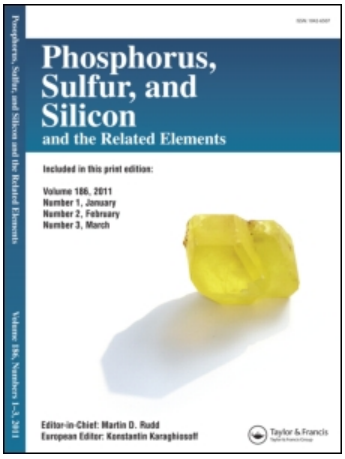


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# KINETICS OF THE INTERACTION BETWEEN 2-NITROETHENYLBENZENE AND SOME S-CONTAINING NUCLEOPHILES

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# KINETICS OF THE INTERACTION BETWEEN 2-NITROETHENYLBENZENE AND SOME S-CONTAINING NUCLEOPHILES

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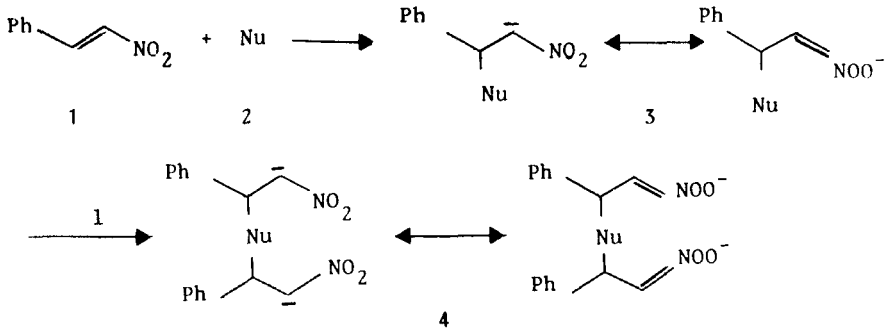
The kinetics of the reaction of 2-nitroethenylbenzene with sulfur-containing nucleophilic reagents such as sodium phenylsulfinate, sodium thiosulfate, sodium bisulfite, sodium sulfide, sodium thiophenolate, and sodium thioglycolate was studied by means of UV spectroscopy. The change in the nucleophilic reactivity of these nucleophiles depending on their basicity was studied. The reactions can be expressed by a second-order kinetic equation. Rate constants, activating energy and enthalpy of activation were calculated at 288–308 K.

*Key words:* Sulfur-containing nucleophiles, 2-nitroethenylbenzene, rate constants, activating energy, enthalpy of activation, nucleophilic reactivity.



## INTRODUCTION

A number of publications dealing with the addition of sulfinic acids,[1,2] thiophenol,[1] sodium bisulfite,[3] hydrogen sulfide[4] and thioglycolic acid[5] to 2-nitroethenylbenzene are available. The reaction of 2-nitroethenylbenzene with these nucleophiles and



| 2 | Nu | 3 | Nu | 4 | Nu |
|---|---|---|---|---|---|
| a | $PhSO_2^-$ | a | $SO_2Ph$ | a | S |
| b | $S_2O_3^{2-}$ | b | $S_2O_3Na$ | | |
| c | $SO_3^{2-}$ | c | $SO_3Na$ | | |
| d | $S^{2-}$ | d | SPh | | |
| e | $PhS^-$ | e | $SCH_2COONa$ | | |
| f | $^-OOC\text{-}CH_2\text{-}S^-$ | | | | |

TABLE I

Kinetic parameters of the addition of S-containing nucleophiles to 2-nitroethenylbenzene at 288, 293, 303, 308 K

| Nuclephile | Substrate | $k.10^{4}$ $M^{-1}s^{-1}$ | E kJ $mol^{-1}$ | $\Delta H^{\neq}$ kJ $mol^{-1}$ |
|---|---|---|---|---|
| 2a | 1 | 11.70 | 51.65 | 47.50 |
| | | 12.51 | | |
| | | 17.34 | | |
| | | 21.63 | | |
| 2b | 1 | 17.45 | 46.35 | 42.70 |
| | | 20.05 | | |
| | | 34.85 | | |
| | | 39.55 | | |
| 2c | 1 | 93.50 | 40.05 | 38.80 |
| | | 124.10 | | |
| | | 221.50 | | |
| | | 238.00 | | |
| 2d | 1 | 345.10 | 39.55 | 37.40 |
| | | 460.25 | | |
| | | 780.40 | | |
| | | 830.60 | | |
| 2e | 1 | 8310 | 36.30 | 34.75 |
| | | 10040 | | |
| | | 17650 | | |
| | | 19400 | | |
| 2f | 1 | 16500 | 34.95 | 32.35 |
| | | 19230 | | |
| | | 30060 | | |
| | | 34930 | | |

with sodium thiosulfate and sodium sulfide has not been the subject of kinetic studies. The aim of the present work was to determine the main kinetic parameters of the reactions between 2-nitroethenylbenzene and the above S-containing nucleophiles. The change in their nucleophilic reactivity depending on their basicity was also studied. The data obtained for nucleophilic addition of sulfinic acids to 2-nitroethenylbenzene[2] were taken into account in the analysis of the results.

## RESULTS AND DISCUSSION

The interaction between **2a–f** and 2-nitroethenylbenzene proceeds as a second-order reaction, first order in each reagent:

$$V = k \cdot [\text{nucleophile}] \cdot [\text{substrate}]$$

Reaction order was determined by Van't Hoff's method, and the half-time method in the concentration range 0.01–0.1 M. The linear dependences 1/[2-nitroethenylbenzene] = $f(\tau)$ were used to determine rate constants of the corresponding sulfur-containing nucleophiles at 288–308 K, and activating energy and enthalpy of activation were calculated using the data obtained. These results are presented in Table I.

Nucleophilic addition of various sulfur anions to 2-nitroethenylbenzene take place at the $\beta$-carbon atom where electron deficit is greatest, forming the final products **3**, respectively **4**, where two moles of sulfide have been added. Within experimental limits, the rates of reactions do not depend on pH of the medium, which is a good reason to consider the nucleophilic attack of sulfur anions as the rate determining stage (Figure 1).

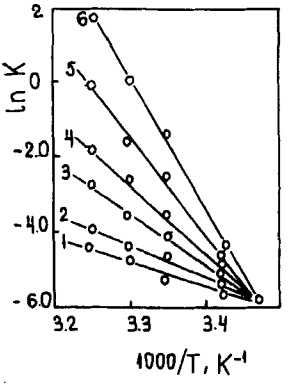



FIGURE 1 Dependence of rate constants on the reaction temperature of 2-nitroethenylbenzene with: 1 – $OOC—CH_2—S^-$; 2 – $PhS^-$ 3 – $S^{2-}$; 4 – $SO_3^{2-}$; 5 – $S_2O_3^{2-}$; 6 – $PhSO_2^-$.

TABLE II

The second-order rate constants for addition of various sulfur anions to 2-nitroethenylbenzene at 273 K

| Nucleophile | $pK_a^*$ | $k.10^4$ $M^{-1}\ s^{-1}$ |
|---|---|---|
| $PhSO_2^-$ | 1.45 | 14.72 |
| $S_2O_3^{2-}$ | 2 | 23.60 |
| $SO_3^{2-}$ | 7 | 166.50 |
| $S^{2-}$ | 7.24 | 575.35 |
| $PhS^-$ | 7.47 | 13130 |
| $^-OOC-CH_2-S^-$ | 10.5 | 23840 |

$pK_a^*$ values of congugated acids of nucleophiles [7-11]

TABLE III

Physical and spectroscopic data of compounds 3–4

| Product | Yield (%) | m.p. (°C) (EtOH/$H_2O$, 1:1 ) | IR (KBr) $\nu$ ($cm^{-1}$) | UV (EtOH/$H_2O$), nm (log $\varepsilon$) |
|---|---|---|---|---|
| 3a | 62 | 298 | 1540,1345,1315, 1120,1090 | 218 (3.60), 261 (2.20),268 (1.83) |
| 3b | 58 | 370 | 1535,1355,1210, 1030,640 | 220 (2.71), 259 (1.97),270 (1.62) |
| 3c | 65 | 360 | 1540,1350,1205, 1035,645 | 219 (2.60),258 (1.85),269 (1.58) |
| 3d | 52 | 345 | 1540,1360,1090 | 217 (2.65), 262 (2.12),269 (1.53) |
| 3e | 67 | 358 | 1695,1535,1410, 1355 | 218 (2.85), 257 (2.16),269 (1.85) |
| 4a | 71 | 379 | 1545,1360,690 | 221 (2.60), 256 (1.90),271 (1.50) |

Microanalyses obtained. Calculated for $C_{14}H_{12}NO_4SNa$ (3a): %C, 53.67; %H, 3.83; %N, 4.47; %S, 10.22; found: %C, 53.35; %H, 3.50; %N, 4.15%S, 9.98. Calculated for $C_8H_7NO_5S_2Na_2$ (3b): %C, 31.27; %H, 2.28; %N, 4.56; %S, 10.42; found: %C, 31.60; %H, 2.19; %N, 4.40; %S, 10.05. Calculated for $C_8H_7NO_5SNa_2$ (3c): %C, 34.91; %H, 2.55; %N, 5.09; %S, 11.64; found : %C, 34.65; %H, 2.21; %N, 4.96; %S, 11.71. Calculated for $C_{14}H_{12}NO_2SNa$ (3d): %C, 59.79; %H, 4.27; %N, 4.98; %S, 11.39; found: %C, 59.52; %H, 4.05; %N, 4.75; %S, 11.06. Calculated for $C_{10}H_5NO_4SNa_2$ (3e): %C, 42.11; %H,3.16; %N, 4.91; %S, 11.23; found: %C, 41.90; %H,2.87; %N, 4.70; %S, 11.00.Calculated for $C_{16}H_{14}N_2O_4SNa_2$ (4a): %C, 51.06; %H, 3.72; %N, 7.45; %S, 8.51; found: %C, 50.82; %H, 3.45; %N, 7.17; %S,8.54.

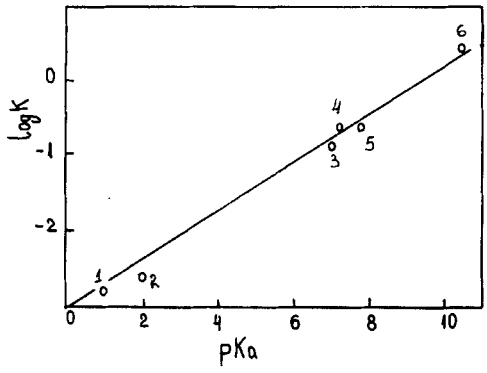



FIGURE 2 Plot of log k vs $pK_a$ for addition of various sulfur anions to 2-nitroethenylbenzene at 303 K. Nucleophile: 1 – $PhSO_2^-$ ; 2 – $S_2O_3^{2-}$ ; 3 – $SO_3^{2-}$ ; 4 – $S^{2-}$ ; 5 – $PhS^-$ ; 6 – $^-OOC—CH_2—S$

The kinetic data of the reaction between 2-nitroethenylbenzene and various sulfur-containing anions give rise to the order of nucleophilicity shown in Table II, revealing a direct dependence on basicity of sulfur anions. The reaction rate of sodium thioglycolate with 2-nitroethenylbenzene is three orders higher than the rate with sodium phenylsulfinate due to the correspondingly higher basicity of the former. In fact, the rate of nucleophilic addition of sulfur-containing anions to 2-nitroethenylbenzene is directly proportional to the basicity of nucleophiles (Figure 2).



## EXPERIMENTAL

Thiophenol and thioglycolic acid, sodium thiosulfate, sodium sulfide and sodium bisulfite are commercial products of Aldrich Chemical Company, Inc. Melting temperatures or decomposition temperatures were determined on a Derivatograph Q (Hungary). Elementary analyses were made using an Elemental Analyser-1104 (Carlo Erba, Italy). IR spectra were obtained on a Specord 75 IR (Germany). UV spectra and kinetic determinations were carried out using a Specord UV-VIS (Germany) (Table III).

*Reaction products.* 0.001 g-mol of the corresponding S-containing nucleophiles **2a–f**, dissolved in a minimum amount of water, was added to a solution of 0.001 g-mol of 2-nitroethenylbenzene in 10 ml ethanol and the mixture kept for 8 hours. The products obtained (**3–4**) were filtered and recrystallized from a 50% aqueous-alcohol solution. The physical and spectral characteristics of the synthesized products are presented in Table III.

*Rate measurement.* S-containing nuclephiles **2a–f** dissolved in a minimum amount of water were added to a solution of 0.001 mol 2-nitroethenylbenzene in ethanol. Aliquots were taken out at regular intervals of time and diluted with ethanol. The 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 literature.[6]

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