

KINETIC STUDY OF STYRENEPSEUDONITROSITE TRANSFORMATION

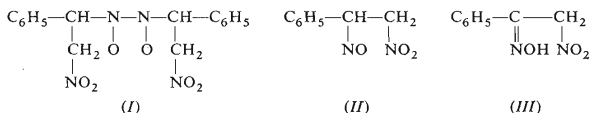
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It has been proved that styrenepseudonitrosite dissolved in acetone is present as 1-nitro-2-nitroso-2-phenylethane (*II*) and undergoes a reversible reaction $P \rightleftharpoons O$ producing 1-nitro-2-isonitroso-2-phenylethane (*III*). Rate constants of the both reverse reactions have been determined at 25, 35 and 45°C. The compounds *II* and *III* are reduced on the dropping mercury electrode giving well developed waves differing by about 0.5 V in their $E_{1/2}$. The polarographical reductions concern nitro group of the both isomers.

The reaction products of dinitrogen trioxide with olefines were called pseudonitrosites more than 70 years ago^{1,2}. Reaction of dinitrogen trioxide and styrene produces styrenepseudonitrosite³, which is formulated in literature as a dimer² (*I*), further denoted by abbreviation D, or as a monomer⁴ (*II*), abbreviation P.



It is known^{4,2} that styrenepseudonitrosite is transformed easily into 1-nitro-2-isonitroso-2-phenylethane (*III*), further denoted by abbreviation O (oxime).

Styrenepseudonitrosite is used in analytical chemistry for indirect determination of styrene, originally a gravimetric determination⁵ and later on a polarographical one^{6,7}. The latter consists in reaction of dinitrogen trioxide with styrene in acetic acid. The polarographic curve (acetate buffer) shows two waves. One was assigned to styrenepseudonitrosite by Šedivec and Flek⁶ who also called the attention to the existence of the other more negative wave. The first wave is used for analytical purposes, its height depending linearly on styrene concentration under precisely defined reaction conditions. Although this method has not yet been sufficiently elucidated from theoretical viewpoint, it is currently used in analytical praxis due to its simplicity and sensitivity in polarographical determination of residual styrene in polycondensates, polymerisates and dispersions⁸.

The aim of this work was to elucidate the character of chemical transformation of the formed styrenepseudonitrosite and the both waves observed during polarographical determination.

EXPERIMENTAL

Apparatus. The polarographical measurements were carried out with a jacketed vessel with mercury on the bottom and with the Kalousek's tempered vessel with the saturated calomel electrode. The polarographic curves were recorded with a V-301 polarograph (Zbrojovka, Brno) and a LP-7 recording polarograph. With reservoir height 55 cm and with zero imposed voltage the mercury outlet velocity was 3.2 mg/s from the capillary used, the drop time being 1.9 s.

Reagents. Styrene was purified by vacuum distillation; it was stabilized with 0.01% hydroquinone and kept in a refrigerator. Styrenepseudonitrosite was prepared according to Wieland³ by introducing dinitrogen trioxide into styrene solution in ether. The substance contained 15.41% N; for $C_8H_8N_2O_3$ calculated 15.56% N. 1-Nitro-2-isonitroso-2-phenylethane was prepared also according to Wieland⁹ by boiling styrenepseudonitrosite with ethanol. The substance contained 15.70% N; for $C_8H_8O_3N_2$ calculated: 15.56% N. 1-Nitro-2-phenylethane was prepared from benzaldehyde and nitromethane¹⁰. The product contained 9.25% N; for $C_8H_7O_2N$ calculated: 9.39% N. Acetone was purified with silver oxide¹¹. The other reagents used were of *p.a.* purity grade.

Polarographical measurements. The investigated substances were dissolved in acetone. The sample of styrenepseudonitrosite had to be prepared always fresh, because it undergoes isomerisation even as solid. Acetone solution of the investigated substance was diluted with aqueous acetate buffer containing 0.2M acetic acid and 0.2M sodium acetate. The final acetone concentration was 40% (by vol.) in all cases. The influence of pH was investigated by changing the acetic acid-acetate ratio at the constant total concentration of the both components (0.4M). The polarographic curves were recorded with solutions from which oxygen was removed by introducing pure nitrogen saturated with the solvent vapours under the solution level for 10 minutes. Concentrations of the substances for polarographical measurements were 10^{-4} to 10^{-3} M.

Kinetic measurements. A fresh sample of styrenepseudonitrosite was dissolved in acetone and tempered to the required temperature. Samples were withdrawn at definite time intervals. Each sample was quickly cooled to the room temperature, and 10 ml was pipetted therefrom into a 25 ml calibrated flask. The volume was completed with acetate buffer, and the solution obtained was polarographed. Only the first more positive wave was evaluated.

Molecular weight determination. The molecular weight of styrenepseudonitrosite was determined by vapour pressure osmometry using a Hewlett-Packard Osmometer 302 B. The measurement was carried out at 30°C, acetone being used as the solvent.

RESULTS AND DISCUSSION

Polarographical Behaviour of the Investigated Substances

Both styrenepseudonitrosite and 1-nitro-2-isonitroso-2-phenylethane are reduced at the dropping mercury electrode to give a well developed wave, $E_{1/2} = -0.3$ V and -0.8 V, respectively (s.c.e.). The wave heights depend linearly on concentration and on the square root of the reservoir height. Increasing pH causes the waves to shift to more negative voltage values. Having the same concentrations (if styrenepseudonitrosite is taken as monomer), the wave of pseudonitrosite is by 10% higher than that of 1-nitro-2-isonitroso-2-phenylethane. For comparison we have recorded also the wave

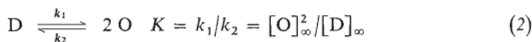
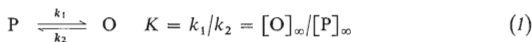
of 1-nitro-2-phenylethene under the same conditions. Polarographic wave of this compound has $E_{1/2} = -0.2$ V (s.c.e.) and is by 15% higher than that of pseudonitrosite of the same concentration.

From the abovementioned experiments we concluded that nitro group is reduced in all the three cases. The wave of styrenepseudonitrosite is identical with the first more positive wave, and that of 1-nitro-2-isonitroso-2-phenylethane is identical with the second more negative wave in the polarographical determination of styrene according to refs^{6,7}.

Kinetic Study of the Reaction

If the solution of styrenepseudonitrosite in acetone is left to stand at the room temperature for several hours, it can be seen that the polarographic wave of styrenepseudonitrosite is decreased and, at the same time, a wave appears having the half-wave potential by 0.5 V more negative, which is identical with the wave of 1-nitro-2-isonitroso-2-phenylethane. The time-concentration dependence of these substances shows characteristics of reverse reactions.

Two reaction schemes can be considered¹², the corresponding equilibrium constants K being defined by ratios of the rate constants of the both reverse reactions or by the equilibrium concentrations:



The time dependence of $[P]$ according to the first scheme is given in Eq. (3) where p stands for $[P]$ at the time $t = 0$.

$$t(k_1 + k_2) = \ln(k_1 p / (k_1 + k_2)) - \ln([P] - [P]_{\infty}). \quad (3)$$

TABLE I

Rate and Equilibrium Constants of the Reaction $P \rightleftharpoons O$

$t, ^\circ\text{C}$	k_1, h^{-1}	$k_2 \cdot 10^2, \text{h}^{-1}$	K
25	0.110	1.26	8.7
35	0.534	2.97	18.0
45	1.46	4.39	33.2
60	—	—	< 100

The time dependence of $[D]$ according to the second scheme is given by Eq. (4) where d stands for $[D]$ at the time $t = 0$.

$$tk_1(8(d - [D]_\infty)/K + 1 = \ln((2d + K/4 - [D] - [D]_\infty)/([D] - [D]_\infty)) + \\ + \ln((d - [D]_\infty)/(d - [D]_\infty + K/4)) \quad (4)$$

The time dependence of $-\ln([P] - [P]_\infty)$ is linear in the whole studied range (i.e. about 24, 8 and 4 hours and $p = 2.175 \cdot 10^{-3}M$, $2.375 \cdot 10^{-3}M$, $2.138 \cdot 10^{-3}M$ for the temperatures 25, 35 and $45^\circ C$, respectively). The time dependence of $\ln((2d + K/4 - [D] - [D]_\infty)/([D] - [D]_\infty))$ is perfectly linear at lower times, after longer time (e.g. after about 15 hours for the temperature $25^\circ C$), when the concentration of the reaction product increases and the order of the reverse reaction is manifested most markedly, the experimental points deviate somewhat from the linear course. This finding confirms the idea that styrenepseudonitrosite is not present as a dimer in the solution, but it is present as monomer, and it undergoes the reversible reaction (1). This was confirmed also by molecular weight determination of styrenepseudonitrosite by the vapour pressure osmometry. The found value of molecular weight 175 agrees well with the calculated value 180.16. The formation of dimer can thus be excluded.

The equilibrium constant of the reaction depends strongly on the temperature. At $60^\circ C$ the reaction equilibrium is shifted to such an extent that the wave of styrenepseudonitrosite cannot be recorded. Table I gives the rate and equilibrium constants values obtained from the time dependence of $-\ln([P] - [P]_\infty)$.

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