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

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The kinetics of the addition of unsubstituted and substituted benzenesulfinic acids to various 2-halogeno-2-nitroethenylarenes was studied by means of UV spectroscopy. The effect of 4-substituents in benzenesulfinic acids and the change in reactivity of the nitroethylene system in 2-halogeno-2-nitroethenylarenes in the presence of various substituents in the benzene ring and various halogens at the double bond were investigated. Kinetic studies were made at 288–308 K, and activating energy and enthalpy of activation were determined.

INTRODUCTION

The results of kinetic studies on nucleophilic addition of unsubstituted and substituted benzenesulfinic acids to 2-nitroethenylbenzene and some of its analogues

$$ArSO_2H \quad + \quad Ar^1 \diagdown\diagup{\overset{X}{\underset{NO_2}{}}} \longrightarrow ArSO_2 \diagdown\diagup{\overset{X}{\underset{NO_2}{\underset{Ar^1}{}}}}$$

| 1 | | | 2 | | | 3 |

1	Ar			2	Ar^1	X
a	Ph			a	Ph	Cl
b	4-MeC_6H_4			b	Ph	Br
c	4-ClC_6H_4			c	4-MeOC_6H_4	Br

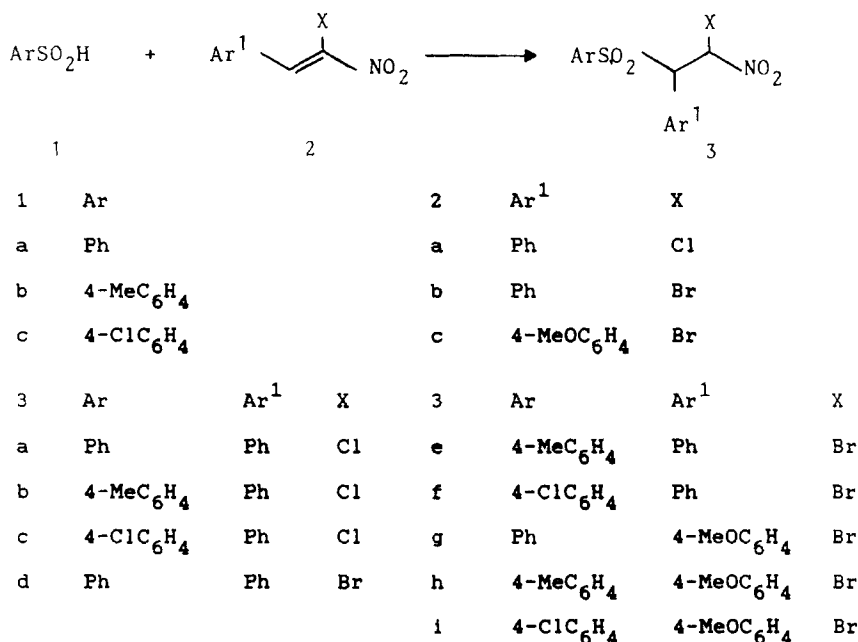| 3	Ar	Ar^1	X	3	Ar	Ar^1	X
a	Ph	Ph	Cl	e	4-MeC_6H_4	Ph	Br
b	4-MeC_6H_4	Ph	Cl	f	4-ClC_6H_4	Ph	Br
c	4-ClC_6H_4	Ph	Cl	g	Ph	4-MeOC_6H_4	Br
d	Ph	Ph	Br	h	4-MeC_6H_4	4-MeOC_6H_4	Br
				i	4-ClC_6H_4	4-MeOC_6H_4	Br

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}	$\Delta H^{\ddagger}$ kJ mol^{-1}
1b	2a	1.24 ± 0.16	49.45	46.55
		1.39 ± 0.28		
		1.54 ± 0.42		
		1.76 ± 0.48		
		2.09 ± 0.66		
1c	2a	0.63 ± 0.02	61.30	58.50
		0.78 ± 0.02		
		0.85 ± 0.03		
		0.97 ± 0.07		
		1.10 ± 0.10		
1b	2b	1.46 ± 0.33	45.85	41.70
		1.58 ± 0.44		
		1.71 ± 0.48		
		1.94 ± 0.55		
		2.24 ± 0.80		
1c	2b	0.88 ± 0.03	59.15	56.65
		0.97 ± 0.07		
		1.13 ± 0.11		
		1.28 ± 0.18		
		1.43 ± 0.32		
		$k.10^5$ $M^{-1}s^{-1}$	E kJ mol^{-1}	$\Delta H^{\ddagger}$ kJ mol^{-1}
1b	2c	1.23 ± 0.15	60.24	57.75
		1.48 ± 0.35		
		1.98 ± 0.57		
		2.25 ± 0.81		
		2.25 ± 0.81		
		2.41 ± 0.95		
1c	2c	0.88 ± 0.03	74.38	70.04
		1.09 ± 0.10		
		1.15 ± 0.12		
		1.32 ± 0.22		
		1.62 ± 0.46		

were published in previous works.[1-2] The present article is a continuation of a series of investigations in this field and is concerned with the kinetics of addition of arenesulfinic acids to 2-halogeno-2-nitroethenylarenes.

The change in the main kinetic parameters of the reaction in the presence of various p-substituents in **1a–c** as well as the change in the reactivity of nitroethylene system under the influence of various halogens at the double bond and depending on the nature of the substituent in the benzene ring of 2-halogeno-2-nitroethenylarenes **2a–c** were studied.

RESULTS AND DISCUSSION

Reaction Order

Nucleophilic addition of p-substituted benzenesulfinic acids to 2-bromo-2-nitroethenylbenzene, 2-chloro-2-nitroethenylbenzene and 1-methoxy-4-(2-bromo-2-nitroethenyl)benzene is a second-order reaction, first-order in each reagent.

$$V = k. [\text{sulfinic acid}]. [\text{2-halogeno-2-nitroethenylarene}]$$

The total order of the reaction was determined by Van't Hoff's method and the half-time method in the concentration range 0.005–10 M^3. Rate constants at five different temperatures were calculated from the slope of the straight lines 1/[2-halogeno-2-nitroethenylarene] = f(τ) (Table I).

Effect of Temperature

The second-order rate constants for the addition of benzenesulfinic acid to 2-bromo-2-nitroethenylbenzene at 288, 293, 298, 303, 308 K are $1.32.10^{-3}$, $1.41.10^{-3}$, $1.60.10^{-3}$, $1.72.10^{-3}$, $2.08.10^{-3}$, $M^{-1}s^{-1}$, respectively. The rate constants of the reaction of 2-chloro-2-nitroethenylbenzene with benzenesulfinic acid at 288, 293, 298, 303, 308 K are $0.98.10^{-3}$, $1.06.10^{-3}$, $1.17.10^{-3}$, $1.29.10^{-3}$, $1.36.10^{-3}$, $M^{-1}s^{-1}$, respectively. The rate constants for the reaction of 1-methoxy-4-(2-bromo-2-nitroethenyl)benzene with benzenesulfinic acid at 288, 293, 298, 303, 308 K are $1.12.10^{-5}$, $1.21.10^{-5}$, $1.62.10^{-5}$, $1.71.10^{-5}$, $2.04.10^{-5}$, $M^{-1}s^{-1}$, respectively. The activating energy and the enthalpy of activation for the reaction of 2-bromo-2-nitroethenylbenzene, 2-chloro-2-nitroethenylbenzene and 1-methoxy-4- (2-bromo-2-nitroethenyl)benzene were calculated as 50.72 kJ mol^{-4} and 48.35 kJ mol^{-1}, 53.60 kJ mol^{-1} and 50.70 kJ mol^{-1}, 65.16 kJ mol^{-1} and 61.83 kJ mol^{-1}, respectively.

Substituent Effect

The data obtained show that the reactivity of the nitroethylene system in 2-halogeno-2-nitroethenylarenes is higher than that of the corresponding 2-nitroethenylarenes. Most probably, this is due to the presence of a halogen atom in α-position in regard to the nitro group.

The rate constants for the reaction of 2-bromo- and 2-chloro-2-nitroethenylbenzene with sulfinic acids are one order higher than those obtained for the reaction of 2-nitroethenylarenes.[1-2] On the other hand, 2-bromo-2-nitroethenylbenzene reacts with arenesulfinic acids (Figure 2) faster than 2-chloro-2-nitroethenylbenzene (Fig-
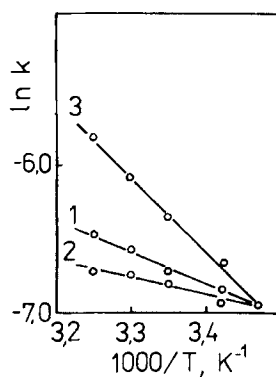
FIGURE 1   Dependence of rate constants on the reaction temperature of 2-chloro-2-nitroethenyl-benzene with: 1—benzenesulfinic acid, 2—4-toluenesulfinic acid, 3—4-chlorobenzenesulfinic acid.
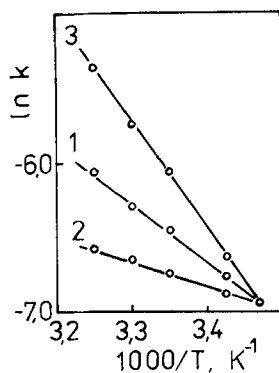

FIGURE 2   Dependence of rate constants on the reaction temperature of 2-bromo-2-nitroethenyl-benzene with: 1—benzenesulfinic acid, 2—4-toluenesulfinic acid, 3—4-chlorobenzenesulfinic acid.
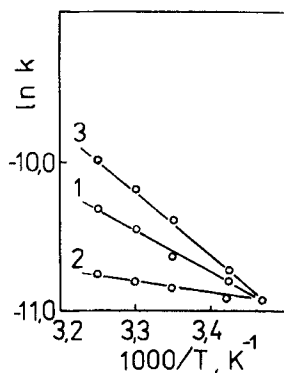

FIGURE 3   Dependence of rate constants on the reaction temperature of 2-methoxy-4-(2-bromo-2-nitroethenyl)benzene with: 1—benzenesulfinic acid, 2—4-toluenesulfinic acid, 3—4-chlorobenzene-sulfinic acid.

ure 1). The presence of a 4-MeO group in the benzene ring of 2-bromo-2-nitroethenylbenzene leads to a decrease in the reaction rate, but it is higher than the rate at which 1-methoxy-4-(2-nitroethenyl)benzene reacts (Figure 3).

Kinetic studies on the reaction of arenesulfinic acids with 1-nitro-3-(2-bromo-2-nitroethenyl)benzene and 1-nitro-4-(2-bromo-2-nitroethenyl)benzene show that it cannot be expressed as a second-order equation. These results confirm the parallel-consecutive course of the reaction, which was proved earlier.[4]

The influence of p-substituents in the benzene ring of sulfinic acids agrees with established dependences.[2]

Mechanism

Having in mind that the reaction of arenesulfinic acids with 2-bromo-2-nitroethenylbenzene, 2-chloro-2-nitroethenylbenzene and 1-methoxy-4-(2-bromo-2-nitroethenyl)benzene is first order regarding each reagent, its most probable mechanism is:
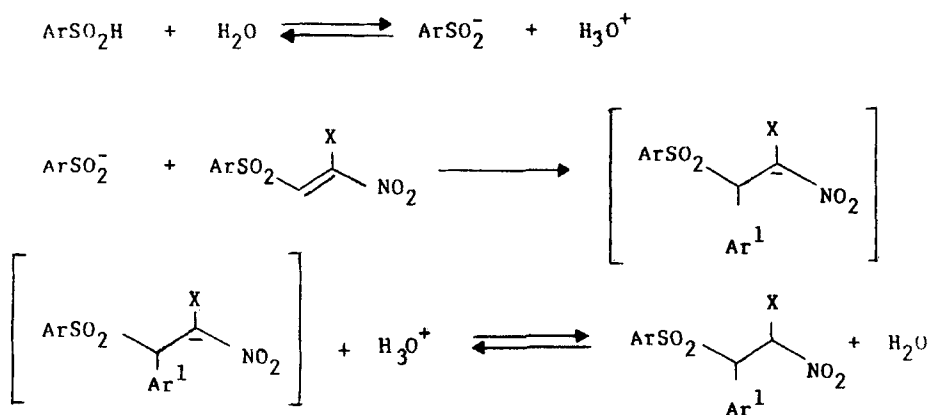
The higher rate of the reaction between arenesulfinic acids and 2-halogeno-2-nitroethenylbenzene may be explained not only by an increase in the electron deficit at the β-carbon atom but also by the possibility of a further delocalization of the negative charge in the formed carbonium ion due to the presence of the halogen. The higher reactivity of 2-bromo-2-nitroethenylbenzene than that of 2-chloro-2-nitroethenylbenzene may be connected with the smaller electronegativity and electron-donating ability of the bromine atom. This leads to a faster formation of carbonium ion and its greater stability.

EXPERIMENTAL

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

Reaction products. Products **3a–i** were synthesized as described in a previous work.[4] These substances are characterized by the following UV absorption maxima, nm (log ε) in ethanol: (**3a**) 220 (2.91), 260

(3.05), 273 (3.15); (**3b**) 223 (2.89), 258 (2.99), 270 (3.00); (**3c**) 219 (2.75); 254 (2.85), 273 (3.12); (**3d**) 224 (2.95), 262 (3.08), 275 (3.16); (**3e**) 222 (2.84), 259 (2.92), 276 (3.02); (**3f**) 221 (2.88), 260.5 (2.97), 274 (3.07); (**3g**) 226 (2.83), 265 (2.95), 283 (3.19); (**3h**) 225 (2.76), 263 (2.89), 285 (3.22); (**3i**) 224 (2.79), 261.5 (2.94), 285.5 (3.16).

Rate measurement. Purified benzenesulfinic acids (0.001 mol) were added to 2-halogeno-2-nitroeth-enylarenes (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 was determined by means of UV spectrophotometry. The second-order constants, the activation energy and the enthalpy of activation were calculated according to the literature.[3]

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