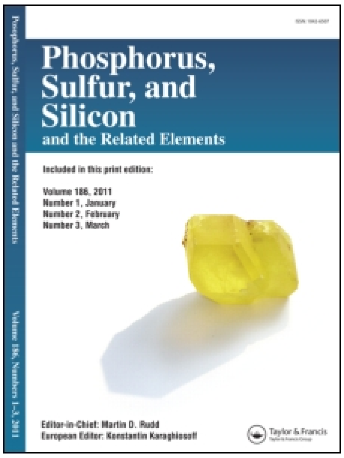

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KINETIC STUDIES ON REACTION OF SULFINIC ACIDS WITH CONJUGATED ALKENES: I. KINETICS OF THE ADDITION OF ARENESULFINIC ACIDS TO β-NITROSTYRENE

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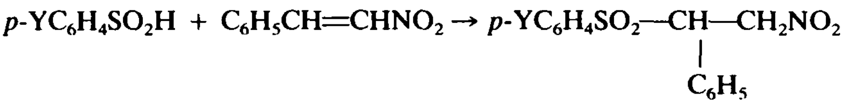
Addition of unsubstituted and substituted benzenesulfinic acids to β-nitrostyrene has been studied kinetically by means of ultraviolet spectrophotometry. The reaction follows the second-order kinetics: $v = k.$ [β-nitrostyrene][sulfinic acid]. The dependence of rate constants on the temperature and influence of *p*-substituents on the kinetic parameters have been investigated. The activating energy and the enthalpy of activation are calculated in the temperature range 288–308 K.

Key words: Sulfinic acids; β-nitrostyrene; reaction order; rate constants; activating energy; enthalpy of activation.

INTRODUCTION

Sulfinic acids add easily to conjugated Michael-type alkenes to yield the corresponding β-substituted sulfones.[1–7] Some of these reactions are studied kinetically.[8,9]

The interaction of sulfinic acids with α,β-unsaturated nitrocompounds to afford Michael-type products has also been observed[10,11] and used for preparation of nitrosulfones. However there is no report on the kinetics of this reaction. We have carried out kinetic studies on the additional unsubstituted and two *p*-substituted benzenesulfinic acids (1) to β-nitrostyrene (2) and the results are described in this paper:



$$p\text{-}YC_6H_4SO_2H + C_6H_5CH{=}CHNO_2 \rightarrow p\text{-}YC_6H_4SO_2{-}\underset{\displaystyle C_6H_5}{\underset{|}{CH}}{-}CH_2NO_2$$

1 2 3

RESULTS AND DISCUSSIONS

Reaction Order

Kinetics of *p*-substituted benzenesulfinic acids to β-nitrostyrene have been investigated. The reaction is second-order, first-order, each in the concentration of sulfinic acids and β-nitrostyrene:

$$V = k[C_6H_5SO_2H]\cdot[C_6H_5CH{=}CHNO_2]$$

Initial concentration of sulfinic acid and β-nitrostyrene were varied between 0.005–10 M and 0.005–10 M, respectively. The study of the chemical reaction order is shown in Table I. This data allow the conclusion that the order of the reaction is 1.75. The linear dependence $1/[\beta\text{-nitrostyrene}] = f(\tau)$ is an additional evidence, the rate constants for five different temperatures are calculated from the resultant slopes.

Effect of Temperature

The second-order for the addition of benzenesulfinic acid to β-nitrostyrene at 288, 293, 298, 303, 308 K are $4.61 \cdot 10^{-4}$, $7.88 \cdot 10^{-4}$, $9.95 \cdot 10^{-4}$, $12.14 \cdot 10^{-4}$, $17.28 \cdot 10^{-4}\ M^{-1}\ s^{-1}$, respectively. The activating energy and enthalpy of activation were calculated on the basis of these data and are 56.86 kJ mol^{-1} and 56.88 kJ mol^{-1}.

Substituent Effect

The reaction of p-substituted benzenesulfinic acids with β-nitrostyrene were carried out at five temperatures. The reactions are accelerated in the presence of an electron-donating group (4-Me) and slowed down in case of an electron-withdrawing group (4-Cl). Second-order rate constants, activating energy and the enthalpy of activation are shown in Table II.

TABLE I

Experimental proof of the benzenesulfinic acid addition order to β-nitrostyrene by methods of Van't Hoff[15] and half-time[15] in 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	1.73	1.68	1.70	1.73
Order value by half-time method	1.76	1.81	1.79	1.77

TABLE II

Substituent effects on the rate constants and activation parameters at 288, 293, 298, 303, 305° K

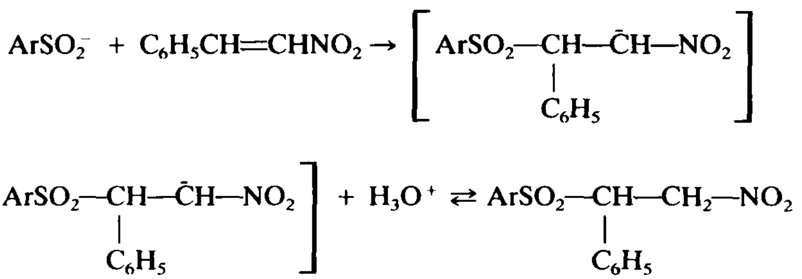
Nucleophile	Substrate	$k \cdot 10^4$ $M^{-1}\ s^{-1}$	E, kJ mol^{-1}	$\Delta H\ddagger$ kJ mol^{-1}
Ib	2	10.6 ± 1.0	49.91	53.42
		11.6 ± 1.1		
		13.6 ± 1.4		
		15.0 ± 1.6		
		20.3 ± 2.1		
Ic	2	3.45 ± 0.4	66.40	59.81
		6.58 ± 0.6		
		7.24 ± 0.9		
		10.81 ± 1.0		
		12.63 ± 1.2		

Mechanism

Sulfinic acids are strong acids (1a pK_a 1.20; 1b pK_a 1.24; 1c pK_a 1.29).[6] Since their absorption maxima in 10^{-4} M solution in 95% ethanol is coincident with the maxima of sulfinate anions,[14] we conclude that they are completely dissociated in our reaction mixture.

Considering this and the fact, that the reaction is first-order in both sulfinic acids and β-nitrostyrene, the following mechanism is plausible:

$$ArSO_2H + H_2O \rightleftarrows ArSO_2^- + H_3O^+$$



$$ArSO_2^- + C_6H_5CH{=}CHNO_2 \rightarrow \left[ArSO_2{-}\underset{\displaystyle C_6H_5}{\underset{|}{CH}}{-}\bar{C}H{-}NO_2 \right]$$

$$\left[ArSO_2{-}\underset{\displaystyle C_6H_5}{\underset{|}{CH}}{-}\bar{C}H{-}NO_2 \right] + H_3O^+ \rightleftarrows ArSO_2{-}\underset{\displaystyle C_6H_5}{\underset{|}{CH}}{-}CH_2{-}NO_2$$

The first step is the addition of the sulfinate anion to the β-carbon atom. This step is accelerated by an electron-donating group (4-Me) at benzene ring in the sulfinic acid. In the second step the intermediate carbanion is protonated to the final product.

EXPERIMENTAL

Materials. β-nitrostyrene (2) and benzenesulfinic acids substituted by 4-Me (1b), H (1a), 4-Cl (1c) groups were prepared and purified as described corresponding to literature.[12–13]

Reaction products. To β-nitrostyrene (0.001 mol) in 95% ethanol was added $C_6H_5SO_2H \cdot xH_2O$ (0.001 mol). The reaction mixtures were kept standing at 25° for 1 h to yield substituted nitroethylarylsulfones, $Y{-}C_6H_4SO_2CH(C_6H_5)CH_2NO_2$. The following data describe the substituents, m.p. (crystallized from acetic acid) and UV absorption peaks in nm (log ε) in ethanol. 4-Me (3b) 149–150°,[10] 222 (3.96), 265 (2.68), 273 (2.31); H (3a) 185–186°,[10] 218 (3.79), 260.5 (2.24), 270 (2.06); 4-Cl (3c) 113–114°, 228 (4.04), 263 (2.82), 272 (2.61). These products were unidentified by their IR spectra.

Rate measurement. Purified benzenesulfinic acids (0.001 mol) were added to β-nitrostyrene (0.001 mol) in ethanol (50 ml). Aliquots 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.[15]

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