

# Kinetic isotope effects of nitrogen and hydrogen in reaction of *N*-*tert*-butyl-*P*-phenylphosphonamidothioic acid with alcohols

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Received 1 July 2004; accepted 10 September 2004

## Abstract

Nitrogen and hydrogen isotope effects for the reaction of *N*-*tert*-butyl-*P*-phenylphosphonamidothioic acid **1** with alcohols (methanol, butanol, *iso*-propanol, *tert*-butanol) were measured in dichloromethane at 30 °C. The observed nitrogen isotope effect  $k_{14}/k_{15}$  is only slightly sensitive to a steric hindrance of the alcohol [ $1.0070 \pm 0.0002$  (MeOH),  $1.0074 \pm 0.0004$  (BuOH),  $1.0062 \pm 0.0004$  (Pr<sup>i</sup>OH),  $1.0087 \pm 0.0007$  (Bu<sup>i</sup>OH)]. The pre-equilibrium step, with proton transfer from oxygen to nitrogen was proved by the inverse hydrogen effect  $k_{\text{ROH}}/k_{\text{ROD}}$  [ $0.778 \pm 0.052$  (MeOH),  $0.863 \pm 0.063$  (BuOH),  $0.883 \pm 0.080$  (Pr<sup>i</sup>OH),  $0.746 \pm 0.084$  (Bu<sup>i</sup>OH)]. The experimental values are consistent with theoretical results of semiempirical calculations on PM3 level for an elimination–addition mechanism and metathiophosphonate PhPSO intermediacy. For the reaction with methanol the addition–elimination mechanism is also possible.

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**Keywords:** Mechanism; Metathiophosphonate; Isotope effect; N-15; Deuterium; Calculations; Ab initio; PM3

## 1. Introduction

Over four decades long intensive studies of nucleophilic substitution at tetracoordinated phosphorus atom [1,2] were recently supplemented with theoretical calculations [3–5], which tried to answer the question of the participation of the elimination–addition mechanism and intermediacy of metaphosphate anion  $\text{PO}_3^-$ .

The theoretical predictions of the nature of the transition states can be examined by means of isotope effects, which are directly related to their structure. Experimental values of isotope effects can test the pro-

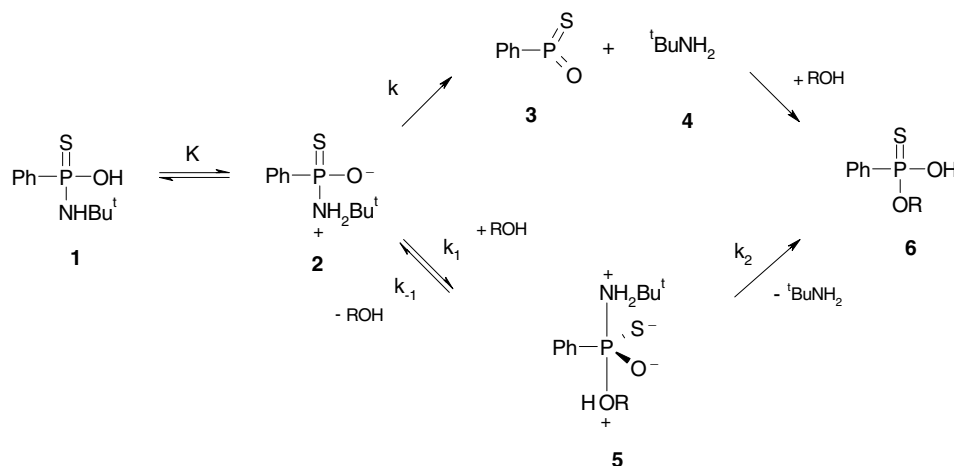
posed mechanism as well as the applied theoretical protocol [6–8].

In our previous studies we have introduced the kinetic isotope effect approach for verification of the involvement of alkyl meta(thio)phosphates as transient intermediates in the fragmentation of phosphoramido(thio)ates [9]. We have proved that the presence of the bulky substituents at nitrogen atom is essential for the suppression of direct substitution at phosphorus and facilitates the elimination–addition mechanism involving the tricoordinated intermediate.

Stereochemical studies [10] of reaction of *N*-*tert*-butyl-*P*-phenylphosphonamidothioic acid **1** with alcohols pointed out to the involvement of a metathiophosphonate **3** (Scheme 1), as should be expected for phosphonamidic acid with sterically demanding substituent at nitrogen. In this work we examine the role of an alcohol in the reaction of **1** by means of isotope effects.

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Scheme 1.

## 2. Experimental

### 2.1. Materials

Synthesis of **1** was carried out according to the known protocol [11]. Deuterated alcohols (methanol- $d_4$ , *iso*-propanol- $d_8$ , butanol- $d_1$ , *tert*-butanol- $d_1$ ), 99 Atom % D (ARMAR, Switzerland), were used without purification. Dichloromethane (P. O. Ch. Poland, analytical grade) and dichloromethane- $d_2$  (99 Atom % D, Aldrich) were dried over  $P_2O_5$  and distilled. Non-deuterated alcohols (P. O. Ch. Poland, Fluka, Aldrich) were dried over magnesium or  $CaH_2$ . Diazomethane in the diethyl ether was generated from Diazald (Aldrich). Methyl derivatives were synthesized by adding diazomethane in diethyl ether to ethereal solution of **1**. Methyl esters (**1-SMe/1-OMe**, 95:5) were purified by column chromatography with  $CH_2Cl_2$ –acetone (1:1) as eluent ( $R_F = 0.42$  for **1-SMe**,  $R_F = 0.85$  for **1-OMe**).

#### 2.1.1. *O*-methyl *N*-*tert*-butyl-*P*-phenylphosphonamidothioate **1-OMe**

Yellow oil;  $\nu_{max}$  ( $CCl_4$ ) 2968, 1376, 1224, 1129, 1040, 784, 696, 648  $cm^{-1}$ ;  $\delta_P$  (101.3 MHz,  $CDCl_3$ ) 73.8;  $\delta_H$  (250.1 MHz,  $CDCl_3$ ) 7.90–7.84 (2H, m,  $H_{Ar}$ ), 7.46–7.41 (3H, m,  $H_{Ar}$ ), 3.82 (3H, d,  $J = 12.5$  Hz,  $OCH_3$ ), 1.14 (9H, s,  $C(CH_3)_3$ );  $\delta_C$  (62.9 MHz,  $CDCl_3$ ) 136.4 (d,  $J = 143.4$  Hz), 131.3 (d,  $J = 3.1$  Hz), 130.9 (d,  $J = 11.3$  Hz), 128.3 (d,  $J = 13.8$  Hz), 53.3 (d,  $J = 5.0$  Hz), 51.2 (d,  $J = 5.0$  Hz), 31.4 (d,  $J = 3.8$  Hz); HRMS (EI):  $M^+$ , found 243.0847.  $C_{11}H_{18}NOPS$  requires 243.0847.

#### 2.1.2. *S*-methyl *N*-*tert*-butyl-*P*-phenylphosphonamidothioate **1-SMe**

Colorless solid, m.p. 75–77 °C (dichloromethane–acetone);  $\nu_{max}$  ( $CCl_4$ ) 3232, 2976, 2928, 1424, 1228, 1216,

1192, 1112, 1016, 760, 696  $cm^{-1}$ ;  $\delta_P$  (101.3 MHz,  $CDCl_3$ ) 35.4;  $\delta_H$  (250.1 MHz,  $CDCl_3$ ) 7.92–7.86 (2H, m,  $H_{Ar}$ ), 7.50–7.46 (3H, m,  $H_{Ar}$ ), 2.18 (3H, d,  $J = 12.5$  Hz,  $SCH_3$ ), 1.35 (9H, s,  $C(CH_3)_3$ );  $\delta_C$  (62.9 MHz,  $CDCl_3$ ) 135.3 (d,  $J = 134.6$  Hz), 131.7 (d,  $J = 3.1$  Hz), 131.3 (d,  $J = 10.1$  Hz), 128.3 (d,  $J = 13.8$  Hz), 53.4 (d,  $J = 3.1$  Hz), 32.0 (d,  $J = 3.1$  Hz), 12.2 (d,  $J = 3.1$  Hz); HRMS (EI):  $M^+$ , found 243.0843.  $C_{11}H_{18}NOPS$  requires 243.0847.

### 2.2. Isotope effects

The solvent hydrogen isotope effect was measured in independent kinetic runs by means of  $^{31}P$  NMR spectroscopy as was described elsewhere [12].  $^{31}P$  NMR spectra were recorded on Bruker DPX 250 Avance spectrometer at 101.20 MHz. The solvent hydrogen isotope effect is an average of at least three runs at different alcohol concentrations (Table 1). In every experiment the concentration of **1** was constant and equal to 0.05 mol/L. For determination of KIE of nitrogen the solutions of **1** (0.05 mol/L) and alcohol (0.5 mol/L) in dichloromethane were sealed under argon in glass ampoules and kept at 30 °C. The reaction was quenched by cooling at 0 °C and diazomethane in ether was added. The solvents were stripped off with a rotary evaporator and the residue was dissolved in  $CDCl_3$ .  $^{31}P$  NMR spectrum was collected with the 90° pulse, gated decoupling and repetition time of 42 s. A fraction of reaction was calculated from the sum of integrations of methylated substrates (Ph-P(S)(NHBu<sup>t</sup>)(OMe)) ( $\delta_P$  73.3) and Ph-P(O)(NHBu<sup>t</sup>)(SMe) ( $\delta_P$  35.6) relative to the total sum of integrations. The chloroform solution was passed through the small column (3 × 0.5 cm) of silica gel 60 (Fluka), the *O*- and *S*-methylated substrate was eluted with chloroform–methanol (98:2) and solvents were removed. Every sample contained at least 65  $\mu$ mol of

Table 1  
Kinetic hydrogen isotope effect for reaction of **1** with alcohols in dichloromethane at 30 °C

R	Concentration (mol/L)	$k \times 10^4$ (s <sup>-1</sup> )		$(k_{\text{ROH}}/k_{\text{ROD}})_{\text{obs}}$
		ROH	ROD	
Me	0.05	4.63 ± 0.18	5.71 ± 0.16	0.778 ± 0.049
	0.15	6.43 ± 0.17	7.68 ± 0.14	
	0.20	6.79 ± 0.27	8.62 ± 0.36	
	0.40	7.62 ± 0.27	10.5 ± 0.23	
	0.50	8.10 ± 0.46	10.5 ± 0.40	
	0.65	7.74 ± 0.19	10.3 ± 0.49	
	0.75	7.96 ± 0.15	10.4 ± 0.32	
Bu	0.05	3.55 ± 0.17	4.15 ± 0.21	0.864 ± 0.053
	0.15	3.18 ± 0.13	3.65 ± 0.12	
	0.50	2.983 ± 0.099	3.453 ± 0.051	
Pr <sup>f</sup>	0.05	3.50 ± 0.15	3.88 ± 0.25	0.884 ± 0.064
	0.15	1.933 ± 0.070	2.27 ± 0.11	
	0.50	1.464 ± 0.052	1.631 ± 0.074	
Bu <sup>f</sup>	0.10	1.444 ± 0.071	1.99 ± 0.11	0.745 ± 0.083
	0.15	1.341 ± 0.045	1.81 ± 0.17	
	0.50	1.002 ± 0.069	1.291 ± 0.047	

substrate. Samples were combusted and the isotopic composition of nitrogen was measured with Europa 20–20 continuous-flow isotope ratio mass spectrometer. The natural isotopic composition of nitrogen was used as a standard. The nitrogen kinetic isotope effect (Table 2) was calculated from the relative isotopic ratios ( $\delta$ )

Table 2  
Kinetic nitrogen isotope effect for reaction of **1** with alcohols in dichloromethane at 30 °C

R	Time (s)	$f$	$\delta(f)$	$(k_{14}/k_{15})_{\text{obs}}$
Me	0	0	-9.00	1.0070 ± 0.0002
	207	0.221	-7.21	
	330	0.289	-6.77	
	473	0.361	-4.89	
	642	0.433	-4.91	
	848	0.503	-4.23	
Bu	0	0	-7.89	1.0071 ± 0.0004
	616	0.276	-6.69	
	985	0.353	-4.82	
	1411	0.408	-3.79	
	1914	0.493	-2.93	
	2531	0.556	-2.38	
Pr <sup>f</sup>	0	0	-7.33	1.0059 ± 0.0004
	1232	0.251	-5.30	
	1971	0.298	-6.01	
	2822	0.353	-4.52	
	3830	0.420	-4.17	
	5062	0.481	-3.45	
Bu <sup>f</sup>	0	0	-8.70	1.0087 ± 0.0007
	1785	0.138	-7.10	
	2853	0.204	-6.05	
	4086	0.307	-5.60	
	5545	0.356	-4.40	
	7330	0.462	-3.30	

measured for different fractions of reaction ( $f$ ), as was described previously [9].

### 2.3. Calculations

Geometries and energies of the reactants and intermediates were determined in the gas phase by energy optimization using PM3 parameters within GAUSSIAN 98 program [13]. No constraints were placed on the systems during optimizations. The resulting structures were identified as genuine minima following frequency determination, which yielded no negative eigenvalues. The structures optimized in the gas phase were taken as starting points for the solution calculations using PM3 parameters with COSMO solvent model ( $\epsilon = 9.0$ ) within MOPAC 2002 package [14]. Geometries and energies of the transition states were determined starting from the reactant or intermediate structures and then stretching the appropriate bonds. Vibrational analysis was performed for each stationary point. Minima and transition states were confirmed to have zero and one imaginary frequency, respectively. Kinetic isotope effects were calculated by means of ISOEFF 98 program [15] according to the Bigeleisen equation [16].

The structure of zwitterion **2** in dichloromethane was optimized at DFT/B3PW91 level of theory with basis set 6-31 + G(d) and PCM solvent model.

## 3. Results and discussion

Reaction of phosphonamidothioic acid **1** with alcohols involves proton transfer and the N–H bond

formation, the P–N bond breakage and the P–O bond formation (Scheme 1). The change of alcohol does not affect significantly the values of the solvent hydrogen isotope effect (Table 1) and the kinetic nitrogen isotope effect, except for the reaction with *tert*-butanol (Table 2). The inverse deuterium solvent effect is consistent with the previous assumption of the formation of zwitterionic form **2** in the pre-equilibrium step. The observed kinetic nitrogen effect values are similar to the effects measured previously for *O*-ethyl *N*-mesitylphosphoramidate and *O*-ethyl *N*-1-adamantylphosphoramido(thio)ate. A relatively high kinetic nitrogen isotope effect was attributed to the elimination–addition mechanism involving the meta(thio)phosphate intermediacy [9].

The reaction of phosphonamidothioic acid **1** with alcohols follows the first order kinetics, which is consistent with the elimination–addition mechanism and the P–N bond breakage in the rate determining step [17,18]. The advantage of isotope effects application is the possibility of mechanism verification by comparison of experimental isotope effect values with calculated ones for different possible mechanisms. For the reaction of **1** with alcohols we considered two alternative mechanistic pathways described on Scheme 1: elimination–addition mechanism involving metathiophosphonate **3** and addition–elimination mechanism with pentacoordinated intermediate **5**.

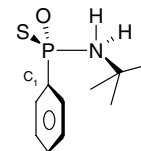
The observed nitrogen effect is given by Eq. (1) [9] for the elimination–addition mechanism and by Eq. (2) for the addition–elimination mechanism [19]:

$$(k_{14}/k_{15})_{\text{exp}} = (K_{14}/K_{15})(k_{14}/k_{15}), \quad (1)$$

$$(k_{14}/k_{15})_{\text{exp}} = (K_{14}/K_{15}) \frac{(k_{14}/k_{15})_1}{(k_{14}/k_{15})_{-1}} \times \frac{(k_{14}/k_{15})_2 + x(k_{14}/k_{15})_{-1}}{1 + x}, \quad (2)$$

where  $K_{14}/K_{15}$  is an equilibrium isotope effect of the pre-equilibrium step of the reaction, the same for both mechanisms,  $k_{14}/k_{15}$  is the kinetic isotope effect on the departure of amine and  $(k_{14}/k_{15})_i$  is the kinetic isotope effect on individual reaction rates ( $i = -1, 1, 2$ ). The partitioning factor  $x$  is equal to  $k_2/k_{-1}$  for nitrogen-14. The Eqs. (1) and (2) were derived from the steady-state approximation for **3** or **5**, respectively.

Our attempts to model the reaction of **1** with alcohols using ab initio methods were not successful, except for the structure of zwitterion **2**. The vibrational analysis of the optimized structure of substrate **1** constantly yielded one imaginary frequency and the transition state of the P–N bond cleavage could not be found. The DFT/B3PW91 optimized structure of zwitterion **2** (Fig. 1) shows that it can be regarded as “base-metathiophosphonate complex”, as was proposed by Todd for monoesters of phosphoramidic acids [20]. The CPSO moiety is



	bond length [Å]	angle [°]
P-N	1.97	
P-O	1.50	
P-S	1.95	
P-C <sub>1</sub>	1.92	
S-P-C <sub>1</sub>		113.7
O-P-C <sub>1</sub>		110.4
S-P-O		124.6

Fig. 1. DFT/B3PW91 optimized structure and selected geometric parameters of zwitterion **2**.

almost planar (the sum of bond angles is 349°) and P–S and P–O distances are close to those observed in crystals of  $\text{ArPS}_2$  (1.90 Å) [21] and  $\text{ArPO}_2$  (1.45 Å) [22], respectively. The calculated P–N bond distance of 1.97 Å is longer than 1.77 Å measured for zwitterionic crystals of  $\text{H}_3\text{N}^+-\text{PO}_3^-$  [23].

The experimental isotope effects were compared to isotope effect values calculated by means of semiempirical calculations on PM3 level, for reaction of **1** with methanol and *tert*-butanol in elimination–addition mechanism, and with methanol only for addition–elimination mechanism. It is known that kinetic isotope effects strongly depend on the changes in force constants around the isotopic atoms and reliable geometries of the reactants and transition states are essential for isotope effects predictions [24]. We were encouraged to use the PM3 model by literature findings that this method gives geometries and bond parameters in good agreement with crystallographic data for different classes of organophosphorus compounds [25].

The optimized structures of the stationary points are presented on Figs. 2 and 3. For the dissociative reaction (Fig. 2) we assumed that the proton transfer between oxygen and nitrogen of **1** occurs without alcohol assistance or via a six-membered ring involving alcohol molecule.

The calculated hydrogen isotope effects for the equilibrium proton transfer and amine departure are given in Table 3. The overall calculated hydrogen isotope effect is practically the same for both alcohols (0.86) and

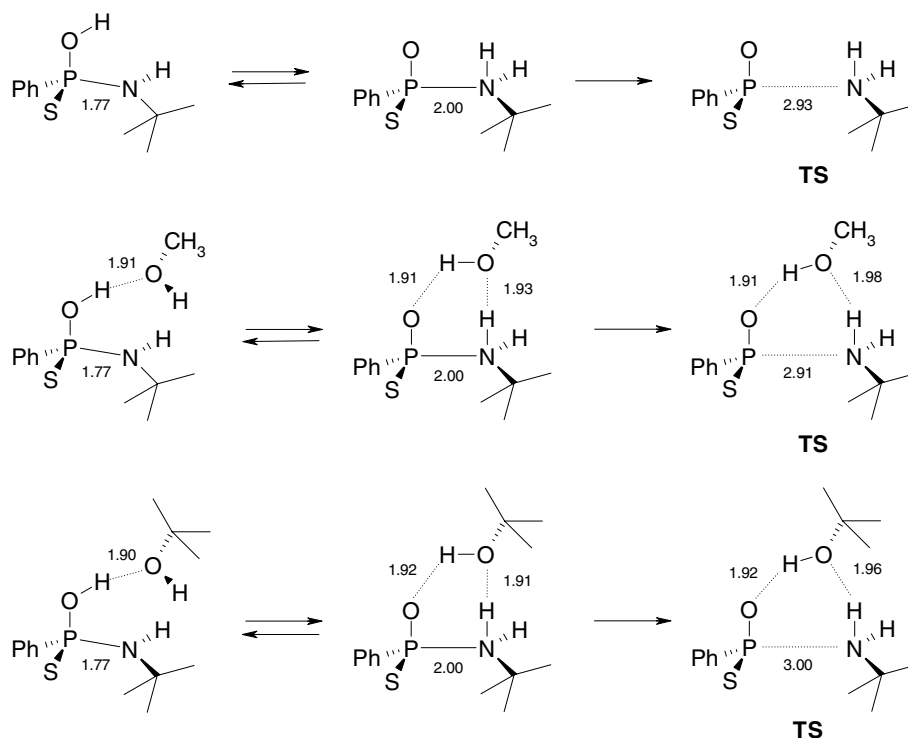


Fig. 2. PM3 optimized structures of the stationary points of the dissociative reaction of **1** in dichloromethane without alcohol (top), with methanol (middle) and *tert*-butanol (bottom). All distances are in angstroms.

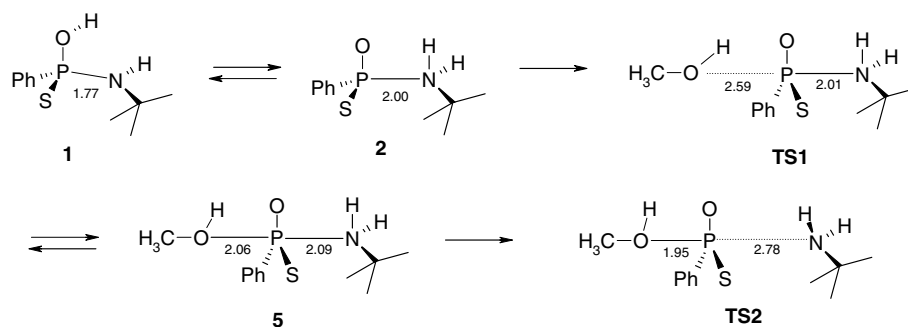


Fig. 3. PM3 optimized structures of the stationary points of the associative reaction of **1** in dichloromethane with methanol. All distances are in angstroms.

Table 3

Calculated nitrogen and hydrogen isotope effects on reaction of **1** with alcohols in dichloromethane – elimination–addition mechanism

Alcohol	$k_H/k_D$	$K_H/K_D$	$(k_H/k_D)$	$k_{14}/k_{15}$	$K_{14}/K_{15}$	$(k_{14}/k_{15})$
None	1.238	0.601	0.744	1.0201	0.989	1.0087
MeOH	1.245	0.684	0.851	1.0203	0.988	1.0082
Bu <sup>t</sup> OH	1.226	0.704	0.862	1.0193	0.987	1.0193

very close to the average experimental isotope effect found for reaction with all alcohols (0.82) (Table 1). The similar value (0.74) of hydrogen isotope effect was found for four-centered proton transfer without alcohol acting as a relay. On the basis of semiempirical theoretical predictions of hydrogen isotope effect the role of alcohol in proton transfer cannot be described explicitly.

The magnitude of the calculated equilibrium nitrogen isotope effect (Table 3) is equal to 0.988 and is very close to the value previously estimated on the basis of the literature data: 0.985 [9]. The values of calculated kinetic nitrogen isotope effect, when corrected for the pre-equilibrium step (Eq. (1)), are in good agreement with experimental data (Table 2).

Table 4

Calculated nitrogen and hydrogen isotope effects on reaction of **1** with methanol in dichloromethane – addition–elimination mechanism

	$k_1$	$k_{-1}$	$k_2$
$k_H/k_D$	1.0383	1.3016	0.9749
$k_{14}/k_{15}$	1.0009	0.9970	1.0165

Thus, the comparison of experimental and calculated isotope effects for the elimination–addition mechanism supports the intermediacy of metathiosphosphate **3**.

The semiempirical calculations for the alternative addition–elimination mechanism were only successful for the reaction with methanol (Fig. 3). The calculated kinetic isotope effects on individual reactions are reported in Table 4. After their application in the Eq. (2) and comparison with the experimental kinetic nitrogen effect value (1.0070), the partitioning factor  $x$  was found to be equal 0.12. This suggests equilibrium between the pentacoordinate intermediate **5** and zwitterion **2** and methanol. Thus, in the case of “small” methanol the addition–elimination mechanism cannot be excluded. However, the reaction of **1** with sterically demanding alcohol, i.e., *tert*-butanol, which would involve an intermediate containing bulky substituents in both apical positions, seems unlikely. Enantiopure **1** was found to react completely non-stereospecifically with *tert*-butanol and with methanol the product was formed with one enantiomer in large excess [10].

#### 4. Conclusions

The intermediacy of metathiosphosphate Ph–PSO in the reaction of *N-tert*-butyl-*P*-phenylphosphonamidothioic acid **1** was examined by means of hydrogen and nitrogen kinetic isotope effects. The comparison of experimental and theoretical results at the semiempirical level (PM3) led us to the conclusion that the reaction follows the unimolecular elimination–addition mechanism. However, in the case of reaction of **1** with methanol, the alternative addition–elimination mechanism is also consistent with experimental data.

#### Acknowledgements

This work was supported by grant 4T09A 117 24 from the State Committee for Scientific Research (KBN, Poland). Computer time was provided by the Interdisciplinary Center for Mathematical and Computational Modeling, Warsaw University (Poland).

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