		293	10.20 ± 0.9		
		298	13.45 ± 0.9		
		303	18.70 ± 1.1		
		308	19.50 ± 1.0		
2c	**1**	288	4.28 ± 0.4	75.50	71.70
		293	5.95 ± 0.6		
		298	8.15 ± 0.5		
		303	10.05 ± 0.4		
		308	12.67 ± 0.4		
2b	**2**	288	10.25 ± 0.9	46.40	44.30
		293	16.50 ± 0.9		
		298	18.40 ± 1.1		
		303	21.05 ± 1.0		
		308	24.70 ± 0.8		
2c	**2**	288	3.15 ± 0.4	53.10	51.90
		293	5.80 ± 0.3		
		298	7.72 ± 0.6		
		303	9.85 ± 0.5		
		308	12.08 ± 0.4		

HPLC was performed using a Series-4-apparatus (Perkin-Elmer) and a programmable multiwaveenght detector. The typical procedure for the prepration of 1-aryl-1-arylsulfonyl-2-nitroethenes **1**: to 1-aryl-1-arylsulfonyl-2-bromo-2-nitroethenes (0.001 mol) in dioxane was added pyridine (0.001 mol). The reaction mixture was kept standing at 8°C V_{o2} to yield the substituted 1-aryl-1-arylsulfonyl-2-mitroethenes. The crystals obtained were filtered and recrystallized from toluene.

Selected Data for 1a

Yield 67%, m.p. 117°C. Found: C, 59.42; H, 4.29: N, 4.62; S, 10.57; Calcd. for $C_{15}H_{13}NO_4S$: C, 59.20; H, 3.80; N, 4.20; S, 10.80. IR (υ, cm^{-1}, KBr): 1530–1330 (υ_{NO2}); 1310–1150 (υ_{SO2}); 1090 ($\upsilon_{s\text{-}Ar}$); 890 (γ=CH); UV (λ_{max}(EtOH), lgε): 211 (2.54); 271 (2.95); ^{1}H NMR (δ, $CDCl_3$): 2.40 (s, 3H′ CH_3); 7.20–7.60 (m, 9H, Ar-H); 8.20 (s, 1H, =CH).

Selected Data for 1b

Yield 71%, m.p. 188°C. Found: C, 50.31; H, 2.99; N, 8.38; S, 9.59; Calcd. for $C_{14}H_{10}N_2O_6S$: C, 49.75; H, 2.67; N, 8.55; IR (υ, cm^{-1}, KBr):

1550–1380 (υ_{NO2}); 1310–1135 (υ_{SO2}); 1085 ($\upsilon_{S\text{-}Ar}$); 850 (γ = CH); UV (λ_{max}, nm (EtOH); lgε): 212 (2.42); 260 (3.10); 280 (2.55); ^{1}H NMR (δ, $CDCl_3$): 7.25–7.65 (m, arom. 9H); 8.24 (s, 1H, =CH).

The Typical Procedure for the Preparation of 1-Aryl-2-arylsulfonyl-2-nitro-1-phenylsulfonylethanes 3a–f

To 1-aryl-2-nitro-1-phenylsulfonylethenes (0.001 mol) in 95% ethanol was added sulfinic acid (0.001 mol). The reaction mixture was kept standing at 20°C for 16 h to yield substituted 1-aryl-2-arylsulfonyl-2-nitro-1-phenylsulfonylethanes. The crystals obtained were filtered and recrystallized from ethanol/dioxane, 10:1.

Selected Data for 3a

IR (υ, cm^{-1}, KBr): 1555–1360 (υ_{NO2}); 1300–1145 (υ_{SO2}); 1080 ($\upsilon_{S\text{-}Ar}$); 810 ($\upsilon_{Ar\text{-}H}$); ^{1}H NMR (δ, $CDCl_3$): 2.40 (s, 3H, CH_3); 5.15 (d, 1H, CH); 6.20 (d, 1H, CH); 7.10–7.65 (m, 13H, Ar-H).

Selected Data for 3b

IR (υ, cm^{-1}, KBr): 1540–1350 (υ_{NO2}); 1350–1150 (υ_{SO2}); 1090 ($\upsilon_{S\text{-}Ar}$); 815 ($\delta_{Ar\text{-}H}$); ^{1}H NMR (δ, $CDCl_3$): 2.42 (s, 3H, CH_3); 5.11 (d, 1H, CH); 6.15 (d, 1H, CH); 7.15–7.70 (m, 13H, Ar-H).

Selected Data for 3c

IR (υ, cm^{-1}, KBr): 1150–1365 (υ_{NO2}); 1310–1140 (υ_{SO2}); 1090 ($\upsilon_{S\text{-}Ar}$); 800 ($\delta_{Ar\text{-}H}$); ^{1}H NMR (δ, $CDCl_3$): 2.44 (s, 3H, CH_3); 6.19 (d, 1H[1], CH); 5.19 (d, 1H, CH); 7.20–7.60 (m.13 H, Ar-H).

Selected Data for 3d

IR (υ, cm^{-1}, KBr): 1555–1360 (υ_{NO2}); 1300–1140 (υ_{SO2}); 1085 ($\upsilon_{S\text{-}Ar}$); 710 ($\delta_{Ar\text{-}H}$); ^{1}H NMR (δ, $CDCl_3$): 5.19 (d, 1H, CH); 6.18 (d, 1H, CH); 7.20–7.90 (m, 13H, Ar-H).

Selected Data for 3e

IR (υ, cm^{-1}, KBr): 1540–1370 (υ_{NO2}); 1310–1150 (υ_{SO2}); 810 ($\upsilon_{Ar\text{-}H}$); ^{1}H NMR (δ, $CDCl_3$): 2.43 (s, 3H, CH_3); 5.12 (d, 1H, CH); 6.21 (d, 1H, CH); 7.15–8.04 (m, 13H, Ar-H).

Selected Data for 3e

IR (υ, cm^{-1}, KBr): 1540–1365 (υ_{NO2}); 1310–1145 (υ_{SO2}); 1090 ($\delta_{Ar\text{-}H}$); ^1H NMR (δ, $CDCl_3$): 5.20 (d, 1H, CH); 6.22 (d, 1H, CH); 7.20–8.00 (m, 13H, Ar-H).

Rate Measurement

Purified sulfinic acid (0.001 mol) was added to 1-aryl-2-nitro-1-phenylsulfonylethene (0.001 mol) in ethanol (50 mL). Aliquots were taken out at requeat intervals of time and diluted with ethanol. Flow concentrations of reagents during the reaction were determined by liquid chromatographic analysis. Second-order constants, the activation energy, and the enthalpy of activation were calculated according to the literature.

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