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Activation and reaction volumes of the reactions of *o*- and *p*-nitrophenylsulfenyl chlorides with styrene and cyclohexene in some solvents

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The effect of hydrostatic pressure below 1000 kg cm^{-2} on the rate of reactions of *o*- and *p*-nitrophenylsulfenyl chlorides with styrene and cyclohexene was studied. The activation and reaction volumes (cm^3 mol^{-1}) for the reactions of *o*-nitrophenylsulfenyl chloride with styrene in acetonitrile (−23.1 and −23.6), 1,2-dichloroethane (−29.2 and −24.7), chlorobenzene (no, −20.2), and anisole (−25.1 and −21.2) and for the reaction of *p*-nitrophenylsulfenyl chloride with styrene in carbon tetrachloride (−39.5±1.5 and −22.0) were determined. In carbon tetrachloride the activation volumes for the reactions of cyclohexene with *o*- and *p*-nitrophenylsulfenyl chlorides (−37.7±2.0 and −40.9±1.2 cm^3 mol^{-1}, respectively) are almost the same and coincide with the data for the reactions with styrene. The considerable decrease in the volume of the transition state in the nonpolar solvent is considered as a consequence of the enhanced electrostriction of carbon tetrachloride in the solvate sphere of the transition state of the reaction, which excludes the nonpolar transition state of the sulfuran type.

Key words: *o*-nitrophenylsulfenyl chloride, styrene, activation volumes, reaction volumes, solvent effect, mechanism.

Complex investigation of the nonpolar Diels—Alder reaction free of electrostriction of the medium during solvation of the transition state made it possible to find that in the series of solvents a noticeable change in the activation or reaction volume is observed only for strong specific interactions of the reactants with the medium.[1,2] It has been shown additionally for the Diels—Alder reaction that the higher volume parameters are observed for the processes involving small, "loosen" reactants with the low packing coefficient in solution.[3,4] Their transition to the activated complex or adduct is always accompanied by a considerable increase in the packing coefficient. The van der Waals activation ($\Delta V^{\neq}_{W}$) and reaction (ΔV_{W}) volumes are often by 2—3 times lower by modulus than the observed volume parameters in solution ($\Delta V^{\neq}$ and ΔV) due to a large contribution of the change in the volume of intermolecular holes in solution. The experimental confirmation has been obtained recently[5] from comparison of the reaction volumes in the solid phase and in solution. It has been shown[6] for lithium perchlorate used as a model of the ion state that the change in the partial molar volume (PMV) due to electrostriction of the solvent reaches tens of cubic centimeters per mole, resulting in even negative PMV value in acetone (−2 cm^3 mol^{-1}). The activation and reaction volumes can be determined from the equations

$$-RT(\partial \ln k/\partial p)_T = (\partial G^{\neq}/\partial p)_T = \Delta V^{\neq} = \Delta V^{\neq}_{W} + \Delta V^{\neq}_{sol}, \quad (1)$$

$$-RT(\partial \ln K/\partial p)_T = (\partial G/\partial p)_T = \Delta V = \Delta V_{W} + \Delta V_{sol}, \quad (2)$$

where $\Delta V^{\neq}_{sol}$ and ΔV_{sol} are the parameters of the solvent.

Taking into account the aforesaid, we should expect low $\Delta V^{\neq}_{W}$ and ΔV_{W} values and their differences for both polar and nonpolar processes. More substantial contributions to the observed $\Delta V^{\neq}$ and ΔV values and their differences are formed due to a change in the solvent packing ($\Delta V^{\neq}_{sol}$ and ΔV_{sol}), especially in the solvate shell of charged states.

Considerable attention was given to studying the elevated pressure effect on the rate of the Menschutkin reaction between the reactants of different structure with different degrees of steric screening of the reaction center and in media with different polarity.[7,8] In the case of the amino-substituted substrates, the transition state always contains localized (to more or less extent) charges achieving the limiting value in the reaction product. Electrophilic addition (Ad_E) of arylsulfenyl chlorides to unsaturated compounds is characterized by the reliable estab-

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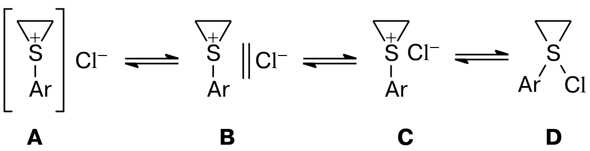
lished features: the interaction affords β-halogenthio esters due to *trans*-addition; the reaction rate depends strongly on the medium polarity; the addition is not accompanied by rearrangement; nucleophilic solvents do not compete with the halide ion and form no solvoadducts.[9—17] The proposed[9] mechanism of the interaction with intermediate formation of the episulfonium ion (**A**, Scheme 1) agrees with the high sensitivity of the reaction rate to the solvent polarity, and the subsequent ring opening upon the nucleophilic attack by the chloride ion results in the experimentally observed *trans*-addition product.

Scheme 1

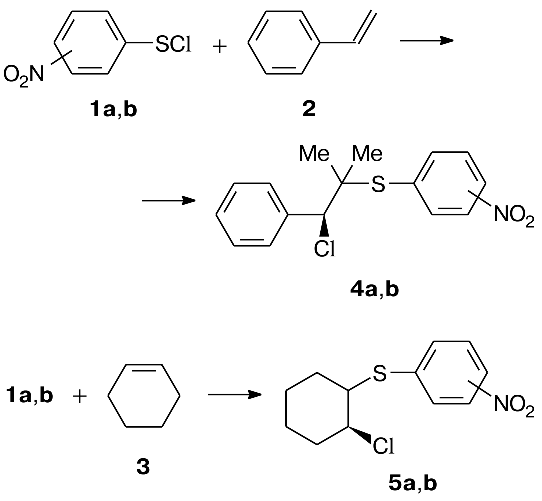


The episulfonium complexes (ESC) are rather stable,[10—12,14,17] especially at low temperature with the counterions such as the BF_4^-, 2,4,6-$(NO_2)_3C_6H_2SO_3^-$, and $SbCl_6^-$ type.

As in the reaction of arylsulfenyl chlorides with alkenes, these salts react readily with nucleophiles to form *trans*-addition products,[10—12,14] which allows them to be considered as intermediates. However, already at room temperature the ESC can include stereoconversion, nucleophiles can add to the ESC obtained from strained cycloalkenes, and the skeletal rearrangement and competitive formation of solvoadducts can occur, which is not observed in the reaction itself. Covalent sulfuran (**D**) agrees better than episulfonium intermediates (**A**, **B**, **C**) with such characteristics of the reaction as *trans*-addition and the absence of skeletal rearrangements and competitive solvoadducts. Anyway, it is still difficult to understand the strong effect of the solvent polarity on the reaction rate. On going from hexane to acetonitrile, the reaction rate constant increases more than by six orders of magnitude.[15] To explain all features of the reaction, one can invoke the change in its mechanism to include[14,17] the whole set of polar and nonpolar structures (see Scheme 1). When the stabilizing factors (favorable electronic effects of substituents in the reactant and substrate, high solvation energy) are strongly supported, the formation of the episulfonium ion (**A** or **B**) is energetically justified. In the case of weak stabilization, the transition state coordinate should shift toward a low-polarity product. How can be checked experimentally the probability that the transition state formed from the episulfonium salt (**A** or **B**) or contact ion pair (**C**), or low-polarity sulfuran with covalent bonds (**D**) is transformed indeed depending on the properties of the reactants or medium polarity? In our opinion, the activation volume of the reaction in nonpolar and polar media can be most informative. High charge separation is retained for the reaction in any media, whereas the contribution of electrostriction in nonpolar solvents should be much larger than that in polar media.[1,8,18,19] If the transition state is formed from the episulfonium complex (**A** or **B**) in polar solvents and from sulfuran (**D**) in nonpolar solvents, then no electrostriction in the solvate sphere of the transition state should be expected.

In the present work, we studied the reactions of *o*- (**1a**) and *p*-nitrophenylsulfenyl chlorides (**1b**) with styrene (**2**) and cyclohexene (**3**) in some solvents at 25 °C and under pressures below 1000 kg cm^{-2}.

Scheme 2



Rather high exothermicity of the reaction **1a** + **2** determined by us using the calorimetric method (−74.9 kJ mol^{-1}, acetonitrile, 25 °C) virtually excludes equilibrium of the process under working conditions and possible difficulties in determination of the rate constants. These data agree with the absence of the competitive reaction of redistribution between the addition product and high excess cyclohexene.[11]

The experimental data on the pressure effect on the reaction rate constants in the studied media are collected in Table 1.

The rate of the reaction **1a** + **2** in carbon tetrachloride turned out to be very low ($k_2 \le 1 \cdot 10^{-6}$ L mol^{-1} s^{-1}) and unsuitable for spectrophotometric study in the optical bomb and, therefore, kinetic measurements were carried out for more reactive *p*-isomer **1b** (see Table 1). At the same time, the rate of the reaction of sulfenyl chlorides **1a**,**b** with cyclohexene in polar media turned out to be too high, which is inconvenient for observation in a barostat.

Table 1. Rate constants (k_2/L mol^{-1} s^{-1}) of some Ad$_E$2 reactions under elevated pressure (p/kg cm^{-2}) in the series of solvents at 25 °C

Acetonitrile		1,2-Dichloroethane		Anisole		Carbon tetrachloride					
p	$k_2 \cdot 10^2$ [a]	p	$k_2 \cdot 10^3$ [a]	p	$k_2 \cdot 10^4$ [a]	p	$k_2 \cdot 10^4$ [b]	p	$k_2 \cdot 10^2$ [c]	p	$k_2 \cdot 10^5$ [d]
0	4.44	0	2.13	0	1.77	0	4.93	0	2.01	0	1.53
0	4.58	160	2.65	0	1.73	145	6.90	203	2.91	0	1.57
200	5.19	290	3.08	150	2.05	250	7.44	325	3.85	464	3.18
285	5.94	370	3.46	295	2.51	295	8.60	386	4.11	546	4.03
397	6.58	515	4.31	450	2.65	325	8.66	520	4.89	867	5.72
475	6.54	630	4.60	500	2.77	325	8.78	564	5.58	930	7.03
507	7.72	770	5.68	573	3.12	495	10.4	763	7.83	936	7.28
695	9.26	960	7.03	685	3.32	515	12.4	852	8.78		
797	9.78			765	4.17	570	12.3				
953	12.03			813	4.22	905	22.9				
				980	4.93	960	26.0				
$\ln k_2 = -3.124 +$ $+ 0.001030p$ $(r = 0.9922)$; $\Delta V^{\neq}_{exp} = -26.0\pm0.8$		$\ln k_2 = -6.136 +$ $+ 0.00124p$ $(r = 0.9982)$; $\Delta V^{\neq}_{exp} = -31.3\pm0.8$		$\ln k_2 = -8.656 +$ $+ 0.001040p$ $(r = 0.9881)$; $\Delta V^{\neq}_{exp} = -26.3\pm1.4$		$\ln k_2 = -7.596 +$ $+ 0.001670p$ $(r = 0.9956)$; $\Delta V^{\neq}_{exp} = -42.2\pm1.5$		$\ln k_2 = -3.877+$ $+ 0.001726p$; $(r = 0.9977)$; $\Delta V^{\neq}_{exp} = -43.6\pm0.8$		$\ln k_2 = -11.069 +$ $+ 0.001599p$; $(r = 0.9969)$; $\Delta V^{\neq}_{exp} = -40.4\pm0.8$	

[a] For reaction **1a** + **2**.
[b] For reaction **1b** + **2**.
[c] For reaction **1b** + **3**.
[d] For reaction **1a** + **3**.

However, the reactions in carbon tetrachloride are favorable. As follows from the data in Table 1, in this medium the activation volumes of all reactions studied are virtually the same. The observed values of the activation volumes were calculated from Eq. (1). The volume parameters of the studied reactions and compressibility of some solvents are collected in Table 2.

The experimental values of the activation volumes ($\Delta V^{\neq}_{exp}$) were corrected to the contribution of the reaction rate change under pressure due to the increase in the reactant concentration upon compression of solutions ($\Delta n\beta_T RT$). The data obtained on the medium effect on the activation and reaction volumes allow one to make some conclusions. First, the reaction volumes (**1a** + **2**, see Table 2) in media with different polarities are rather constant (−22.3±1.4 cm^3 mol^{-1}), which agrees with the low polarity of the reactants and products. Second, the strong increase in the electrostriction of the solvent in the transition state of the reaction (see Table 2) is proportional to the change in the baric dielectric constant of the solvent**[18]** ($\partial\varepsilon^{-1}/\partial p$, see Table 2). These results contradict the assumption on the nonpolar (**D**) type of the transition state of the reaction under study. Moreover, the sharp decrease in the partial molar volume of the transition states of the reactions **1b** + **2**, **1b** + **3**, and **1a** + **3** in carbon tetrachloride corresponds to strong electrostriction of this

Table 2. Rate constants (k_2/L mol^{-1} s^{-1}) and partial molar volumes (V) for compounds **1a**, **2**, and **4a**; reaction volumes (ΔV) and activation volumes ($\Delta V^{\neq}$/cm^3 mol^{-1}), compressibility coefficients (β_T), and baric dielectric constants ($\partial\varepsilon^{-1}/\partial p$) in some solvents at 25 °C*

Solvent	k_2	V			$-\Delta V$ (**1a** + **2**)	$-\Delta V^{\neq}$	$\beta_T \cdot 10^6$	$\partial\varepsilon^{-1}/\partial p \cdot 10^6$
		1	**2**	**4a**				
CH_2ClCH_2Cl	$2.13 \cdot 10^{-3}$	126.9	117.4	219.6	24.7	29.2	78.8	17.9
MeCN	$4.41 \cdot 10^{-2}$	121.4	114.7	212.5	23.6	23.1	113	4.0
PhCl	$3.36 \cdot 10^{-5}$	123.4	115.9	219.1	20.2	—	74.5	13.7
PhOMe	$1.75 \cdot 10^{-4}$	125.3	115.2	219.3	21.2	25.1	66.0	13.5
CCl_4	$\leq 1\ 10^{-6}$ (**1a** + **2**)	123.1	115.6	216.7	22.0	39.5 (**1b** + **2**)	107	38
	$4.93 \cdot 10^{-4}$ (**1b** + **2**)					40.9 (**1b** + **3**)		
	$2.01 \cdot 10^{-2}$ (**1b** + **3**)					37.7 (**1a** + **3**)		
	$1.53 \cdot 10^{-5}$ (**1a** + **3**)							

* Compressibility coefficients (β_T/bar^{-1}) and baric dielectric constant ($\partial(1/\varepsilon)/\partial p$/bar^{-1}) are borrowed from Ref. 18.

solvent, which can appear only during solvation of high-polarity states.

Experimental

Arylsulfenyl chlorides **1a**,**b** (Aldrich) were purified by recrystallization from hexane; **1a**, m.p. 75—76 °C (*cf.* Ref. 20: m.p. 75 °C); **1b**, m.p. 46—47 °C (*cf.* Ref. 21: m.p. 48—49 °C). Solvents were purified by known methods.[22] Under all conditions studied (solvent, temperature, pressure), the unchanged absorption of compounds **1a**,**b** in time was checked. Spectral purity of compounds **1a**,**b** was monitored after the reaction completed from the correspondence of the residual absorption to the expected absorption of the adduct. Styrene was distilled *in vacuo* before measurements. Product **4a**, m.p. 63—64 °C (from pentane) (*cf.* Ref. 23: m.p. 55.5—57.5 °C). Found (%): C, 57.30; H, 4.03; N, 4.65. $C_{14}H_{12}ClNO_2S$. Calculated (%): C, 57.24; H, 4.12; N, 4.77. The reaction products with cyclohexene have been described earlier.[11,20] Kinetic measurements were carried out by a change in the absorption of reactants **1a**,**b** in the reaction mixture (420—445 nm, SF-46). The concentrations of styrene and cyclohexene, which do not absorb in this region, usually were 0.2 mol L^{-1} and exceeded the concentration of sulfenyl chlorides by more than 20 times. Correction to absorption of the adducts was calculated from their absorption spectra. Since additives noticeably affected the reaction rate in carbon tetrachloride, all kinetic measurements were performed at a fixed alkene concentration. The occurrence of the reaction with styrene according to Markovnikov′s rule has been proved earlier.[9] The procedure of kinetic measurements under elevated pressure has been described.[1,19] The corrected activation volume (see Table 2) was calculated from the experimental value ($\Delta V^{\neq}_{\text{exp}}$, see Table 1) and the correction ($\Delta n\beta_T RT$) to an increase in the reaction rate under pressure due to compression of the solutions:

$$\Delta V^{\neq}_{\text{corr}} = \Delta V^{\neq}_{\text{exp}} - \Delta n\beta_T RT. \qquad (3)$$

Here $\Delta n = -1$ is the change in the number of moles during the reaction, β_T is the compressibility coefficient of the solvent,[18,24] constant R = 84.78 cm^3 kg cm^{-2} K^{-1} mol^{-1}, and T is the temperature (in Kelvin).

The PMV values of compounds **1a**, **2**, and **4a** were calculated from data on the density of dilute solutions (m_A is the molality of substance A in solution) using the equation

$$(1000 + m_A M_A)/d = V_A m_A + 1000/d_0. \qquad (4)$$

The extrapolation of the dependence of $(1000 + m_A M_A)/d$ on m_A gives the value of V_A at $m_A = 0$.

The operating procedure of a DMA-602 precision densimeter has been described previously.[19] The temperature of the resonating tube was maintained constant with an accuracy of $\pm 2 \cdot 10^{-3}$ °C. In 1,2-dichloroethane the reaction volume was calculated by two methods: from the difference in PMV of the adduct and reactants (–24.7±0.4 cm^3 mol^{-1}) and using the kinetic method (–24.3±0.4 cm^3 mol^{-1}) from the dependence of the solution density in time ($1/d_{(t)}$) on the adduct concentration (c_P).

$$1/d_{(t)} = 1/d_{(t=0)} + c_P\,\Delta V_r/(1000 d_{(t=0)}). \qquad (5)$$

The enthalpy of the reaction (–74.9±1.2 kJ mol^{-1}) between reactants **1a** and **2** in acetonitrile at 25 °C was calculated from the data on the thermal effect of the reaction (–54.2±0.7 kJ mol^{-1}) when mixing a weighed sample of crystals **1a** with a styrene solution (0.021 mol L^{-1}) in the calorimeter cell (153 mL) and from the heat of dissolution (20.7±0.5 kJ mol^{-1}) of crystalline sulfenyl chloride **1a** in acetonitrile.

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