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Abstract

Full Text

Chemistry

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Study of the Oxidation Rate of Substituted 1,5-Diphenylthiocarbohydrazides by the Spectrophotometric Method

(Presented by Academician N. N. Semenov, October 17, 1962)

Substituted 1,5-diphenylthiocarbohydrazides (I) are oxidized relatively readily to substituted 1,5-diphenylthiocarbazones (II), and the latter, in turn, under oxidative dehydrocyclization in harsher conditions are converted into substituted diphenyltetrazolium thiobetaines (III)[1-4].

$$\begin{matrix}\mathrm{RNHNH}\\ \mathrm{RNHNH}\end{matrix}\!\!\diagup\!\!\diagdown\mathrm{C=S}\ \underset{\mathrm{H}}{\overset{\mathrm{O}}{\rightleftarrows}}\ \begin{matrix}\mathrm{RN=N}\\ \mathrm{RNHNH}\end{matrix}\!\!\diagup\!\!\diagdown\mathrm{C=S}\ \underset{\mathrm{H}}{\overset{\mathrm{O}}{\rightleftarrows}}\ \begin{matrix}\mathrm{R-N^{+}=N}\\ \mathrm{R-N-N}\end{matrix}\!\!\diagup\!\!\diagdown\mathrm{C-S^{-}}$$

(I) (II) (III)

Oxidation of I to II can proceed as an oxidation–reduction reaction, in which dismutation of two molecules of diarylthiocarbohydrazide occurs[2,5]

$$2\begin{matrix}\mathrm{RNHNH}\\ \mathrm{RNHNH}\end{matrix}\!\!\diagup\!\!\diagdown\mathrm{C=S}\ \rightleftarrows\ \begin{matrix}\mathrm{RN=N}\\ \mathrm{RNHNH}\end{matrix}\!\!\diagup\!\!\diagdown\mathrm{S=S}+\mathrm{RNHCSNHNH_2}+\mathrm{RNH_2}$$

Taking into account that the derivatives of 1,5-diphenylthiocarbohydrazide studied by us possess reducing properties, it was of interest to study the rate of their oxidation. Arylthiocarbohydrazides (I) are colorless substances, and their solutions in various solvents are not colored. It turned out that solutions of thiocarbohydrazides in nonpolar solvents begin, with time, to acquire a green color characteristic of solutions of the corresponding diarylthiocarbazones (II) in the same solvents[6,7]. We used this property to study the oxidation rate of the substituted 1,5-diphenylthiocarbohydrazides synthesized by us and to calculate the activation-energy values of this reaction. The experiments were carried out in a Geppler ultrathermostat of type NB. Benzene solutions (concentration $2 \cdot 10^{-5}$ g-mol/l) were placed in identical glass test tubes of 100 ml volume, with closing glass stoppers. Samples of the solutions were taken at definite time intervals with a "Fortuna" pipette and measured on a spectrophotometer. The optical density at 500 mμ was taken as the zero point. The optical density of

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Figure 1. Rate of oxidation of 1,5-di-(p-carbethoxyphenyl)-thiocarbohydrazide in benzene. 1 —at 20°, 2 —at 40°

Figure 1: Figure 1. Rate of oxidation of 1,5-di-(p-carbethoxyphenyl)-thiocarbohydrazide in benzene. 1 —at 20°, 2 —at 40°

the initial solutions was taken as the initial point. To determine the amount of thiocarbazone formed at each given moment, calibration curves were obtained for the thiocarbazones whose thiocarbohydrazides were studied by us.

Fig. 1. Rate of oxidation of 1,5-di-(*p*-carbethoxyphenyl)-thiocarbohydrazide in benzene. 1 —at 20°, 2 —at 40°.

Figure 1 shows the nature of the kinetic curves for 1,5-di-(*p*-carbethoxyphenyl)-thiocarbohydrazide in benzene.

As is seen from the kinetic curves, they correspond to reactions of the first order with respect to product II:

$$(\Delta x)_\infty - \Delta x = (\Delta x)_\infty l^{-kt}. \tag{1}$$

In this formula, Δx is the change in optical density at the time t, and Δx_∞ is the same at the end of the photochemical reaction. The difference $(\Delta x)_\infty - \Delta x$ denotes the value of the optical density at each given moment of time.

Formula 1 may be represented in the form:

$$\lg\left(1 - \frac{\Delta x}{\Delta x_\infty}\right) = kt \lg l, \tag{2}$$

which should be plotted as a straight line in the coordinates:

$$\left[\lg\left(1 - \frac{\Delta x}{\Delta x_\infty}\right), t\right].$$

In Fig. 2 are shown the semilogarithmic anamorphoses of the kinetic curves, which are straight lines.

The values of the oxidation rate constants were determined for two temperatures, 20 and 40°. From these data, an estimate is also made of the activation energy for a series of substituted 1,5-diphenylthiocarbazides (see Table 1).

From the data given in Table 1 it is seen that, under the conditions studied by us, 1,5-di-(*p*-tolyl)thiocarbazide proved to be the most resistant to oxidation.

Fig. 2. Semilogarithmic anamorphoses of the kinetic curves of 1,5-di-(*n*-carbethoxyphenyl)thiocarbazide.
1 —at 20°, 2 —at 40°

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Table 1

No.	Compound	20° k_1, min^{-1}	40° k_2, min^{-1}	E, kcal/mol
1	$C_6H_5NHNHCSNHC_6H_5$	$6.0 \cdot 10^{-3}$	$32.7 \cdot 10^{-3}$	15.6
2	$CH_3C_6H_4NHNHCSNHC_6H_4CH_3$	$1.3 \cdot 10^{-3}$	$6.3 \cdot 10^{-3}$	7.9
3	$CH_3C_6H_4NHNHCSNHC_6H_4CH_3$	$2.8 \cdot 10^{-3}$	$27.9 \cdot 10^{-3}$	21.2
4	$CH_3SC_6H_4NHNHCSNHC_6H_4SCH_3$	$5.8 \cdot 10^{-3}$	$30.7 \cdot 10^{-3}$	15.4
5	$C_2H_5OOCC_6H_4NHNHCSNHNHC_6H_4COOC_2H_5$	$3.6 \cdot 10^{-3}$	$16.9 \cdot 10^{-3}$	15.2
6	$ClC_6H_4NHNHCSNHNHC_6H_4Cl$	$7.8 \cdot 10^{-3}$	$16.10 \cdot 10^{-3}$	11.0

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