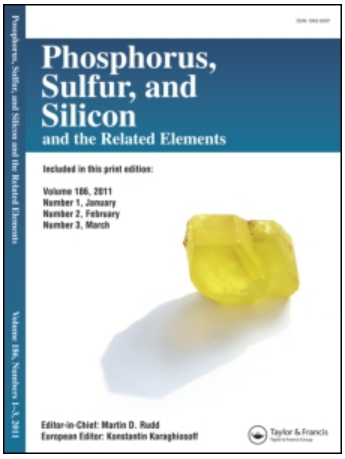

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Kinetic Studies on the Reaction of Sulfinic Acids with Conjugated Alkenes: IV. Kinetics of the Addition of Arenesulfinic Acids to 2-nitro-1-phenyl-1-phenylsulfonylethene

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KINETIC STUDIES ON THE REACTION OF SULFINIC ACIDS WITH CONJUGATED ALKENES: IV. KINETICS OF THE ADDITION OF ARENESULFINIC ACIDS TO 2-NITRO-1-PHENYL-1-PHENYLSULFONYLETHENE

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The addition of unsubstituted and substituted benzenesulfinic acids to 2-nitro-1-phenyl-1-phenylsulfonylethene was studied kinetically by means of LC. The reaction follows the second-order kinetics: $v = k$[2-nitro-1-phenyl-1-phenylsulfonylethene]·[sulfinic acid]. The dependance of the rate constants on the temperature, and the influence of the p-substituents on the kinetic parameters were studied. The activation energy and the enthalpy of activation were calculated in the temperature range 288–308 K.

Keywords: 2-nitro-1-phenyl-1-phenylsulfonylethene; activation energy; enthalpy of activation; rate constants; sulfinic acids

INTRODUCTION

The study of the reactivity of 1-aryl-1-arylsulfonyl-2-nitroethenes when interacting with nucleophilic reagents is a natural continuation of our work on the addition reactions of S-containing nucleophiles with heteroconjugated alkenes.[1–3] From a theoretical point of view, it is interesting to study the change in the activity of the double bonds toward the nucleophilic reagents depending on the nature of the substituents at α- and β-carbon atoms.

The present work is a study of the change in the kinetic parameters of nucleophilic addition of sulfinic acids to 2-nitro-1-phenyl-1-phenylsulfonylethene compared with those characterizing the reactivity of 2-nitrostyrene. On the basis of the quantitative parameters obtained,

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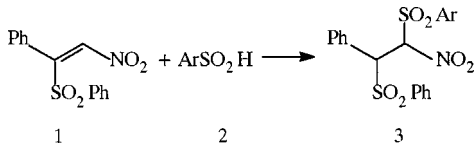
some conclusions were made concerning the reactivity of 2-nitro-1-phenyl-1-phenylsulfonylethene towards S-containing nucleophils.

RESULTS AND DISCUSSION

The interaction between 2-nitro-1-phenyl-1-phenylsulfonylethene and sulfinic acids takes place according to the following scheme:



1 2 3 (1)

2-arylsulfonyl-2-nitro-1-phenyl-1-phenylsulfonylethanes (**3**) are obtained by mixing equimolar amounts of (**1**) and (**2**) in a medium of ethanol. The yields are 65–85% and there are no by-products. The compounds obtained are colourless crystalline substances, very soluble in chloroform, acetone, and dioxane. All compounds give satisfactory elemental analyses for $C \pm 0{,}3$; $H \pm 0{,}3$; $N \pm 0{,}2$; $S \pm 0{,}3\%$. In the IR-spectra of compounds **3a–c**, there are intensive absorption bands at $1540 \pm 10(\nu_{as}^{NO_2})$, $1360 \pm 10(\nu_{s}^{NO_2})$, $1300 \pm 10(\nu_{as}^{SO_2})$, 1150–1130$(\nu_{s}^{SO_2})$, $1080 \pm 10\,cm^{-1}(\nu_{S\text{-}Ar})$. NMR-spectra of 2-arylsulfonyl-2-nitro-1-phenyl-1-phenylsulfonylethanes contain aromatic multiplets in the interval 7.10–7.88 ppm. Two doublets can be seen at 5.11 and 6.20 ppm. The presence of a methyl group in H3b results in a singlet at 2.40 ppm. Simultaneously with the syntheses carried out, the kinetics of the addition of sulfinic acids to 2-nitro-1-phenyl-1-phenylsulfonylethene was also studied.

Reaction Order

The kinetics of the addition of p-substituted benzenesulfinic acids to 2-nitro-1-phenyl-1-phenylsulfonylethene were studied. The overall reaction is second order but it is first order regarding each reagent. The inital concentration of sulfinic acids and 2-nitro-1-phenyl-1-phenylsulfonylethene was varied from 0.005 to 10 M. The experimental results for the chemical reaction order are show in Table I. These data make it possible to draw the conclusion that the order of the reaction is 1.86. The linear dependance 1/[2-nitro-1-phenyl-1-phenylsulfonylethene] = $f(\tau)$ is another proof of the above conclusion. The rate constants for five different temperatures were calculated from the resultant slopes.

TABLE I Experimental Proof of the Benzenesulfinic Acids Addition Order to 2-Nitro-1-Phenylsulfonylethene by Methods of Van't Hoff and Half-Time in the Concentration Range 0.005–10 M, T = 298 K

Concentration range C, M	0.0005–0.01	0.001–0.1	0.1–1	1–10
Order value by Van't Hoff method	1.82	1.85	1.80	1.84
Order value by half-time method	1.86	1.89	1.89	1.91

Effect of Temperature

The second-order values for the addition of benzenesulfinic acid 3a to 2-nitro-1-phenyl-1-phenylsulfonylethene at 288, 293, 298, 303, 308 K are $7{,}70.10^{-4}$; $9{,}55.10^{-4}$; $12{,}30.10^{-4}$; $18{,}55.10^{-4}$; $21{,}50.10^{-4}$ $M^{-1}s^{-1}$, respectively. The activation energy and the enthalpy of activation, calculated on the basis of these data, are found to be 60.15 kJ.mol^{-1} and 63.25 kJ $\cdot$ mol^{-1}.

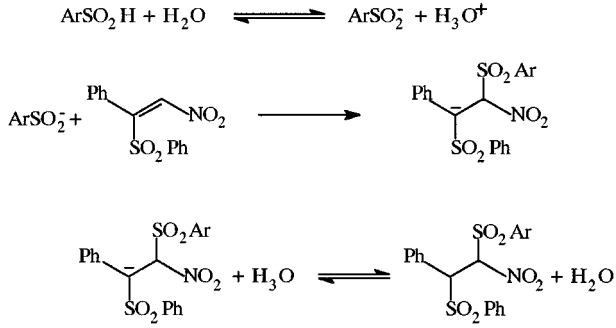
Substituent Effects

The addition reactions between p-substituted benzenesulfinic acids and 2-nitro-1-phenyl-1-phenylsulfonylethene were carried out at five temperatures. The reactions were accelerated or slowed down depending on the presence of an electron-donating or electron-withdrawing group, respectively. The second-order rate constants, the activation energy and the enthalpy of activation are shown in Table II.

TABLE II Substituent Effect on the Rate Constants and Activation Parameters at Different Temperature

Nucleophile	Subst. rate	Temp.	$k \cdot 10^4$ $M^{-1}s^{-1}$	E, kJ $\cdot$ mol^{-1}	$\Delta H^{\neq}$ kJ $\cdot$ mol^{-1}
2b	1	288	8.83 ± 1.1	55.72	50.65
		293	10.14 ± 0.9		
		298	12.56 ± 1.2		
		303	19.07 ± 0.8		
		308	28.87 ± 1.3		
2c	1	288	2.78 ± 0.3	72.10	67.35
		293	5.54 ± 0.6		
		298	7.08 ± 0.4		
		303	10.50 ± 0.6		
		308	12.10 ± 0.7		

The kinetic data obtained for the addition reaction under study and the fact that sulfinic acids are strong acids make it possible to suggest the most probable mechanism of their addition to 2-nitro-1-phenyl-1-phenylsulfonylethene.



(2)

The limiting step of that process is the addition of the sulfinic anion to the α-carbon atom and the formation of a carbanion, which quickly accepts a proton to form the final product. Comparing the kinetic parameters of the reaction under study with those characterising the interaction between sulfinic acids and 2-nitrostyrene[4] it can be seen that the carbon-carbon double bond in 2-nitro-1-phenyl-1-phenylsulfonylethene is less active towards the nucleophilic reagents.

EXPERIMENTAL

General

Melting points were determined on a Melt-Temp apparatus and are uncorrected. Microanalyses were obtained using an elemental Analyser-1104 (Carbo Erba). IR- and NMR-spectra were obtained using a Specord 75 IR and Bruker (350 MHz).

Materials

2-nitro-1-phenyl-1-phenylsulfonylethene and sulfinic acids were prepared and purified as described in the literature.[5–6]

General Procedure

To 2-nitro-1-phenyl-1-phenylsulfonylethene (0.001 mol) in 95% ethanol was added sulfinic acid (0.001 mol). The reaction mixture was kept standing at 20°C, 16 h, to yield the substituted 1-aryl-1,2-diarylsulfonyl-2-nitroethanes. The crystals obtained were filtered and

crystallized from ethanol/dioxane, 10:1. The substituents were 4-Me (**3b**) m.p. 174°C, H(3a), m.p. 186–187°C, 4-Cl(3c), m.p. 168°C.

Rate Measurement

Purified sulfinic acid (0.001 mol) was added to 2-nitro-1-phenyl-1-phenylsulfonylethene (0.001 mol) in ethanol (50 ml). Aliquots were taken out at reaction intervals of time and diluted with ethanol. The flow concentration of the reagents during the reaction were determined by liquid chromatographic analysis. HPLC was performed using a Series-4 apparatus (Perkin-Elmer) and a programmable multiwavelength detector. The second-order constants, the activation energy and the enthalpy of activation were calculated according to literature.[7]

REFERENCES

[1] D. I. Aleksiev and S. Ivanova, *Phosphorus, Sulfur and Silicon*, **101,** 103 (1995).
[2] D. I. Aleksiev and S. Ivanova, *Phosphorus, Sulfur and Silicon*, **101,** 15 (1995).
[3] D. I. Aleksiev and S. Ivanova, *Zh. Org. Khim.*, **30**(5), 720 (1995).
[4] D. I. Aleksiev, S. Ivanova, and Kr. Tashkova, *Phosphorus, Sulfur and Silicon*, **85,** 73 (1993).
[5] Eighth European Symposium on Organic Chemistry, Sitges, Barcelona, Spain, August 29–September 3, 1993, 465, book of abstracts.
[6] Y. Ogata, Y. Sawaki, and M. Isono, *Tetrahedron*, **25,** 2715 (1969).
[7] N. M. Emanuel and P. G. Knorre, Kurs khimicheskoi kinetiki, Vishaia Shkola, Moskva, 166 (1974).