## Quantitative Estimation of the $\alpha$ -Effect in the Reactions Yielding Phosphorus-Containing Thiosemicarbazides

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Received May 20, 2005

**Abstract**—The  $\alpha$ -effect in the reactions of *O*,*O*-diaryl phosphorohydrazidothioates with phenyl isothiocyanate in benzene at 25°C was quantitatively evaluated from the kinetic data. The probable reaction mechanism was suggested, and the causes of the  $\alpha$ -effect in these reactions are discussed. An approximate linear correlation is observed between the  $\alpha$ -effect in the reactions of *O*,*O*-diaryl phosphorohydrazidothioates with phenyl isothiocyanate, basicity constants of the hydrazides, and  $\sigma^p$  constants of the substituents at the P atom. The value of the  $\alpha$ -effect is largely determined by the structure of the transition state. **DOI:** 10.1134/S1070363206080111

It was found previously that phosphorus acid hydrazides exhibit increased reactivity toward phenyl isocyanate, which was attributed to the  $\alpha$ -effect [1, 2].

It is also known that these reactions occur via cyclic transition states; hence, the manifestation of the  $\alpha$ -effect and its value are determined by the reaction mechanism [1–3]. It was suggested that organophosphorus hydrazine derivatives would show increased reactivity toward substrates of definite type.

In this study, aimed to check the above assumption, we examined the kinetics of the reactions of O,O-diaryl phosphorohydrazidothioates with phenyl isothiocyanate. It is known that hydrazine derivatives react with isothiocyanates in benzene relatively slowly [4]. Therefore, we attempted to quantitatively evaluate the  $\alpha$ -effect in these reactions if it takes place. We found that O,O-diaryl phosphorohydrazidothioates react with phenyl isothiocyanate in benzene quantitatively to form thiosemicarbazides:

$$\underset{R'C_{6}H_{4}O}{\overset{S}{\underset{H}{}}}_{P-NHNH_{2}} + \underset{S=C=N-C_{6}H_{5}}{\overset{RC_{6}H_{4}O}{\underset{R'C_{6}H_{4}O}{\overset{S}{\underset{H}{}}}}_{P-NHNHC(S)NHC_{6}H_{5}}$$

The kinetics of these reactions are described by second-order equations. The rate constants calculated by these equations do not noticeably change during the process.

To check whether the starting compounds or reaction products exert a catalytic effect on the reactions of the hydrazides with phenyl isothiocyanate, we studied the kinetics of these reactions at different concentrations of the reactants (hydrazides, 0.000625– 0.002 M; phenyl isothiocyanate, 0.000625–0.00625 M) and with preliminary addition of the reaction products (0.000625 M) to the initial solutions. We found that neither the starting reactants nor the reaction products (thiosemicarbazides) affect the rates of the reactions of phosphorus-containing hydrazides with phenyl isothiocyanates, as indicated by the rate constants ranging from  $0.949 \times 10^{-4}$  to  $0.970 \times 10^{-4}$  1 mol<sup>-1</sup> s<sup>-1</sup>.

Experimental data on the effect of substituents in phenyl groups on the reactivity of O,O-diaryl phosphorohydrazidothioates toward phenyl isothiocyanate show that the activity of the hydrazides is proportional to their basicity constants (determined in 50% ethanol, see table). The Brønsted equation for the reactions of O,O-diaryl phosphorohydrazidothioates with phenyl isothiocyanate is as follows:

$$\log k = (-19.5 \pm 2.0) + (5.91 \pm 0.73) p K_{\rm BH^+}, \qquad (1)$$
  
n 7, r 0.961, s 0.116.

Thus, variation of the reactivity of the examined hydrazides is related to variation of their basicity.

Therefore, it could be expected that aniline would be more reactive than O,O-diaryl phosphorohydrazidothioates toward phenyl isothiocyanate. However, actually less basic phosphorus acid hydrazides are more reactive (see table). Hence, abnormally high reactivity of O,O-diaryl phosphorohydrazidothioates cannot be attributed solely to their basicity, and other factors should be take into account.

As shown previously, the effect of polarizability on reactions of this type is insignificant. Apparently, the increased reactivity of O,O-diaryl phosphorohydrazidothioates is due to the effect of the nitrogen atom bearing a lone electron pair in the position adjacent to the nucleophilic center, i.e., to the so-called  $\alpha$ -effect.

In this study we characterized this  $\alpha$ -effect quantitatively. The  $\alpha$ -effect is manifested as a positive deviation of the point for the  $\alpha$ -nucleophile from the Brønsted straight line for compounds with normal reactivity [6]. The  $\alpha$ -effect is evaluated quantitatively as the ratio of the rate constant of the reaction with a given hydrazide to that of the reaction with an arylamine having the same basicity [3]. The values of the  $\alpha$ -effect in the reactions of *O*,*O*-diaryl phosphorohydrazidothioates with phenyl isothiocyanate, estimated using in some cases the rate constants calculated from the Brønsted equation for the reactions of aromatic amines with phenyl isothiocyanate in benzene {the basicity constants were determined in 50% ethanol; Eq. (2) [3]}, are given in the table.

$$\log k = -9.44 + 1.17 p K_{\rm BH^+}, \qquad (2)$$
  
r 0.997, s 0.088.

It is seen that the substituents in the aromatic rings of the hydrazides influence the value of the  $\alpha$ -effect: electron-donor substituents enhance, and electron-acceptor substituents, on the contrary, suppress it. The larger the difference between the  $\beta$  constants in the Brønsted equations for hydrazides and amines, the

stronger the influence of substituents on the value of the  $\alpha$ -effect. Thus, it is possible to determine from the Brønsted  $\beta$  constants how introduction of electron-donor and electron-acceptor substituents will influence the value of the  $\alpha$ -effect.

Analysis showed that the value of the  $\alpha$ -effect varies in the same direction with the basicity constants of the hydrazides and  $\sigma^{p}$  constants of substituents at the P atom in the hydrazides [7]. The correlations are described by Eqs. (3) and (4), respectively.

$$\alpha \text{-Effect} = (-7059 \pm 1879) + (2735 \pm 699) pK_{\text{BH}^+}, \quad (3)$$
  
 $n \ 7, \ r \ 0.868, \ s \ 0.110,$   

$$\alpha \text{-Effect} = (242 \pm 42) - (930 \pm 225) \Sigma \sigma^{\text{p}}, \quad (4)$$

n 7, r 0.879, s 106.

The  $\alpha$ -effect is attributed at present to several factors, but none of them, considered separately, fully explains the nature of this phenomenons [1, 2, 8]. Assuming that the  $\alpha$ -effect is largely determined by the structure of the transition state [9, 10], we can explain the increased reactivity of phosphorus acid hydrazides by a specific structure of the transition state. Hydrazine derivatives, being bifunctional reagents, can form cyclic complexes in the transition state [1].

It was shown that reactions of hydrazine derivatives with isocyanates involve a nucleophilic attack of the isocyanate carbon atom by the hydrazide. The bimolecular addition of the hydrazide to the electrophilic carbon atom of the isocyanate occurs in one step via a cyclic transition state [11]. The similar structure of the transition state can be realized in the reactions of O,O-diaryl phosphorohydrazidothioates with phenyl isothiocyanate, taking into account our results and the relevant published data [12–16]. Thus, the general mechanism of the noncatalytic reaction of O,O-diaryl phosphorohydrazidothioates with phenyl isothiocyanate in benzene is, presumably, as follows:

$$\begin{array}{c} \operatorname{RC}_{6}H_{4}O \underset{\mathbb{R}'C_{6}H_{4}O}{\overset{\mathbb{S}}{\underset{\mathbb{R}'C_{6}}{\underset{\mathbb{R}'C_{6}H_{4}O}{\overset{\mathbb{S}}{\underset{\mathbb{R}'C_{6}}{\underset{\mathbb{R}'C_{6}}{\underset{\mathbb{R}'C_{6}}{\underset{\mathbb{R}'C_{6}}{\underset{\mathbb{R}'}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}$$

According to the mechanism suggested, the reaction occurs in one step via a cyclic transition state A, with the hydrogen bonding of the S and N atoms of phenyl isothiocyanate with the H atoms of the imino and amino groups of the hydrazide and formation of a new bond between between the nucleophilic N atom

RUSSIAN JOURNAL OF GENERAL CHEMISTRY Vol. 76 No. 8 2006

Quantitative evaluation of the  $\alpha$ -effect in the reactions of O,O-diaryl phosphorohydrazidothioates  $[(RC_6H_4O) \cdot (R'C_6H_4O)PSNHNH_2]$  with phenyl isothiocyanate in benzene at 25°C

R	R'	р <i>К</i> <sub>ВН</sub> + [5]	$k \times 10^4,$ 1 mol <sup>-1</sup> s <sup>-1</sup>	α-Effect
<i>p</i> -CH <sub>3</sub>	<i>p</i> -СН <sub>3</sub>	2.76	$3.90 \pm 0.24$	634
<i>p</i> -CH <sub>3</sub>	Н	2.74	$2.39 \pm 0.17$	410
m-CH <sub>3</sub>	<i>m</i> -CH <sub>3</sub>	2.73	$2.48 \pm 0.19$	437
Н	Η	2.70	$0.958 \pm 0.029$	183
Н	<i>p</i> -Cl	2.68	$0.920 \pm 0.025$	185
p-Cl	p-Cl	2.63	$0.465 \pm 0.014$	107
<i>m</i> -Cl	<i>m</i> -Cl	2.58	$0.372 \pm 0.011$	98.2
Aniline		4.19	$0.0301 \pm 0.0016$	

of the hydrazide and the electrophilic C atom of the isothiocyanate. This is accompanied by cleavage of the C=N bond in the isothiocyanate and N-H bond in the hydrazide, with the proton transfer from the amino group of the hydrazide to the isocyanate group (formation of a new N-H bond) and formation of the reaction product, thiosemicarbazide derivative.

The occurrence of reactions via cyclic transition states is energetically favorable, and therefore such reactions should be relatively fast.

## EXPERIMENTAL

Benzene for kinetic studies was purified according to [17]. *O*,*O*-Diaryl phosphorohydrazidothioates were prepared from the corresponding acid chlorides and hydrazine hydrate and were purified as described in [18, 19]. Phenyl isothiocyanate was vacuum-distilled just before use.

The reaction progress was monitored by the content of unchanged phenyl isothiocyanate [4, 20]. The kinetic experiments were performed in benzene at  $25 \pm$  $0.05^{\circ}$ C. The initial concentrations (M) were as follows: *O*,*O*-diaryl phosphorohydrazidothioates 0.000625– 0.002 and phenyl isothiocyanate 0.000625–0.00625. Three replicate experiments were performed in each case; the experiments involved 6–8 measurements and were performed to no less than 80% conversion.

The accuracy of the results was evaluated by methods of mathematical statistics [21] at a confidence level of 0.95.

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