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Kinetic Regularities of Reactions of *O,O*-Diaryl Phosphorohydrazidothioates with Phenyl Isothiocyanate in Benzene

N. L. Yanchuk and L. N. Ivanets

Gnatyuk Ternopol State Pedagogical University, Ternopol, Ukraine

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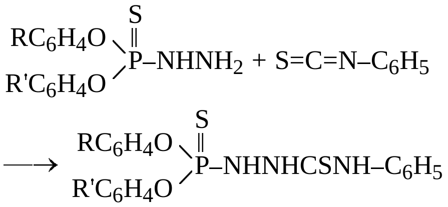
Abstract—The effect of the temperature on the rate of reactions of *O,O*-diaryl phosphorohydrazidothioates with phenyl isothiocyanate in benzene is studied, and the activation parameters of the reactions are calculated. It is established that the reaction series under study obeys the isokinetic relationship with an enthalpy control and an isokinetic temperature of 690±24 K. The effect of electronically diverse substituents on phosphorus on the reactivity of *O,O*-diaryl phosphorohydrazidothioates is additive. It is described by the Hammett equation with σ^P constants.

In the present work we present the results of a kinetic study of reactions of *O,O*-diaryl phosphorohydrazidothioates with phenyl isocyanate, aimed at assessing structure–reactivity relationship for the hydrazides in hand.

The reactions of *O,O*-diaryl phosphorohydrazidothioates with phenyl isothiocyanate proceed quantitatively and irreversibly to form thiosemicarbazides.



$$(RC_6H_4O)(R'C_6H_4O)P(=S)\text{–}NHNH_2 + S{=}C{=}N\text{–}C_6H_5 \longrightarrow (RC_6H_4O)(R'C_6H_4O)P(=S)\text{–}NHNHCSNH\text{–}C_6H_5$$

The kinetics of these reactions are described by an irreversible second-order reaction equation (partial first order in hydrazide and phenyl isothiocyanate), as evidenced by the fact that the reciprocal current concentration linearly varies with time.

The effect of substituents of different electronic nature in the aromatic rings of *O,O*-diaryl phosphorohydrazidothioates on the rates of their reactions with phenyl isothiocyanate was studied in the temperature range 25–55°C. The resulting reaction rate constants are listed in Table 1.

The reactions under study are described by the Arrhenius equation. The polytherms of the log rate constants of phosphorus-containing thiosemicarbazide formation are linear, as evidenced by high correlation coefficients of the Arrhenius equation [Table 2, Eqs. (1)–(7)]. This allowed the activation parameters of the reactions (Table 3) to be found from the temperature dependences of the rate constants measured at four temperatures and known relationships [1]. The activation entropy ($\Delta S^{\neq}$), enthalpy ($\Delta H^{\neq}$) and Gibbs energy ($\Delta G^{\neq}$) were calculated for 25°C.

Table 1. Rate constants of reactions of *O,O*-diaryl phosphorohydrazidothioates **I**–**VII** with phenyl isothiocyanate in benzene at various temperatures

Comp. no.	R	R'	298 K	308 K	318 K	328 K
I	*p*-CH_3	*p*-CH_3	0.390 ± 0.024	1.36 ± 0.10	4.71 ± 0.24	9.75 ± 0.23
II	*p*-CH_3	H	0.239 ± 0.017	0.631 ± 0.033	2.94 ± 0.16	6.74 ± 0.27
III	*p*-CH_3	*p*-CH_3	0.248 ± 0.019	0.716 ± 0.037	3.24 ± 0.30	5.76 ± 0.21
IV	H	H	0.0958 ± 0.0029	0.559 ± 0.016	2.09 ± 0.13	6.29 ± 0.19
V	H	*p*-Cl	0.0920 ± 0.0025	0.370 ± 0.021	1.47 ± 0.11	2.74 ± 0.12
VI	*p*-Cl	*p*-Cl	0.0465 ± 0.0014	0.129 ± 0.005	0.611 ± 0.028	2.40 ± 0.18
VII	*m*-Cl	*m*-Cl	0.0372 ± 0.0011	0.123 ± 0.009	0.662 ± 0.014	1.36 ± 0.11

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Table 2. Parameters of the equation $\log k = \log A + b \times 10^3 \times T^{-1}$ for reactions of *O,O*-diaryl phosphorohydrazidothioates **I–VII** with phenyl isothiocyanate in benzene (298–328 K)

Equation	Hydrazide	$\log A$	$-b$	r	s
1	**I**	12.19 ± 0.92	4.64 ± 0.29	0.996	0.066
2	**II**	12.83 ± 1.17	4.91 ± 0.37	0.995	0.084
3	**III**	12.01 ± 1.51	4.66 ± 0.47	0.990	0.108
4	**IV**	15.86 ± 1.53	5.91 ± 0.48	0.994	0.109
5	**V**	12.56 ± 1.46	4.93 ± 0.46	0.992	0.104
6	**VI**	14.64 ± 1.25	5.68 ± 0.39	0.995	0.089
7	**VII**	13.40 ± 1.52	5.31 ± 0.20	0.992	0.109

Table 3. Activation parameters of reactions of *O,O*-diaryl phosphorohydrazidothioates **I–VII** with phenyl isothiocyanate in benzene

Comp. no.	E_a, kJ mol^{-1}	$-\Delta S^{\neq}_{298}$, J mol^{-1} K^{-1}	$\Delta H^{\neq}_{298}$, kJ mol^{-1}	$\Delta G^{\neq}_{298}$, kJ mol^{-1}
I	90.8 ± 4.2	13.8 ± 1.7	88.3 ± 6.2	92.5 ± 8.0
II	90.7 ± 4.1	18.2 ± 1.4	88.2 ± 5.6	93.6 ± 7.8
III	91.3 ± 4.0	15.9 ± 2.0	88.8 ± 6.0	93.6 ± 9.0
IV	95.4 ± 4.8	10.1 ± 1.2	92.9 ± 7.0	95.9 ± 6.1
V	96.2 ± 5.1	7.7 ± 0.8	93.7 ± 7.2	96.1 ± 7.4
VI	98.2 ± 5.3	6.7 ± 0.3	95.7 ± 6.2	97.8 ± 5.0
VII	99.2 ± 3.7	5.2 ± 0.3	96.7 ± 3.4	98.2 ± 3.6

Table 4. Parameters of the equations $y = Cx + D$ for kinetic characteristics of reactions of *O,O*-diaryl phosphorohydrazidothioates with phenyl isothiocyanate in benzene ($n = 7$)

Equation	y	x	C	$-D$	r	s
8	$\log k_{298}$	pK_a	5.91 ± 0.73	19.5 ± 2.0	0.961	0.116
9	$\log k_{308}$	pK_a	5.38 ± 0.47	17.8 ± 1.3	0.981	0.075
10	$\log k_{318}$	pK_a	5.13 ± 0.64	16.5 ± 1.7	0.962	0.101
11	$\log k_{328}$	pK_a	4.55 ± 0.59	14.6 ± 1.6	0.960	0.093
12	$\log k_{298}$	$\Sigma\sigma^P$	-1.94 ± 0.24	4.03 ± 0.05	0.962	0.115
13	$\log k_{308}$	$\Sigma\sigma^P$	-1.82 ± 0.14	3.46 ± 0.03	0.986	0.064
14	$\log k_{318}$	$\Sigma\sigma^P$	-1.75 ± 0.16	2.85 ± 0.03	0.979	0.077
15	$\log k_{328}$	$\Sigma\sigma^P$	-1.56 ± 0.14	2.47 ± 0.26	0.981	0.065

Substituents of different electronic nature in *O,O*-diaryl phosphorohydrazidothioates affect both kinetic and thermodynamic parameters of the reactions. Hence, enhancing electron-donor power of the substituents decreases the activation energy, enthalpy, and Gibbs energy. Therewith, the activation entropy decreases in absolute value. Electron-acceptor substituents produce the opposite effect. In this reaction series, there is an enthalpy–entropy compensation effect: Enhancing electron-donor power of substituents in *O,O*-diaryl phosphorohydrazidothioates decreases the activation enthalpy and increases the activation entropy. The activation energies of reactions of *O,O*-diaryl phosphorohydrazidothioates with phenyl isothiocyanate in benzene are about 6 times those of reactions of the same substrates with phenyl isocyanate [2].

The reactivity of *O,O*-diaryl phosphorohydrazidothioates toward phehyl isothiocyanate varies in parallel the basicity constants of the hydrazides. The dependence of the log reaction constants on the basicity constants of the hydrazides [2] is described by the Brønsted equation [Table 4, Eqs. (8)–(11)].

As follows from the data in Table 1, the reactivity of *O,O*-diaryl phosphorohydrazidothioates is much dependent on the position and nature of substituents in the aromatic rings. The effect of substituents on the reactivity of *O,O*-diaryl phosphorohydrazidothioates described by the Hammett equation with σ^P constants [3] [Table 4, Eqs. (12)–(15)]. The absolute values of the reaction constant ρ of 1.94–1.56 in the temperature range under study suggest enhanced sensitivity of this reaction series to the structure of the *O,O*-diaryl phosphorohydrazidothioate compared to the same reaction with phenyl isocyanate [2].

The log rate constants of the reaction under study nicely correlate with the σ^P constants of the substituents on the phosphorus atom. The ρ values are negative, which is characteristic of nucleophilic reactions. As the temperature increases, the reaction constant only slightly decreases in absolute value, implying that the isokinetic temperature [4] of these reactions falls far beyond is the temperature range studied.

To find out if there is the isokinetic relationship in this reaction series in the temperature range studied, we made use of known criteria [4–6]. Evidence showing that a given reaction series obeys the isokinetic law [7] is obtained from an analysis of correlation equations of kinetic and activation parameters.

One of the most reliable criteria for the isokinetic relationship is a linear dependence of log reaction rate constants at two different temperatures. According to the Exner method [4, 8, 9] based on an analysis of the tangent slope of $\log k_{T_2} = \chi \log k_{T_1}$ + const dependences, where $T_2 > T_1$, the isokinetic temperature is readily calculated with known χ. The isokinetic temperature calculated from the $\log k_{318} - \log k_{308}$ dependence (16) is 674 K.

$$\log k_{318} = (0.413 \pm 0.021) + (0.942 \pm 0.102) \log k_{308}, \quad (16)$$
$$n\ 7,\ r\ 0.972,\ s\ 0.089.$$

The existence of the isokinetic relationship follows from the $\Delta H^{\neq}_{298} - \Delta S^{\neq}_{298}$ dependence (17):

$$\Delta H^{\neq}_{298} = (99.8 \pm 1.1) + (0.699 \pm 0.994) \Delta S^{\neq}_{298}, \quad (17)$$
$$n\ 7,\ r\ 0.962,\ s\ 1.08.$$

In this case, the isokinetic temperature is 699 K. Furthermore, the activation parameters of the reaction fit the linear dependence E_a–$\log A$ (18), and the isokinetic temperature in these coordinates is 697 K.

$$E_a = (-74.2 \pm 2.2) + (13.3 \pm 1.7) \log A, \quad (18)$$
$$n\ 7,\ r\ 0.962,\ s\ 1.08.$$

The average isokinetic temperature β [Eqs. (16)–(18)] is 690 ± 24 K. As seen, the isokinetic temperature falls far above the temperature range studied and is thus unavailable for experimental verification.

The existence of the isokinetic relationship creates certain prerequisites for predicting Hammett reaction constants of reactions of the type in hand. It is known that the temperature dependence of ρ in cases where isokinetic relationship is obeyed is given by Eq. (19) [5].

$$\rho = \alpha(1 - \beta/T). \quad (19)$$

By writing Eq. (19) for two arbitrary temperatures T and T_0 and dividing the resulting equations term-by-term, we obtain, after simple transformations, Eq. (20).

$$\rho = \rho_0 \frac{T_0}{\beta - T_0} \frac{\beta - T}{T}. \quad (20)$$

From Eq. (20) we can calculate ρ for each temperature, using the isokinetic temperature of the series and the reaction constant of this series ρ_0 at T_0. Examples of such calculations are listed in Table 5. From this data we can conclude that the calculated ρ values satisfactorily fit experimental.

Reliability of all the calculated correlation parameters for all the equations was checked by means of Student's *t* criterion [10]. It was shown that all the parameters are statistically significant with the probability exceeding 95%.

Table 5. Reaction constants (ρ) of reactions of *O,O*-diaryl phosphorohydrazidothioates with phenyl isothiocyanate in benzene at various temperatures

Temperature, K	Reaction constant ρ		Δρ
	experimental	calculated	
298	1.94	1.94	0
308	1.82	1.83	0.01
318	1.75	1.73	0.02
328	1.56	1.63	0.07

In our recent kinetic study we showed [11] that reactions of *O,O*-diaryl phosphorohydrazidothioates with phenyl isothiocyanate involve a cyclic transition complex [11]. The existence of the isokinetic relationship in this series point to a common reaction mechanism with all the members of the reaction series in the temperature range studied.

EXPERIMENTAL

Benzene for kinetic studies was purified according to [12]. *O,O*-Diaryl phosphorohydrazidothioates were prepared and purified according to [13, 14]. Phenyl isothiocyanate was distilled in a vacuum directly before use.

Reaction rate was controlled following the concentration of unreacted phenyl isothiocyanate [15, 16]. Each experiment was repeated three times and included 6–8 measurements. The conversion was no less than 80%. The kinetics of the formation of phosphorus-containing thiosemicarbazides were studied at 298, 308, 318, and 328 K. The activation parameters were calculated by known equations [1]. The accuracy of the resulting data was assessed by mathematical statistics (confidence probability 0.95) [17].

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