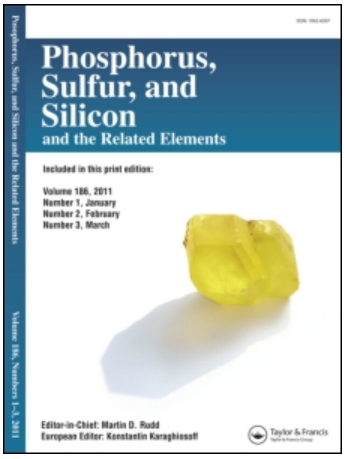

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Kinetic Studies on the reaction of Sulfinic Acids with Conjugated Alkenes: II. Kinetics of the Addition of Arenesulfinic Acids to 4-Substituted 2-Nitroethenylarenes

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KINETIC STUDIES ON THE REACTION OF SULFINIC ACIDS WITH CONJUGATED ALKENES: II. KINETICS OF THE ADDITION OF ARENESULFINIC ACIDS TO 4-SUBSTITUTED 2-NITROETHENYLARENES

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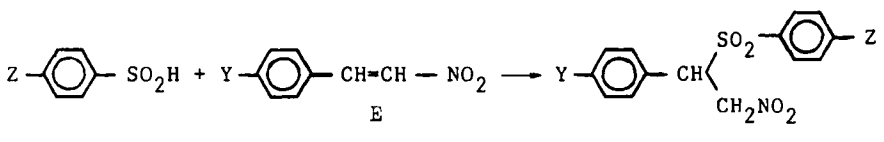
The kinetics of the addition of arenesulfinic acids to 4-substituted 2-nitroethenylarenes was studied by means of UV spectrophotometry. The effect of 4-substituting groups in benzenesulfinic acids, and the change in reactivity of nitroethylene system due to typical electron-donating and electron-withdrawing groups were investigated. The substituent effect on benzenesulfinic acid fits Hammett's equation, *p*-value at 298 K being −1.12 (r = 0.987). Kinetic studies were carried out at 288–308 K, and the activating energy and the enthalpy of activation were determined.

Key words: Sulfinic acids, 1-nitro-4-(2-nitroethenyl)benzene, 1-methoxy-4-(2-nitroethenyl)benzene, rate constants, activating energy, enthalpy of activation.

INTRODUCTION

Kinetic data concerning nucleophilic addition of some arenesulfinic acids to β-nitrostyrene were reported in a previous work.[1] Further points of interest are the change in the main kinetic parameters of the reaction due to various *p*-substituting groups in arenesulfinic acids, and the change in the reactivity of the nitroethylene system due to highly electron-donating and electron-withdrawing groups in 4-position in the benzene ring of 1-(2-nitroethenyl) benzene. To achieve this aim, a number of kinetic studies were made on the addition reaction of benzenesulfinic acids and two of its *p*-substituted analogs to 1-nitro-4-(2-nitroethenyl)benzene and 1-methoxy-4-(2-nitroethenyl)-benzene:



(1)

1

(a) Z=H
(b) Z=CH_3
(c) Z=Cl

2

(a) Y=NO_2
(b) Y=CH_3O

3

(a) Y=NO_2 Z=H
(b) Y=NO_2 Z=CH_3
(c) Y=NO_2 Z=Cl
(d) Y=CH_3O Z=H
(e) Y=CH_3O Z=CH_3
(f) Y=CH_3O Z=Cl

RESULTS AND DISCUSSION

Reaction Order

Nucleophilic addition of *p*-substituted benzenesulfinic acids to 1-nitro-4-(2-nitroethenyl)benzene and 1-methoxy-4-(2-nitroethenyl)-benzene takes place in the second reaction order, but it is first order regarding each reagent. This is also confirmed by the linear dependence 1/[1-nitro-(1-methoxy-)-4-(2-nitroethenyl)benzene] = f(τ). The slopes of these straight lines were used to determine the rate constants at five different temperatures.

Effect of Temperature

The second-order rate constants for the addition of benzenesulfinic acid to 1-nitro-4-(2-nitroethenyl)benzene at 288, 293, 298, 303, 308 K are $1.99.10^{-3}$, $2.23.10^{-3}$, $2.35.10^{-3}$, $2.91.10^{-3}$, $3.32.10^{-3}$ $M^{-1}s^{-1}$, (Figure 1) respectively. The rate constants for the reaction of 1-methoxy-4-(2-nitroethenyl)benzene with benzenesulfinic acid at 288, 293, 298, 303, 308 K are $0.98.10^{-6}$, $1.13.10^{-6}$, $1.65.10^{-6}$, $2.02.10^{-6}$, $2.17.10^{-6}$ $M^{-1}s^{-1}$, respectively (Figure 2). The activating energy and the enthalpy of activation for the reaction of 1-nitro-4-(2-nitroethenyl)benzene were calculated as 55.31 kJ mol^{-1} and 52.60 kJ mol^{-1}. The results for the reaction of 1-methoxy-4-(2-nitroethenyl)benzene were 71.32 kJ mol^{-1} and 68.65 kJ mol^{-1}, respectively.

Substituent Effect

Second-order rate constants, activating energy and the enthalpy of activation for the addition of p-substituted benzenesulfinic acids to 1-nitro-4-(2-nitroethenyl)benzene and 1-methoxy-4-(2-nitroethenyl)benzene are given in Table I.

The kinetic data obtained show that the 4—Me group in the sulfinic acid accelerates its addition to 2-nitroethenylarener, and the 4—Cl group has the opposite

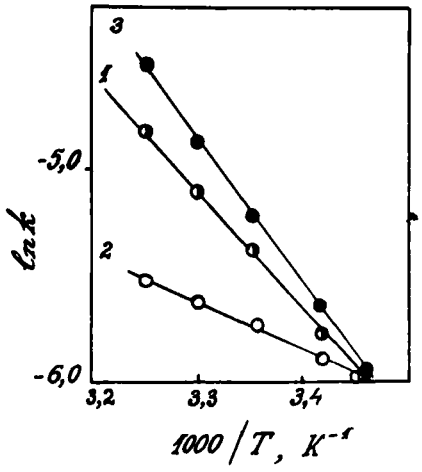


FIGURE 1 Dependence of rate constants on the reaction temperature of 1-nitro-4-(2-nitroethenyl)benzene with: 1) benzenesulfinic acid, 2) 4-toluenesulfinic acid, 3) 4-chlorobenzenesulfinic acid.

TABLE I

Substituent effects on the rate constants and activation parameters at 288, 293, 298, 303, 308°K

Nucleophile	Substrate	$k.10^3$ $M^{-1}s^{-1}$	E kJ mol^{-1}	$\Delta H^{\neq}$ kJ mol^{-1}
1b	2a	2.08±0.6	49.42	44.19
		2.28±0.8		
		2.84±1.1		
		3.18±1.4		
		3.62±1.7		
1c	2a	1.44±0.3	59.26	55.74
		1.67±0.4		
		2.07±0.6		
		2.22±0.7		
		2.41±0.9		
		$k.10^6$ $M^{-1}s^{-1}$	E kJ mol^{-1}	$\Delta H^{\neq}$ kJ mol^{-1}
1b	2b	1.18±0.1	68,52	63.74
		1.43±0.3		
		1.96±0.5		
		2.10±0.6		
		2.35±0.8		
1c	2b	0.56±0.01	80.62	76.54
		0.88±0.03		
		1.06±0.09		
		1.28±0.2		
		1.59±0.4		

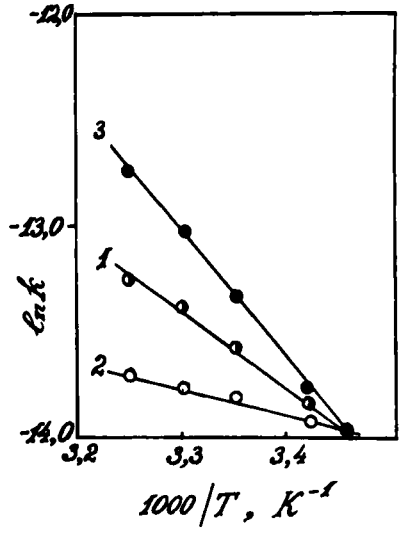
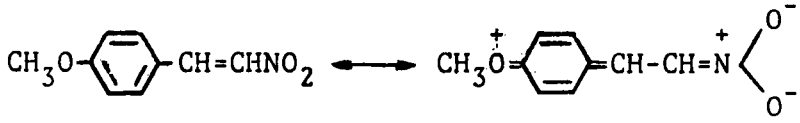


FIGURE 2 Dependence of rate constants on the reaction temperature of 1-methoxy-4-(2-nitroethenyl)benzene with: 1) benzenesulfinic acid, 2) 4-toluenesulfinic acid, 3) 4-chlorobenzenesulfinic acid.

effect. It can also be seen that the 4—NO_2 group in 1-nitro-4-(2-nitroethenyl)benzene increases reaction rate by one order, and the 4—CH_3O group in 1-methoxy-4-(2-nitroethenyl)benzene decreases reaction rate by two orders compared to the reaction rate of 1-(2-nitroethenyl)benzene.[1] The considerable decrease in the reactivity of 1-methoxy-4-(2-nitroethenyl)benzene is probably connected with decreased electrophilic characteristics of the β-carbon atom.



(2)

Publications are available discussing the peculiarities of IR-spectra of 1-methoxy-4-(2-nitroethenyl)benzene and its decreasing reactivity with increasing contribution of the bipolar ion in the hybrid structure.[2]

EXPERIMENTAL

General Comments. Melting points were determined on a Melt-Temp apparatus and are uncorrected. Microanalyses were made using an Elemental Analyzer-1104 (Carlo Erba, Italy). IR spectra were obtained on a Specord 75 IR (Germany). Kinetic determinations were carried out using a Specord UV-VIS (Germany).

Materials. Benzenesulfinic acids substituted by H (**1a**), 4—CH_3 (**1b**), 4—Cl (**1c**) were prepared and purified as described in the literature.[3] 1-nitro-4-(2-nitroethenyl)benzene (**2a**) and 1-methoxy-4-(2-nitroethenyl)benzene (**2b**) were synthesized according to published procedures.[4,5]

General Procedure. 0.001 mol sulfinic acid was added to 0.001 mol of the corresponding nitroethenylarene dissolved in 10 ml ethanol. 1-nitro-4-(2-nitroethenyl)benzene (**2a**) was allowed to react with sulfinic acids (**1a–c**) for 12 hours, and 1-methoxy-4-(2-nitroethenyl)benzene (**2b**) reacted with (**1a–c**)

for 48 hours at 18–20°C. The yields (%), m.p. (°C), UV absorption peaks in nm (log ε) in ethanol of the nitrosulfones (**3a–f**) (scheme 1) were determined. (**3a**) 67, 125 (EtOH/Dioxane, 10:1), 218 (2.86), 265 (3.08), 271 (3.11); (**3b**) 97, 195 (EtOH/Dioxane, 10:1), 220 (2.72), 261.5 (2.98), 273 (3.02); (**3c**) 93, 179 (EtOH/Dioxane, 10:1), 222 (2.75), 262.5 (2.83), 275 (3.10); (**3d**) 89, 134 (EtOH), 228 (2.86), 266 (2.95), 301 (3.12); (**3e**) 85, 142 (EtOH), 227.5 (2.79), 266.5 (2.98), 306 (3.18); (**3f**) 51, 158 (EtOH), 220.5 (2.70), 263 (2.55), 303 (2.93). These products were identified by their IR spectra and microanalyses.

Rate Measurements. Purified benzenesulfinic acids (0.001 mol) were added to 2-nitroethenylarenes (0.001 mol) in ethanol (50 ml). Alliquots were taken out at regular intervals of time and diluted with ethanol. The flow concentration of the reagents during the reaction were determined by means of UV spectrophotometry. The second-order constants, the activating energy and the enthalpy of activation were calculated according to literature.[6]

REFERENCES

1. D. I. Aleksiev, S. Ivanova and Kr. Tashkova, *Phosphorus and Sulfur*, **85,** 73 (1993).
2. T. Ia. Paperno and V. V. Perekalin, "Infrakrasnie spektri nitrosoedinenii," Leningrad, 1974, 46.
3. Y. O. Gata, Y. Sawaki and M. Isono, *Tetrahedron*, **25,** 2715 (1969).
4. T. Nashimura, *Bull. Chem. Soc. Japan*, **27,** 617 (1954).
5. K. Gairaund and C. Lappin, *J. Org. Chem.*, **18,** 1 (1953).
6. N. M. Emanuel and P. G. Knorre, "Kurs khimicheskoi kinetiki," Vishaia shkola, Moskva, 1974, 166.