ISSN 1070-3632, Russian Journal of General Chemistry, 2006, Vol. 76, No. 5, pp. 720–725. © Pleiades Publishing, Inc., 2006.
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Effect of Reaction Medium on the Kinetic Rules of Formation of Phosphorus-Containing Picrylhydrazides

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Received April 12, 2005

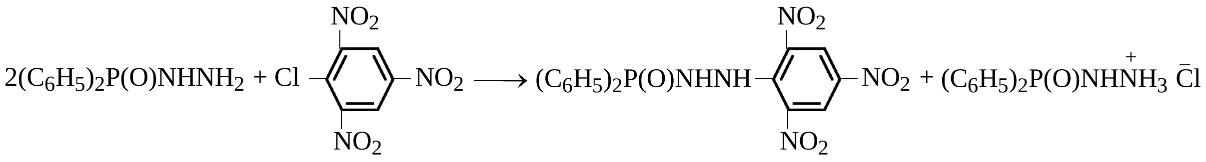
Abstract—Rate constants of the reaction of diphenylphosphinic acid hydrazide with picryl chloride in the solvents of different nature may be quantitatively connected with their physicochemical characteristics by means of the linear tetraparametric Coppel–Palm equation. The rule obtained permits to carry out quantitative analysis of the solvatational effects of solvents under study. Reaction rate depends mainly on the solvent basicity and polarity. Reaction mechanism is discussed and possible scheme of solvatation is offered.

DOI: 10.1134/S1070363206050100

The kinetic rules of the reactions of nucleophilic aromatic substitution in the series of activated derivatives of benzene and substituted hydrazine in the solvents of different nature have not been sufficiently studied up to now. Small attenion was focused on the quantitative evaluation of the physicochemical properties of the solvents in these reactions [1]. For establishing the reaction mechanism the investigation of the effect of solvent on the kinetics of the process is of special interest.

In this connection it seemed important to study an effect of the medium nature on the reaction rate of hydrazine organophosphorus derivatives with picryl halides. That is why in the present work the reaction kinetics of diphenylphosphinic acid hydrazide with picryl chloride in solvents of different nature **I**–**XXIV** is studied (see the table) at 25°C. Kinetic data were used for investigation of the mechanism of specific and nonspecific solvatation of starting reagents with solvents.

Experiments showed that the reaction of diphenylphosphinic acid hydrazide **XXV** with picryl chloride **XXVI** in different solvents similarly to the previously studied reaction in benzene [8] proceeded quantitatively and irreversibly according to the equation presented below to form the phosphorus-containing picrylhydrazide **XXVII**.



$$2(C_6H_5)_2P(O)NHNH_2 + Cl-C_6H_2(NO_2)_3 \longrightarrow (C_6H_5)_2P(O)NHNH-C_6H_2(NO_2)_3 + (C_6H_5)_2P(O)NH\overset{+}{N}H_3\,\overset{-}{Cl}$$

XXV **XXVI** **XXVII** **XXVIII**

Kinetisc of this reaction is described by the second order equation. The observed rate constants (k, l mol^{-1} s^{-1}), calculated with this equation practically do not alter in the course of the process, what shows on the correctness of this equation for the calculations of obtained data in all the solvents under study. The values of the rate constants and the parameters of solvents are presented in the table.

From the table it follows that the lowest reaction rate (k) is observed in saturated hydrocarbons and their halide derivatives **I**–**IV**. As is generally known, interaction of such solvents with reagents may be caused only by nonspecific solvatation arising from the electrostatic interaction between the molecules of solvent and of dissolved substance. In the case of electrostatic interaction only a linear dependence between the logarithms of the rate constant and of the values $[(\varepsilon - 1)/(2\varepsilon + 1)]$, characterizing the solvent polarity, is usually observed [9, 10]. But from the data of the table and the equation (1) it follows that for the reaction of picryl hydrazide formation in the studied sol-

Rate constants (k) of the reaction of diphenylphosphinic acid hydrazide with picryl chloride in the solvents **I–XXIV** at 25°C and the parameters of solvents

Comp. no.	Solvent	k, $\mathrm{l\,mol^{-1}\,s^{-1}}$	ε [2, 3]	n_D^{20} [2, 3]	Y	P	E [2, 4, 5]	B [3, 6, 7]
I	Hexane	0.0201 ± 0.0003	1.89	1.3750	0.186	0.2289	0	0
II	Heptane	0.0205 ± 0.0002	1.92	1.3877	0.190	0.2358	0	0
III	Cyclohexane	0.0223 ± 0.0002	2.02	1.4262	0.202	0.2563	0	0
IV	Tetrachloromethane	0.0255 ± 0.0022	2.24	1.4603	0.226	0.2742	0	0
V	Benzene	0.0418 ± 0.0013	2.28	1.5011	0.230	0.2947	2.1	48
VI	Toluene	0.0489 ± 0.0009	2.38	1.4969	0.239	0.2926	1.3	58
VII	Mesitylene	0.0573 ± 0.0017	2.28	1.4994	0.230	0.2938	0.8	77
VIII	Nitromethane	0.0816 ± 0.0012	38.6	1.3819	0.481	0.2326	5.1	65
IX	Nitrobenzene	0.105 ± 0.005	34.8	1.5546	0.479	0.3215	0	67
X	Anisole	0.112 ± 0.002	4.33	1.5170	0.345	0.3025	1.4	155
XI	Benzonitrile	0.116 ± 0.007	25.2	1.5282	0.471	0.3084	0	155
XII	Acetonitrile	0.124 ± 0.006	37.5	1.3416	0.480	0.2106	5.2	160
XIII	Methylacetate	0.143 ± 0.007	6.68	1.3619	0.396	0.2218	1.6	170
XIV	Dioxane	0.192 ± 0.005	2.21	1.4424	0.224	0.2543	4.2	237
XV	Diethyl ether	0.217 ± 0.012	4.34	1.3527	0.345	0.2167	0	280
XVI	Ethyl acetate	0.250 ± 0.009	6.02	1.3724	0.385	0.2275	1.6	181
XVII	Dibutyl ether	0.283 ± 0.004	3.06	1.3993	0.289	0.2420	0	285
XVIII	Tetrahydrofurane	0.381 ± 0.014	7.39	1.4076	0.405	0.2451	0	287
IX	*N*,*N*-Dimethylformamide	0.454 ± 0.018	36.7	1.4272	0.480	0.2584	2.6	291
XX	*N*,*N*-Dimethylacetamide	0.623 ± 0.019	37.8	1.4356	0.480	0.2627	2.4	343
XXI	Tributyl phosphate	0.948 ± 0.021	6.78	1.4246	0.397	0.2555	6.3	336
XXII	*N*,*N*-Diethylacetamide	1.15 ± 0.04	–	–	–	–	–	335
XXIII	Dimethylsulfoxide	1.34 ± 0.06	48.9	1.4783	0.485	0.2826	3.2	362
XXIV	Hexamethylphosphotriamide	2.62 ± 0.09	29.6	1.4582	0.475	0.2730	0	471

vents the common Kirkwood dependence is not observed.

$$\log k = -2.11 + 3.61[(\varepsilon - 1)/(2\varepsilon + 1)], \qquad (1)$$
$$n\ 23,\ r\ 0.705,\ s\ 0.428.$$

The rate constant value obtained for the reaction in *N*,*N*-diethylacetamide **XXII** was not used in the calculation of the correlational equations due to the lack of some of parameters for this solvent. Hence, the absence of the common Kirkwood dependence and the sharp increase in the reaction rate in aromatic hydrocarbons **V**–**VII** as compared to the protoinert solvents **I**–**IV** inspite of the closeness in the values of their permittivity, as well as other donor solvents **VIII**–**XXIV** shows on the existence of the effect of the specific solvation in this process. In donor solvents the reaction proceeds much more effectively than it may be expected from the consideration of their values of permittivity (ε). Really the highest reaction rate is observed in the oxygen- and nitrogen-containing solvents **VIII**–**XXIV** (amides, sulfoxides, esters and ethers, nitriles, etc) related to the electrondonating substances and good acceptors of hydrogen atoms at hydrogen bonding in the donor–acceptor complexes. Formation of bonds of the N–H···O(N) type must increase electronic density on the nitrogen atom of hydrazide, and hence, increase of its nucleophilicity what probably provides the highest reaction rates in these solvents.

Hence, from the above-delivered it follows that the difference in the reaction rate in various media arises not only from nonspecific solvation, but also from the ability to enter or not enter the specific interactions with reagents.

For the quantitative analysis of solvational effects in the reaction under study we used the tetraparametric Coppel–Palm equation (2). It reflects the additive effect of various properties of the medium, that is of its polarity and polarizability (nonspecifis solvation), and of its electrophilicity and basicity (specific solvation) on the reaction rate [2].

$$\log k = \log k_0 + yY + pP + eE + bB. \qquad (2)$$

Here Y and P are respectively the polarity and polarizability of a solvent expressed as functions of the dielectric constant $[(\varepsilon - 1)/(2\varepsilon + 1)]$ and the refraction index $[(n^2 - 1)/(n^2 + 2)]$. *E* and *B* are the empirical parameters of electrophilicity and basicity of solvents respectively; k_0 is the rate constant of the reaction in gas phase; *y*, *p*, *e*, and *b* are the coefficients characterizing the sensitivity of the reaction to the corresponding parameter. Correlational depensence of logarithms of the reaction rate constants from all the above-mentioned parameters of solvents is well described by the equation (3).

$$\log k = -2.18 + 0.800Y + 1.43P + 0.0211E + 0.00373B, \quad (3)$$
$$n\ 23,\ r\ 0.989,\ s\ 0.097.$$

The partial correlation coefficients for separate parameters are: r_1 0.705, r_2 0.193, r_3 0.343, r_4 0.973 (r_1, r_2, r_3, and r_4 are the partial correlation coefficients between lgk and the functions *Y*, *P*, *E*, and *B* respectively).

Obtained data show that the reaction under study is sensitive to all types of solvation. Effect of nonspecific solvation is mainly expressed by the polarity of solvent due to more significant increment of the electrostatic effect (r_1 0.705) as compared to polarizability expressed by dispersional interactions (r_2 0.193). Specific solvation is caused mainly by the significant positive effect of nucleophilic solvation (r_4 0.973) and the insignificant effect of electrophilic solvation (r_3 0.313) on the rate of the process. Positive values of the regression coefficients for *Y*, *P*, *E*, and *B* show that the proceeding of the reaction is favored by the nonspecifis solvation, as well by the nucleophilic solvatation of hydrazide and the electrophilic solvation of picryl chloride due to the presence of the nucleophilic center on the chlorine atom in the latter compound. As the regression coefficients do not give the opportunity to evaluate the significance of separate parameters, for the evaluation of their effect on the reaction rate the correlational characteristics of triparametric equations were calculated in which separate addends were alternately excluded, that is one of the parameters was equalized to zero.

$$\log k = -2.09 + 1.83P + 0.0325E + 0.00411B, \quad (4)$$
$$n\ 23,\ r\ 0.982,\ s\ 0.121,$$

$$\log k = -1.82 + 0.886Y + 0.0152E + 0.00368B, \quad (5)$$
$$n\ 23,\ r\ 0.986,\ s\ 0.106,$$

$$\log k = -2.11 + 0.925Y + 1.13P + 0.00373B, \quad (6)$$
$$n\ 23,\ r\ 0.987,\ s\ 0.103,$$

$$\log k = -1.99 + 3.49Y - 0.427P + 0.0224E, \quad (7)$$
$$n\ 23,\ r\ 0.710,\ s\ 0.447.$$

From the Eqs. (4)–(7) it follows that the property of solvent determining the rate of the process is its basicity *B* (the electon-donating properties). At the exclusion of this parameter the correlation is practically absent. [equation (7), *r* 0.710]. Polarity of a solvent also contributes the essential but the significantly smaller effect as seen from the decrease in the correlational coefficient from 0.989 [Eq. (3)] to 0.982 [Eq. (4)] at the exclusion of this parameter. Positive meaning of the value e and also the decrease in the correlation coefficient from 0.989 [equation (3)] to 0.987 [Eq. (6)] at the exclusion of this parameter tells about the electrophilic assistance for the proceeding of this reaction. The polarizability and the electrophilicity of solvents affects slightly the rate [Eq. (5), *r* 0.986, and Eq. (6), *r* 0.987].

Exclusion of the variables of small significance (the polarizability and the electrophilicity) from the equation according to the recommendations of IUPAC [11] and the transfer to twoparametric equations showed that the rate of the process is mainly determined by the basicity and the polarity of a solvent and with high accuracy is described by twoparametric linear equation (8) with the insignificant decrease in correlation coefficient.

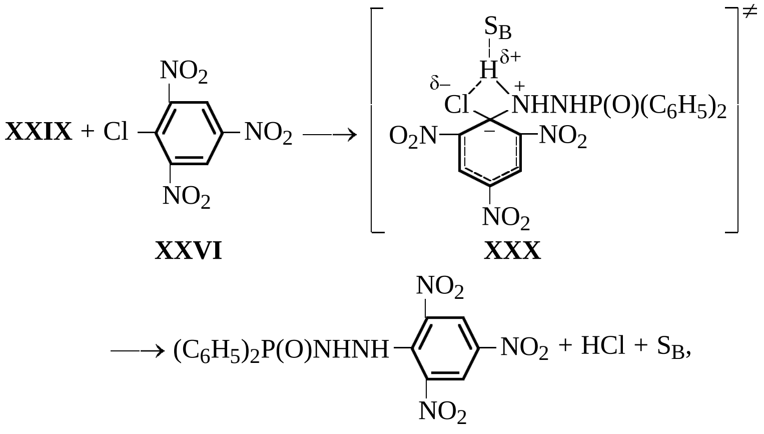
$$\log k = -1.82 + 0.968Y + 0.00369B, \quad (8)$$
$$n\ 23,\ r\ 0.985,\ s\ 0.107.$$

On the basis of the above correlations and also considering the equation (1) it may be concluded that the main contribution to reaction rate in donor solvents **V**–**XXIV** is the nucleophilic assistance to the reaction process. Hence, the effect of solvents under investigation is determined by their electron-donating properties and mainly by the ability of hydrogen bonding [1].

We have shown previously [12] that the reaction under study is not complicated by the catalytic effect of starting substances or the reaction products. It is also found that in the noncatalyzed reaction which evidently proceeds according to S_NAr mechanism the rate-limiting step is the σ-complex formation. Considering the fact that the specific solvation with donor solvents is regarded as the catalysis with these substances, the mechanism of the reaction of picrylation of diphenylphosphinic acid hydrazide in the solvents under investigation may be given by the schemes (9)–(11).

A significant positive contribution of nucleophilic solvation to the rate of the process of nucleophilic solvatation well corresponds to the high sensitivity of such reactions to the catalytic additives of organic

$$\underset{\textbf{XXV}}{(C_6H_5)_2P(O)NHNH_2} + \underset{\textbf{V–XXIV}}{S_B} \rightleftarrows \underset{\textbf{XXIX}}{(C_6H_5)_2P(O)NHHNH—H\cdots S_B}, \qquad (9)$$



XXVII

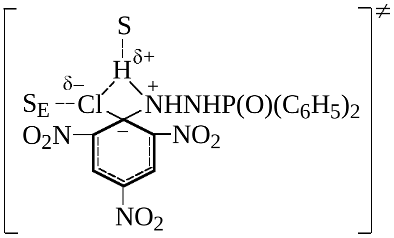
$$(C_6H_5)_2P(O)NHNH_2 + HCl \longrightarrow (C_6H_5)_2P(O)NH\overset{+}{N}H_3\,\overset{-}{Cl}. \qquad (11)$$

bases and to the mechanism of catalysis [12]. Actually if the formation of σ-complex is the limiting step of the reaction of diphenylphosphinic acid hydrazide with picryl chloride, the alteration in the rate may be observed only on this step. According to the scheme (9) the electron-donating solvent (S_b) **V**–**XXIV** forms H-complex **XXIX** with nucleophile **XXV**. This complex exhibits higher nucleophilicity than the starting hydrazide due to the localization of electronic density on nitrogen. Association of hydrazide with the molecule of the electron-donating solvent is a fast and equilibral process. Increasing in the nucleophilicity of hydrazide facilitates formation of new bond with the carbon atom of picryl chloride **XXVI** on the subsequent rate-limiting stage. It proceeds through the four-centered cyclic transition stage **XXX** which then transforms to the reaction products [schemes (10) and (11)].

The mechanism of this reaction is based on the formation of new C–N bond and the rupture of C–Cl and N–H bonds. Formation of N–H bond and hence the cleavage of C–Cl and N–H bonds on the rate-limiting stage [scheme (10)] is assisted with the formation of the H···Cl hydrogen bond between the leaving hydrogen and chlorine atoms in the cyclic four-centered transition state **XXX**. In the medium of the electron-donating solvent the hydrogen atom of the amino group of hydrazide due to its more acidic character arising from the formation of the hydrogen bond with the electron-donating solvent ($H\cdots S_B$) will be connected with the leaving atom of chlorine by the stronger hydrogen bond than in the proton-inert solvent, what in its turn will favor the cleavage of the C–Cl bond.

Hence, the electron-donating solvent promotes formation of the cyclic transition state where the hydrogen atom is coordinated with three atoms: the leaving chlorine, the solvent S_B and the nitrogen atom of hydrazide, the attacking nucleophile. This conclusion agrees with the established sensitivity to formation of the hydrogen bond with the leaving group and the catalyst [13]. In this case the solvent facilitates the ejection of hydrogen atom from the amino group of the σ-complex by formation of hydrogen bond. It also facilitates the formation of the hydrogen bond between the leaving atoms of hydrogen and chlorine.

From the experimental data it follows that the solvents also exhibit insignificant electrophilic solvation what is possible because of the presence of nucleophilic center in the molecule of picryl chloride. Considering the electrophilic solvation transition state of the reaction under study will be described by the formula **XXXI**.



XXXI

In this case the solvatation of chlorine atom of σ-complex with the electrophilic center of solvent is observed (S_E is the electrophilic solvent). Such electrophilic solvation favors the formation of the new

C–N bond and facilitates the cleavage of C–Cl bond. From the obtained data it follows that the effect of electrophilicity of solvent is positive, that is the electrophilic properties of solvent favor some increase in the reaction rate. Formation of σ-complex and its decomposition through the cyclic four-centered transition state **XXXI** proceeds compatibly on the rate-limiting stage.

Hence, the main contribution to the increase in the reaction rate in electron-donating solvents **V**–**XXIV** is the nucleophilic solvation of the starting hydrazide by means of formaton of the hydrogen bond with it (complex **XXIX**). This process is assisted by the electrophilic solvation of the obtained transition state **XXXI**.

EXPERIMENTAL

Diphenylphosphinic acid hydrazide was prepared from corresponding acid chloride and hydrazine hydrate in anhydrous benzene [14, 15]. Pycryl chloride was purified for kinetic measurements according to the procedure [16]. Hexane and heptane for kinetic measurements were dried over phosphorus pentoxide and distilled over its fresh portion, and then over sodium. Cyclohexane was passed through a column whose upper part was filled with the silica gel and the lower one with the active aluminum oxide, and then distilled over sodium. Tetrachloromethane was purified by shaking consiquently with sodium hydroxide and the diluted hydrochloric acid. Then it was dried over freshly calcinated calcium chloride and phosphorus pentoxide and then distilled. Benzene was purified analogously to [17]. Toluene of the “pure” grade was treated with concentrated sulfuric acid, washed with water, then with solution of sodium hydroxide, dried over calcium chloride and fractionated over sodium wire. Mesitylene of the “pure” grade was dried over calcium chloride and twice distilled over sodium at reduced pressure. Nitromethane and nitrobenzene of the “pure for analysis” grade were dried over calcium chloride and twice distilled in a vacuum. Anisole of the “pure” grade was kept for 3 h at 100°C over sodium hydroxide and then twice distilled at reduced pressure over sodium. Benzonitrile of the “chemically pure” grade was refluxed for 5 h with phosphorus pentoxide and then twice distilled without the drying agent at reduced pressure. Acetonitrile of the “pure for analysis” grade was boiled for 3 h over phosphorus pentoxide and then twice distilled each time over the fresh portion of phosphorus pentoxide, and then without a drying agent. Methyl and ethyl acetate of the “pure” grade were washed with the saturated water solution of sodium chloride and then dried for a week over the magnesium sulfate. After that these solvents were twice distilled over phosphorus pentoxide and then without a drying agent. Dioxane was refluxed for 2 h over solid potassium hydroxide for removing of peroxides. After that it was refluxed for 3 h over sodium and then distilled. Diethyl ether, dibutyl ether, and THF of the “pure” grade were purified by refluxing over potassium hydroxide and then distilled on a fractionating column over sodium. DMF of the “pure” grade was kept for 3–4 h at reduced pressure under nitrogen to remove the volatile amines. After that the first fraction was distilled off, and the residue was refluxed for 2 h with hexamethylenediisocyanate (10 ml l^{-1}) and then triple fractionated on the fractionation column collecting the fraction boiling at 55°C (20 mm Hg). *N*,*N*-Dimethylacetamide and *N*,*N*-diethylacetamide of the “pure” grade were several (3–4) times distilled in a vacuum collecting the fractions boiling at 84°C (32 mm Hg) and 48°C (6 mm Hg) respectively. Tributyl phosphate of the “pure” grade was distilled in a vacuum. DMSO of the “pure” grade was distilled at reduced pressure over barium oxide and then twice without a drying agent; the first and the last fractions were thrown away. Hexamethyl phosphoritriamide of the “pure” grade was boiled over barium oxide and then exposed to fractional distillation. Obtained middle fraction was purified by fractionation in a vacuum over phosphorus pentoxide. The physicochemical properties of all the substances used well corresponded to the published data.

Reaction progress was monitored by potentiometric evaluation of the amount of unreacted hydrazide according to the previously described procedures [18]. Kinetic measurements were carried out at 25 ± 0.05°C. The starting concentrations of reagents were 0.00125 mol l^{-1} for diphenylphosphinic acid hydrazide and 0.000625 mol l^{-1} for picryl chloride.

For the evaluation of the solvational coefficients *y*, *p*, *e*, and *b* in the Coppel–Palm equation experimental data were presented as a system of n linear equations (*n* is the number of solvents). This system of equations was solved by means of the root-mean-square method on a pesonal computer. The accuracy of obtained results was evaluated by the mathematical statistics methods (the confidential probability 0.95) [19].

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