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Reactivity of sodium arenesulfinates in the substitution reaction to γ-functionalized allyl bromides

Galina Khamis[a], Stoyanka Stoeva[a]* and Dimitar Aleksiev[a]

The kinetics of nucleophilic bimolecular substitution reactions of γ-functionalized allyl bromides with non-substituted and *p*-substituted sodium arenesulfinates has been studied. Both the structure of allyl bromides and nucleophilicity of arenesulfinate ions exerted a significant effect on the values of the kinetic parameters such as the second-order rate constants *k*, activation energy E_A, and changes in the entropy $\Delta S^{\neq}$, enthalpy $\Delta H^{\neq}$, and free energy $\Delta G^{\neq}$ of the formation of the activated complex from reactants. Based on the evaluation of kinetic parameters, the reactants could be arranged, according to their decreasing reactivity in the S_N2-reactions as follows: *p*-toluenesulfinate ion > benzenesulfinate ion > *p*-chlorobenzenesulfinate ion and 4-bromo-2-butenenitrile > 1,3-dibromopropene, respectively. Comparison was also made between the kinetic data obtained and some delocalization reactivity indexes for both the substrates and nucleophiles. The enthalpy–entropy compensation effect was observed for the reactions of sodium arenesulfinates with γ-functionalized allyl bromides. Copyright © 2009 John Wiley & Sons, Ltd.

Keywords: kinetic resolution; nucleophilic substitution; substituent effects; sulfinate S-allylation

INTRODUCTION

The reactions of sulfinic acids or their salts with some electrophiles, resulting in the formation of new C—S bonds constitute one of the most important methods for the synthesis of sulfones.[1] As reported in some publications,[2–8] the chemical properties of sulfones make them very useful reagents in the organic synthesis, since these products serve as synthetic intermediates in the preparation of various chemically and biologically significant compounds. The syntheses of sulfones have been extensively described by Schank,[9] in his review, and new, independent reports concerning the modification and optimization of these types of important reactions have also appeared.[10–19]

Relatively fewer studies, associated with the quantitative evaluation of the reactivity of arenesulfinic acids toward saturated and unsaturated electrophilic reactants, containing carbon–carbon double bond have been published so far. Ogata *et al.* studied the kinetics of nucleophilic addition of substituted arenesulfinic acids to acrylonitrile[20] as well as *p*-benzoquinone.[21,22] These reactions were found to follow second-order kinetics. The authors also found that, at pH 2–4, the rate-determining step was the addition of arenesulfinate ion to *p*-benzoquinone, whereas, at pH 4–6, addition as well as deprotonation reactions took place with commensurable rates. The basic kinetic parameters of the nucleophilic additions of *p*-substituted arenesulfinic acids to 2-haloacrylonitriles were also determined.[23] Lindberg[24] studied the kinetics of the nucleophilic substitution reactions of arenesulfinate ions with bromoacetamide and bromoacetate. The nucleophilicity of sulfinate ions was found to decrease with the introduction of electron-withdrawing groups such as chlorine atom and nitro group in the aromatic nucleus. In all cases, the interaction between bromoacetamide and *p*-substituted arenesulfinates took place at a higher rate.[24] On the other hand, the kinetic studies conducted by Jarvis and Tong[25] showed that the reactivity in the reactions of sodium benzenesulfinate with α-halo-*p*-nitrobenzyl phenyl sulfones decreased in the order $k_{Br} > k_I > k_{Cl}$, depending on the type of halogen.

A number of authors studied the interactions of arenesulfinic acids with γ-substituted allyl halides, which resulted in the formation of structurally diverse allyl phenyl sulfones.[10,15,17,26] However, information about the quantitative evaluation of these kinds of reactions was not found. The aim of the present work is associated with the kinetic studies of the reactions between some non-substituted and *p*-substituted sodium arenesulfinates with γ-functionalized allyl bromides. The effect of substituents in the reactants on the changes of basic kinetic parameters of these reactions was discussed. Moreover, comparison of the results concerning the delocalization reactivity indexes of arenesulfinate ions and γ-substituted allyl bromides was made.

EXPERIMENTAL

General remarks

All substituted and non-substituted sodium benzenesulfinates were prepared by a known procedure, employing reduction of the corresponding benzenesulfonylchlorides with 50% excess of

* *Correspondence to: S. Stoeva, Department of Organic Chemistry, Bourgas Assen Zlatarov University, 8010 Bourgas, Bulgaria. E-mail: sstoeva2001@yahoo.com*

a *G. Khamis, S. Stoeva, D. Aleksiev Department of Organic Chemistry, Bourgas Assen Zlatarov University, 8010 Bourgas, Bulgaria*

sodium sulfite.[17,27] 4-Bromo-2-butenenitrile was prepared according to the procedure described by Masuyama *et al*.[26] 1,3-Dibromopropene was obtained by dehydrobromination of 1,2,3-tribromopropane in the presence of sodium hydroxide.[28] The compounds thus synthesized were characterized by elemental analysis and IR spectroscopy. Elemental microanalyses were performed using a *Carlo Erba 1104* instrument (Italy). Infrared spectra were recorded with a *Specord 75 IR* instrument (Germany). The samples were either prepared as KBr pellets or pressed between NaCl plates as neat films. The absorption of adducts, formed due to the interaction of sodium benzenesulfinates with *p*-benzoquinone was determined at room temperature in aqueous-ethanol medium by using a UV-Vis spectrophotometer (Germany). Absorption maxima at 322–324 nm were registered for all the adducts.

Rate measurements

The reaction mixture, containing an aqueous solution of sodium arenesulfinate (8 ml, 1 mmol), γ-functionalized allylic bromide (1 mmol), dissolved in ethanol (8 ml) as well as glacial acetic acid (0.06 ml, 1.05 mmol) was placed into a glass tube. Sodium arenesulfinates were prepared by the interaction of equimolar amounts of arenesulfinic acids with sodium hydroxide, dissolved in double-distilled water. The glass reactor was placed into a thermostat to maintain the temperature between 308 and 333 K, ($\pm$0.1 K accuracy). Aliquots of 0.1 ml were periodically taken for each of the eight experimental points. They were transferred into 50 ml flasks, cooled in ice water. Glacial acetic acid (0.1 ml) and water–ethanol solution (2 ml, 1:1 volume ratio) of *p*-benzoquinone (1 mmol) were also added. The flask was then thermostated at 293 K for 20 min, and a constant volume of the solution (50 ml) was maintained therein.

Due to the rapid interaction of unreacted arenesulfinic acids with *p*-benzoquinone, a change of the light-yellow color of the solution in the flask was observed. The corresponding adducts such as 2,5-dihydroxy-4′-substituted diphenyl sulfones were thus obtained. The reaction took place at a high velocity at room temperature (293–298 K) in a water–ethanol medium and at pH 2–4.[21,22] In this particular case, pH was maintained to be within 3.17–3.63 by using an acetate buffer. Following the absorption measurements for the adducts by employing a UV-spectrophotometer with absorbance maxima registered within 322–324 nm, the concentrations of the unreacted arenesulfinic acids were determined by means of a standardized linear dependence method as reference.[29] Four parallel runs were conducted for each experimental point. The accuracy of UV-analysis when determining the current concentrations of arenesulfinic acids for the experimental series studied changed within the 0.025–0.029% range.

The experimentally obtained results, concerning the changes in the concentrations *versus* the time of their interaction with 4-bromo-2-butenenitrile and 1,3-dibromopropene, respectively, were processed by employing the integral method for the kinetic evaluation of homogeneous liquid-phase reactions in a batch reactor at several constant temperatures.[30,31] These results were found to be in good agreement with a second-order kinetics model. The correlation coefficient values exceeded 0.988, which proved with a good approximation the linear dependences. Verification of the adequacy of the kinetic equation with respect to the experimental data was conducted by applying the *Fisher* criterion (F_{exp}), according to the equation:[30,31]

$$F_{exp} = \frac{\hat{s}_C^2}{s_C^2} \quad (1)$$

where s_C^2 is the dispersion of reproducibility, measured in mol^2 L^{-2}; and $\hat{s}_C^2$ is the dispersion of adequacy in mol^2 L^{-2}.

The values of the dispersion of reproducibility for the corresponding experimental series are presented in Table 1.

The *Fisher* criterion was calculated for each of the reactions at temperatures corresponding to the middle of the interval in which these reactions were conducted, and at a level of significance $\alpha = 0.05$. Observing this value of α has been recommended for studying and evaluating organic reactions.[30,31] The experimental values of *Fisher* criterion (F_{exp}) were found to be lower than the reference (tabulated) value (F_{table}), which, in this case was set at 8.941.[31]

Kinetic processing of the experimental results

Integral processing of experimental data was conducted, applying the well-known second-order kinetics equation $r = kC_AC_Y$, with the first order toward each of reactants (sodium arenesulfinates and 4-bromo-2-butenenitrile or 1,3-dibromopropene). At $C_{Ao} = C_{Yo}$ and stoichiometric coefficients equaling unity, this equation can be expressed as follows:[30,31]

$$\frac{1}{C_{Ao}} = \frac{1}{C_{Ai}} + k\tau \quad (2)$$

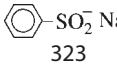
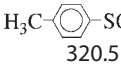
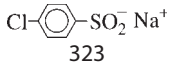
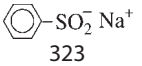
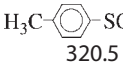
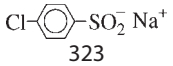
where C_{Ao} is the initial concentration of the corresponding arenesulfinic acid, in mol L^{-1}; C_{Ai} is the current concentration of the reacted arenesulfinic acid, in mol L^{-1}; k is the second-order rate constant, in L mol^{-1} min^{-1}; and τ is the reaction time, in minutes.

To determine the activation parameters of the studied reactions, Arrhenius and Eyring equations were used. [32–34]

Calculation of electronic descriptors

Molecular geometries of the corresponding sodium benzenesulfinates, benzenesulfinic acids, 4-bromo-2-butenenitrile, and

Table 1. Values of the dispersion of reproducibility (s_C^2) and *Fisher* criterion (*F*exp) calculated at *T*av for the reaction of sodium arenesulfinates with 4-bromo-2-butenenitrile and 1,3-dibromopropene

Substrates	Br—CH$_2$—CH=CH—C≡N			Br—CH$_2$—CH=CH—Br		
Nucleophiles						
T (K)	323	320.5	323	323	320.5	323
s_C^2	$4.71 \cdot 10^{-12}$	$2.54 \cdot 10^{-13}$	$9.33 \cdot 10^{-13}$	$2.47 \cdot 10^{-13}$	$1.67 \cdot 10^{-11}$	$1.34 \cdot 10^{-12}$
F_{exp}	1.993	3.025	3.657	2.965	3.072	3.266

1,3-dibromopropene were optimized. Then the quantum-chemical descriptors were calculated using the AM1 Hamiltonian method of the MOPAC 93 program, a semi-empirical molecular modeling routine.[35,36] The following local electronic descriptors were determined: donor superdelocalizibility of a sulfur atom (SE(S)) of arenesulfinate ions (Y-C_6H_4-SO_2^-, where Y = H, CH_3, or Cl); acceptor superdelocalizability of an allylic carbon atom (SN(C_{allyl})) in 4-bromo-2-butenenitrile and 1,3-dibromopropene, respectively; charges of a sulfur atom (q(S)) and those of an allylic carbon atom (q(C_{allyl})) for the same reactants; the partial electron density of C_{allyl} on the lowest unoccupied molecular orbital (LUMO) in substrates (fN(C_{allyl})). Higher values of SE and SN corresponded to stronger nucleophilicity and electrophilicity of the atomic reaction centers, respectively.[37]

RESULTS AND DISCUSSION

Interaction of sodium benzenesulfinates with γ-functionalized allyl bromides gives rise to the formation of substituted allyl phenyl sulfones, according to Scheme 1.

The reaction was conducted in a slightly acidic water–alcohol medium,[17] in order to prevent the possible isomerization of allyl phenyl- to vinyl phenyl sulfones.[38] It may be assumed that the substitution of bromine at the allylic (C_{allyl}) carbon atom by the corresponding arenesulfinate ion occurs according to S_N2-mechanism. The following considerations supporting this assumption are put forward: (i) primary allylic halides participate in the reaction with a reaction center (C_{allyl}), which is structurally similar to that of primary haloalkanes, and no steric hindrances are involved;[39,40] (ii) the presence of electron-withdrawing substituents such as CN and Br in the molecular structure of substrates could hamper the formation of stable allyl cations in accordance with S_N1-type mechanism but, on the other hand, would significantly increase the electrophilicity of C_{allyl} in the S_N2-type reaction, particularly, in the presence of a cyano group; and (iii) in the experimentally prepared sulfones, no rearrangement products were detected; the presence of only products of direct allylic substitution was actually proved.[17] What is more, for the interaction of sodium benzenesulfinates with highly functionalized primary (*Z*)-ketoallyl halides, Kotti *et al.*[41] have also described that, in similar cases, S_N2 nucleophilic substitution reactions take place.

The implementation of this reaction in polar medium was a prerequisite for the full dissociation of sodium arenesulfinates. The strong acidity of arenesulfinic acids is well known. They are completely dissociated in water, except at high acidities.[42] For example, p*K*a values of benzenesulfinic, *p*-toluenesulfinic, and *p*-chlorobenzenesulfinic acids determined in water at 298 K are 1.45, 1.55, and 1.15, respectively.[22] Moreover, the effective formation of hydrogen bonds between solvents containing hydroxyl groups such as a mixture of ethanol and water, and the negatively charged oxygen atoms in the sulfinate ions left the sulfur atom as the only nucleophilic center, which was determined by its unshared electron pair.[33,42] Both the low electronegativity and facile polarizability of the sulfur atom caused its effective bonding to the electrophilic reaction site (C_{allyl}), according to the principles of interaction between 'soft' bases and acids.[39] As a result, the final products were the corresponding sulfones, formed in accordance with Scheme 1. Their composition and structure were confirmed previously by elemental microanalysis, IR, ^{1}H NMR, and ^{13}C NMR.[17]

The kinetic studies, accompanying the preparation of allyl phenyl sulfones described above, were conducted at the temperature interval of 308–333 K. The changes in the concentration of arenesulfinic acids *versus* reaction time during their interaction with 4-bromo-2-butenenitrile and 1,3-dibromopropene at 323 K are shown in Figs 1 and 2, respectively. Similar kinetic curves were also obtained for each of the reaction temperatures at 70–94% conversion of arenesulfinic acids. The experimental data processing was performed, by employing the well-known second-order kinetics equation, i.e., the first order with respect to each of the reactants. The assumption of such a kinetic model was based on the suggested synchronic reaction mechanism, with the participation of both the reactants in the formation of an activated complex. The validation of the kinetic equation for this bimolecular process was conducted by determination of the experimental values of the *Fisher* criterion (F_{exp}) for each of the reactions (Table 1) and its comparison with the corresponding tabular value, which, in this case, was $F_{table} = 8.941$. This value was 2.5–3 times as high as the experimental one, which corresponded well to the $F_{exp} \leq F_{table}$ requirement.[30,31] Therefore, the

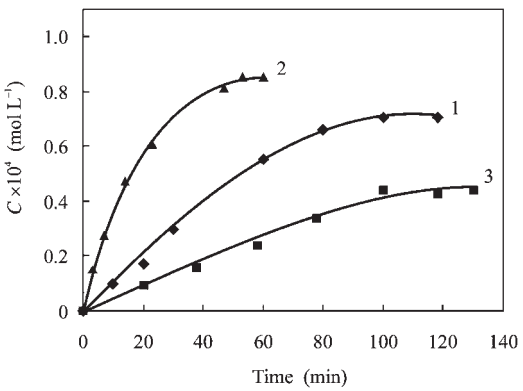
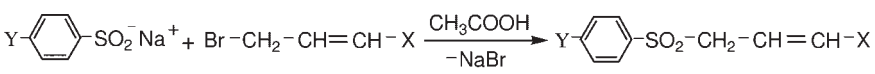


Figure 1. Time dependence of the concentrations of benzenesulfinic acid (1), *p*-toluenesulfinic acid (2), and *p*-chlorobenzenesulfinic acid (3) for their interaction with 4-bromo-2-butenenitrile at 323 K



1 **2** **3**

X	CN	CN	CN	Br	Br	Br
Y	H	*p*-CH_3	*p*-Cl	H	*p*-CH_3	*p*-Cl
3	**a**	**b**	**c**	**d**	**e**	**f**

Scheme 1. Synthesis of substituted allyl phenyl sulfones

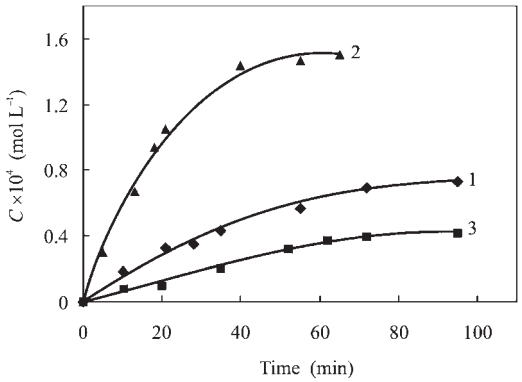


Figure 2. Time dependence of the concentrations of benzenesulfinic acid (1), *p*-toluenesulfinic acid (2), and *p*-chlorobenzenesulfinic acid (3) for their interaction with 1,3-dibromopropene at 323 K

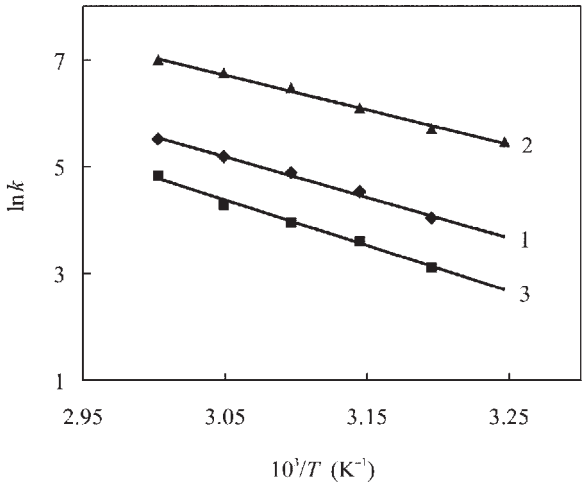


Figure 3. Arrhenius plots for the interaction of benzenesulfinic acid (1), *p*-toluenesulfinic acid (2), and *p*-chlorobenzenesulfinic (3) with 4-bromo-2-butenenitrile

suggested second-order kinetic equation adequately described the experimental results obtained.

The values of the rate constants *k*, as a function of temperature are presented in Table 2. The rate constants had relatively high values, which is usually observed for S_N2 reactions in allylic systems.[39] Moreover, the temperature elevation of 10° within the 308–333 K intervals resulted in a two- to threefold increase in the corresponding *k*-values. This trend was more clearly pronounced for those experimental series, in which nucleophiles of lower reactivity such as *p*-chlorobenzenesulfinate ion had participated. Such a trend was in agreement with the basic mathematical formalism of the Arrhenius equation.[32]

Based on the Arrhenius plot of rate constants as shown in Figs 3 and 4 for the two experimental series, the values of the activation energy E_A and the pre-exponential factor (*A*) were determined (Table 3). The corresponding values of the changes in entropy, enthalpy, and free energy for the formation of the activated complex from the reactants, participating in the S_N2-reactions are also listed in Table 3. The lowest values of these parameters were observed for the reaction of the *p*-toluenesulfinate anion with both the 4-bromo-2-butenenitrile and 1,3-dibromopropene. Apparently, this resulted from the hyperconjugation effect, involving both the methyl group and benzene nucleus, which led to a more effective conjugation between the π-electrons of the

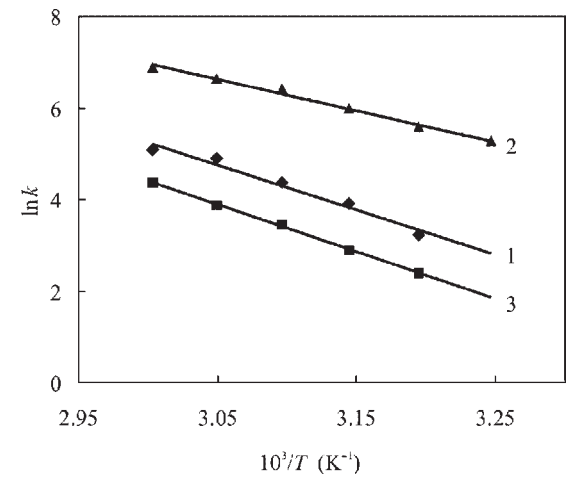


Figure 4. Arrhenius plots for the interaction of benzenesulfinic acid (1), *p*-toluenesulfinic acid (2), and *p*-chlorobenzenesulfinic (3) with 1,3-dibromopropene

Table 2. Values of the rate constants *k* (L mol^{-1} min^{-1}) at different temperatures for the reaction of non-substituted and *p*-substituted sodium arenesulfinates with 4-bromo-2-butenenitrile and 1,3-dibromopropene

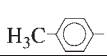
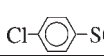
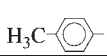
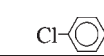
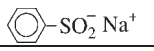
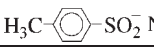
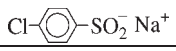
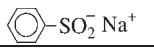
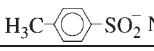
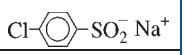
	Rate constants, *k* (L mol^{-1} min^{-1})					
Substrates	Br—CH_2—CH=CH—C≡N			Br—CH_2—CH=CH—Br		
Nucleophiles						
308 K	—	232.2 ± 10.6	—	—	193.3 ± 1.4	—
313 K	56.3 ± 2.4	301.9 ± 5.9	22.6 ± 1.1	25.4 ± 1.2	265.9 ± 3.6	11.4 ± 0.1
318 K	91.8 ± 2.8	434.2 ± 10.9	36.9 ± 1.7	49.9 ± 1.7	397.4 ± 15.8	18.3 ± 0.7
323 K	130.5 ± 4.5	638.3 ± 25.6	52.8 ± 2.6	78.4 ± 2.4	609.1 ± 15.9	31.9 ± 1.5
328 K	178.6 ± 7.7	851.2 ± 30.1	72.4 ± 2.7	132.9 ± 3.3	772.2 ± 21.2	47.9 ± 2.6
333 K	248.4 ± 10.5	1084.1 ± 28.1	124.6 ± 6.1	163.3 ± 7.7	965.6 ± 38.6	78.1 ± 1.6

Table 3. Basic kinetic parameters of the reaction of non-substituted and *p*-substituted sodium arenesulfinates with 4-bromo-2-butenenitrile and 1,3-dibromopropene

Substrates	Br—CH_2—CH=CH—C≡N			Br—CH_2—CH=CH—Br		
Nucleophiles						
E_A (kJ mol^{-1})	63.09 ± 0.02	54.04 ± 0.04	70.77 ± 0.02	81.45 ± 0.06	56.59 ± 0.12	84.94 ± 0.01
A (min^{-1})	$2.01 \cdot 10^{12}$	$3.32 \cdot 10^{11}$	$1.48 \cdot 10^{13}$	$1.11 \cdot 10^{15}$	$7.75 \cdot 10^{11}$	$1.65 \cdot 10^{15}$
$\Delta S^{\neq}$ (J mol^{-1} K^{-1})	−52.40 ± 0.11	−67.32 ± 0.10	−35.81 ± 0.14	0.096 ± 0.002	−60.26 ± 0.16	3.40 ± 0.03
$\Delta H^{\neq}$ (kJ mol^{-1})	60.41 ± 0.02	51.40 ± 0.04	68.09 ± 0.02	78.77 ± 0.06	53.95 ± 0.12	82.26 ± 0.01
$\Delta G^{\neq}$ (kJ mol^{-1})	77.33 ± 0.01	72.80 ± 0.17	79.66 ± 0.12	78.74 ± 0.08	73.12 ± 0.05	81.16 ± 0.02
p	$1.83 \cdot 10^{-3}$	$3.05 \cdot 10^{-4}$	$1.35 \cdot 10^{-2}$	1.01	$7.12 \cdot 10^{-4}$	1.51

ring and sulfinate ions, and, also, enhanced their nucleophilicity. The higher nucleophilicity of the sulfur atom in *p*-toluenesulfinate anion was also confirmed by its higher donor superdelocalizability (SE(S) = 0.2496 (a.u.)^2/eV), as compared to that of benzenesulfinate and *p*-chlorobenzenesulfinate ions (Table 4). Among the sulfinate ions explored, the weakest nucleophilic center was established at the sulfur atom in sodium *p*-chlorobenzenesulfinate, which was associated with the electron-withdrawing inductive effect of chlorine atom, making the benzene ring 'more positive',[40] and hampering the conjugation to the sulfonyl group.

Substituents such as the cyano group and bromine atom, located at γ-position toward the reaction center in the substrates markedly influenced the reactivity of C_{allyl} therein. As seen from Table 2, the rate constant values for the interaction of both the non-substituted and *p*-substituted arenesulfinates with 4-bromo-2-butenenitrile were higher than those for the corresponding interaction with 1,3-dibromopropene. This is apparently associated with the enhanced C_{allyl}-type electrophilicity of 4-bromo-2-butenenitrile under the influence of both the negative inductive and resonance effects of the cyano group. Such an influence of bromine, attached to vinyl group in 1,3-dibromopropene, was not observed, since its negative inductive effect was, at least partially, compensated by the positive resonance one, which led to a lower electrophilicity of the reaction center (C_{allyl}). The difference in the substrate reactivity was particularly well pronounced in their interaction with benzenesulfinate and *p*-chlorobenzenesulfinate anions. In this case, the *k*-values for 4-bromo-2-butenenitrile were 1.50–2.24 times as high as those determined for 1,3-dibromopropene as substrate.

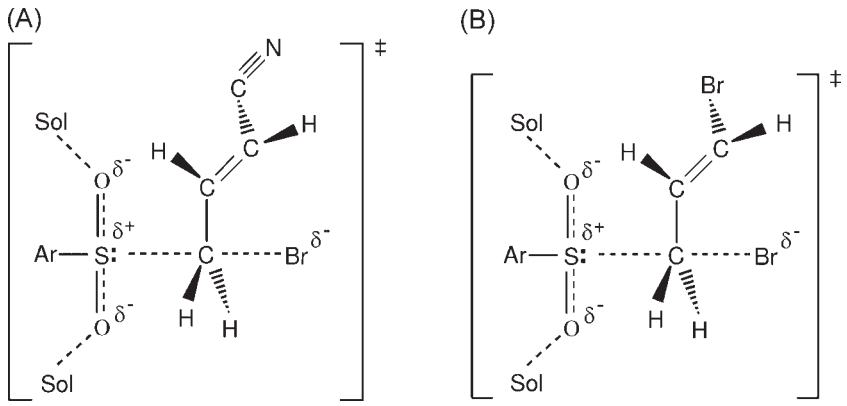
Table 4. Reactivity indices of arenesulfinate ions

	Arenesulfinate ions	
Y-C_6H_4-SO_2H	SE(S) (a.u.)^2/eV	q(S) (a.u.)
H	0.2444	1.4824
p-CH_3	0.2496	1.4768
p-Cl	0.2419	1.4808

The delocalization reactivity indexes of substrates (4-bromo-2-butenenitrile and 1,3-dibromo-propene) are presented in Table 5. Regardless of the fact that higher values of the acceptor superdelocalizability of C_{allyl} in 1,3-dibromopropene were determined (SN(C_{allyl}) varied from 0.2475 to 0.2612 (a.u.)^2/eV), compared to 4-bromo-2-butenenitrile (SN(C_{allyl}) varied from 0.2374 to 0.2468 (a.u.)^2/eV), the reactivity of the former chemical was lower. Moreover, the atomic charges at the electrophilic site (q(C_{allyl})) in these substrates differed slightly and could not explain and define the differences in their reactivity. However, the lower minimum and maximum values of the partial electron density of C_{allyl} at the lowest unoccupied molecular orbital (LUMO) in 4-bromo-2-butenenitrile (fN(C_{allyl})), compared to those in 1,3-dibromopropene (Table 5), obviously determined the easier formation of its bond with sulfur in the corresponding arenesulfinate ion. Therefore it could be assumed that the interaction between sodium arenesulfinates and γ-substituted allyl bromides was more likely to be determined by orbital factors, rather than by factors associated with the electronic charge. This originated from the fact, that, in the activated complex, a bond between the 'soft' nucleophilic center (S-atom in the reagents) and the 'soft' electrophilic center (C_{allyl} in substrates) was formed. In such cases, the LUMO of the electrophilic center should possess a relatively low energy.[33] On the other hand, the lower

Table 5. Reactivity indices of 4-bromo-2-butenenitrile (1) and 1,3-dibromopropene (2)

		SN(C_{allyl}) ((a.u.)^2/eV)		q(C_{allyl}) (a.u.)		fN(C_{allyl}) (eV)	
No.	Compound	min.	max.	min.	max.	min.	max.
1	Br—CH_2—CH=CH—CN	0.2374	0.2468	−0.2026	−0.2132	−0.0273	−0.3263
2	Br—CH_2—CH=CH—Br	0.2475	0.2612	−0.1946	−0.2042	−0.0422	−0.4335



Scheme 2. Types of activated complexes formed in the interaction of arenesulfinate ions with 4-bromo-2-butenenitrile (A) and 1,3-dibromopropene (B)

enthalpies of activation for the interaction of arenesulfinate ions with 4-bromo-2-butenenitrile ($\Delta H^{\neq} = 51.40–68.09$ kJ mol^{-1}), compared to those with 1,3-dibromopropene ($\Delta H^{\neq} = 53.95–82.26$ kJ mol^{-1}) (Table 3) indicated the higher stability of the activated complexes of the S_N2-reaction with the participation of the former substrate (Scheme 2).

In this particular case, the stability of the complex **A** was not only determined by the possibility of conjugation of the allylic π-electron system with the *p*-orbital of the reaction center (C_{allyl}),[39,43] but, also, by its conjugation with the π-electrons of the cyano group.

In the course of interaction of benzenesulfinate and *p*-chlorobenzenesulfinate ions with 1,3-dibromopropene as a substrate of reduced electrophilicity at the reaction center (C_{allyl}), an increase in the entropy of activation (slightly positive values) was observed (Table 3). A decrease in the electrophilicity of C_{allyl} in 1,3-dibromopropene favors the formation of a late transition state with these neutral S-nucleophiles, associated with a long S—C bond. The change in the entropy of activation in that case could be related to the change in the transition state of the S_N2-reactions studied,[44] more particularly, from the early formation of the transition state with entropy-controlled reactivity to the late formation of transition state with enthalpy-controlled reactivity.

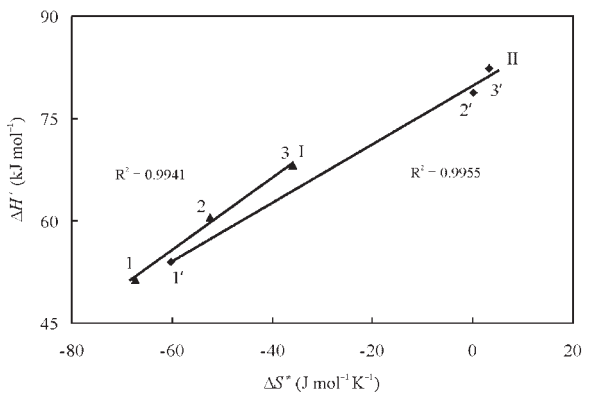


Figure 5. Compensation plots ($\Delta S^{\neq}$ *vs.* $\Delta H^{\neq}$) for the interaction of *p*-toluenesulfinic acid, benzenesulfinic acid, and *p*-chlorobenzenesulfinic acid with 4-bromo-2-butenenitrile (line I, points 1, 2, 3) and 1,3-dibromopropene (line II, points 1′, 2′, 3′)

The steric factor *p* values correlated with the entropy changes during the formation of the activated complex (transition state). The lower negative $\Delta S^{\neq}$-values, and, the lower *p*-values suggest the rapid formation of the activated complex between reactants. This is particularly well pronounced for the interaction of the *p*-toluenesulfinate anion with both the 4-bromo-2-butenenitrile and 1,3-dibromopropene. Based on the *p*-values shown in Table 3, it could be assumed that, with the interactions of any of the reagents with the corresponding substrates, the electrophilicity of the reaction center (C_{allyl}) in the latter plays a determining role.

Plots of $\Delta H^{\neq}$ *versus* $\Delta S^{\neq}$ for the two experimental series gave straight lines (Fig. 5). Hence, the reactions of arenesulfinates with 4-bromo-2-butenenitrile (line I) and 1,3-dibromopropene (line II) were characterized by the isokinetic relationship or kinetic compensation effect.[44] The values of the corresponding isokinetic temperatures β(I) = 528 K and β(II) = 430 K were higher than the experimental temperature range (308–333 K).

CONCLUSIONS

The kinetics of the nucleophilic substitution reaction of sodium arenesulfinates with γ-functionalized bromides was studied. The principal kinetic and thermodynamic parameters associated with these reactions such as *k*, E_A, *A*, *p*, $\Delta H^{\neq}$, $\Delta S^{\neq}$ и $\Delta G^{\neq}$ were determined. On the basis of their values, it can be assumed that sodium *p*-toluenesulfinate had the highest reactivity for the interaction with any of the substituted allyl bromides. On the other hand, bromine atom bound to C_{allyl} in 4-bromo-2-butenenitrile was replaced by the corresponding arenesulfinate anion at a reaction rate, about twice as high as that associated with the similarly bound bromine atom in 1,3-dibromopropene. Juxtaposition of the data from the kinetic studies, obtained with the involvement of some local electron reactivity indexes of sodium arenesulfinates and γ-substituted allylbromides was also made.

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