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General Base Catalysis by Organic Bases of the Reaction of Diphenylphosphinic Hydrazide with Phenyl Isocyanate in Benzene

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Abstract—The kinetics of the reaction of diphenylphosphinic hydrazide with phenyl isocyanate in the presence of organic bases in benzene at 25°C were studied. The catalytic activity of the bases correlates with spectroscopic and thermodynamic Taft (pK_{HB}), Koppel–Palm (*B*), and Gutmann (*DN*) parameters. A common general base mechanism of the catalysis of semicarbazide formation by bases belonging to different classes of organic compounds is offered and discussed.

Organic catalysts exhibit a high catalytic activity in nucleophilic additions of hydrazine derivatives [1, 2]. At the same time, the catalytic activity of such compounds in reactions of phosphorus-containing hydrazides with isocyanates have scarcely been studied. The problem of searching for effective catalysts for such practically important processes is actual. In the purposeful search for highly active organic catalysts for systems in which starting compounds enhance their reactivity via donor–acceptor interaction with catalysts of special interest are organic bases containing different basic centers and belonging to different classes of compounds. It is important to find out the possibility of realization of the above mechanism and to correlate the catalytic properties of bases with the nature and structure of electrophilic reagents.

To this end, in the present work we studied the catalytic activity of benzenes and nitrogen- and oxygen-containing compounds **I**–**XVIII** that belong to different classes and capable of specific interactions with reagents in the reaction of diphenylphosphinic hydrazide (**XIX**) with phenyl isocyanate (**XX**) in benzene at 25°C. We correlated the catalytic activity with the class of organic bases, their structure, the nature and structure of electrophilic reagents, and also different basicity parameters of catalysts.

It was established that semicarbazide **XXI** formation in the presence of the catalysts under investigation proceeds irreversibly according to the following scheme.

$$\underset{\textbf{XIX}}{(C_6H_5)_2(O)PNHNH_2} + \underset{\textbf{XX}}{O{=}C{=}N{-}C_6H_5} \longrightarrow \underset{\textbf{XXI}}{(C_6H_5)_2(O)PNHNHCONHC_6H_5}.$$

Control experiments showed that the catalytic reaction proceeds quantitatively and is not complicated by side processes. The substituted semicarbazide formed by the reaction has no effect on the catalytic process. Small additives of organic bases to the reaction mixture accelerate the reaction significantly, i.e. act as catalysts.

The rate of the reaction in benzene in the presence of organic catalysts is described by Eq. (1).

$$dx/dt = k_0(a - x)(b - x) + k_b(a - x)(b - x)m. \quad (1)$$

Here k_0 and k_b are the rate constants of the noncatalytic ($l\ mol^{-1}\ s^{-1}$) and catalytic ($l^2\ mol^{-2}\ s^{-1}$) reactions, respectively; *a*, *b*, and *m* are the initial concentrations of hydrazide, phenyl isocyanate, and catalyst (M); *x* is the yield of the reaction product (M); and *t* is time (s). From Eq. (1) it follows that the overall apparent rate constant is described by Eq. (2).

$$k = k_0 + k_b m. \quad (2)$$

The apparent rate constant *k* ($l\ mol^{-1}\ s^{-1}$) was found by a second-order reaction equation, since in was shown that the reciprocal current reagent concentrations linearly vary with time at varied catalyst concentrations and the rate constants are invariable in the course of the process. The catalytic rate constants k_b listed in Table 1 were found by Eq. (2) {k_0 0.449 ± 0.012 $l\ mol^{-1}\ s^{-1}$) [3]}.

Small bases additives significantly accelerate the

Table 1. Effect of organic bases on the rate of the reaction of diphehylphosphinic acid hydrazide with phenyl isocyanate in benzene at 25°C

Comp. no.	Catalyst	pK_{BH^+} [4, 5]	pK_{HB} [4]	*DN* [6, 7]	B [7, 8]	k_b, $l^2 mol^{-2} s^{-1}$	k_b/k_0, M
I	Toluene	–	–	–	58	0.498±0.063	1.11
II	Mesitylene	–	–	–	77	0.511±0.067	1.14
III	Nitromethane	–	–	2.7	65	0.539±0.061	1.20
IV	Nitrobenzene	–12.14	0.73	4.4	67	0.544±0.056	1.21
V	Anisole	–6.82	0.02	–	155	1.58±0.35	3.52
VI	Benzonitrile	–10.70	0.80	11.9	155	2.51±0.25	5.59
VII	Acetonitrile	–	0.90	14.1	160	2.64±0.34	5.87
VIII	Methyl acetate	–5.2	1.00	16.5	170	4.08±0.31	9.08
IX	Ethyl acetate	–3.96	1.09	17.1	181	4.72±0.24	10.5
X	Diethyl ether	–2.42	1.01	19.2	280	6.60±0.19	14.7
XI	Dioxane	–3.22	0.73	14.6	237	12.5±1.5	27.8
XII	Dibutyl ether	–5.40	1.02	–	285	6.71±0.42	14.9
XIII	Tetrahydrofuran	–2.08	1.26	20.0	287	7.80±0.28	17.4
XIV	*N,N*-Dimethylformamide	–1.50	2.06	26.6	291	23.0±2.3	51.2
XV	*N,N*-Dimethylacetmide	–0.36	2.38	27.8	343	31.7±2.4	70.6
XVI	*N,N*-Diethylacetamide	–	2.47	32.2	335	47.9±3.2	106
XVII	Dimethyl sulfoxide	–1.04	2.53	29.8	362	40.9±1.6	91.0
XVIII	Pyridine	5.25	1.88	33.1	472	66.2±4.1	147

reaction, and the reaction rate significantly increases with increasing catalyst concentration. The apparent rate constants *k* linearly vary with catalyst concentration (up to the concentration 0.05 M).

From Table 1 it follows that organic bases **I**–**XVIII** are effective catalysts for the process of formation of phosphorus-containing semicarbasides. At the same time, noteworthy are great differences in the activity of bases belonging to differerent classes of compounds. The catalytic activity measured by the k_b/k_0 ratio span the range 1.11–147. Hence, the catalytic activity of the catalysts studied varies 130 times. The most active catalyst is pyridine (**XVIII**) whose nucleophilic solvation ability is the highest. It is known that nitrogen- and oxygen-containing bases act as strong hydrogen acceptors in hydrogen-bond formation in donor–acceptor complexes. The formation of fairly strong hydrogen bonds of $N–H\cdots O(N)$ type increases the electron density on the nitrogen atom of the amino group of the hydrazide, thus enhancing the nucleophilicity of the latter and ensuring the highest reaction rates in the presence of these bases. It is known that the aromatic ring can exhibit nucleophilic properties and forms weak hydrogen bonds with proton donors. But, as the specific solvation with aromatic hydrocarbons is not so effective as with nitrogen- and oxygen-containing compounds, the reaction rates in the presence of toluene (**I**) and mesitylene (**II**) are the lowest. The catalytic activity of bases belonging to different classes of organic compounds increases in the order aromatic hydrocarbons < nitro compounds < nitriles < ethers ≈ carboxylic esters < carboxamides < sulfoxides < tertiary amines. This trend is evidently explained by the electron-donor properties and ability of these compounds to hydrogen-bond formation, which, too, enhance in the above order.

Note that the character of the structural effect of electrophilic reagents on the catalytic activity of organic bases in this reaction is similar [9]. This fact shows that hydrogen-bond formation on catalysis plays a decisive role in the reactions with all the substrates. In the series of the electrophilic reagents we studied previously and in the present work, the sensitivity to the catalytic effect of organic bases increases in the order phenyl isocyanate < picryl chloride < phenyl isothiocyanate < mesityl isothiocyanate, even though the rate of a noncatalytic reaction of diphenylphosphinic hydrazide with the above-mentioned substrates varies in the opposite order. The fact that the catalytic activity of organic bases increases in going from phenyl isocyanate to mesityl isothiocyanate agrees with the commonly accepted postulate that catalysts act more effectively in slower reactions. Hence, the trend in variation of the catalytic activity of bases with the nature and structure of electrophilic reagents provides evidence for hydrazide–catalyst complex formation and thus for a general base mechanism of the catalysis.

To find out the mechanism of the catalytic action of various organic bases, it is expedient to quantitatively correlate the activity of catalysts with parameters characterizing their properties. With this purpose we correlated the logarithms of catalytic rate constants k_b with the basicity of catalysts (pK_{BH^+}) in water (Table 1). However, no satisfactory correlation was obtained. This implies lack of ionic dissociation with complete proton transfer from hydrazide to catalyst. It was recently showed [5] that the strength of organic bases in protoinert media is best evaluated on the Taft pK_{BH} scale which reflects the ability of the nucleophilic center of a catalyst to hydrogen-bond formation [4, 10–12]. The corresponding data analysis showed that the catalytic rate constants vary in parallel with the ability of bases to hydrogen-bond formation. The effect of the catalysts on the reaction rate was quantitatively described in terms of pK_{HB} values by means of Eq. (3) (data in dioxane **XI** were not used, because they much deteriorated the correlation coefficient).

$$\log k_b = (-0.0985 \pm 0.1631) + (0.728 \pm 0.105)pK_{HB};$$
$$n\ 14,\ r\ 0.900,\ s\ 0.289. \qquad (3)$$

The resulting data suggest that catalysts of different nature act by a common mechanism. Most probably, this is a general base catalysis mechanism that involves formation of a hydrogen-bonded complex like **XXII**. Really, we can hardly develop an alternative mechanism for such weak bases as aromatic hydrocarbons, nitro compounds, nitriles, ethers, and carboxylates. Their catalytic activity can be explained in no other way than by hydrogen-bond formation, which is characteristic of general base catalysis [5]. Similarly, the catalytic activity of carboxamides and sulfoxides is in the first turn determined by their ability to hydrogen-bond formation [5]. It was previously shown [13] that the high catalytic activity of tertiary amines in thiosemicarbazide formation primarily contributed by the electron-donor properties of the catalysts and their ability to hydrogen-bond formation. The latter fact better agrees with base rather than nucleophilic catalysis. Correlation (3) that includes both strong and weak bases, too, provides evidence for the proposed mechanism. Note also that isocyanates exhibit weak coordination properties and do not form complexes even with very strong electron donors [14–16].

Donor number (*DN*) is an important characteristic of electron-donor compounds. This quantitative characteristic has been offered by Gutmann [6, 17] as a parameter of Lewis basicity. It characterizes the overall strength of interaction of an electron donor with an electron acceptor. The catalytic activity of bases considerably depends on their nature, and, as follows from Table 1, it increases with increasing donor number. We found that the dependence of the logarithms of catalytic rate constants on the donor numbers of catalysts is quantitatively described by the linear equation (4) (data for dioxane were not used).

$$\log k_b = (-0.514 \pm 0.031) + (0.0702 \pm 0.0014)DN;$$
$$n\ 13,\ r\ 0.997,\ s\ 0.049. \qquad (4)$$

It is known that the nucleophilicity of compounds can be quantitatively characterized in terms of a Koppel–Palm general basicity (*B*) [8, 18]. The dependence of the logarithms of catalytic rate constants on *B* is described by Eq. (5).

$$\log k_b = (-0.563 \pm 0.105) + (0.00576 \pm 0.00042)B;$$
$$n\ 18,\ r\ 0.960,\ s\ 0.206. \qquad (5)$$

Considering dependences (3)–(5) it is easy to propose that both the spectoscopic Taft (pK_{BH}) and Koppel–Palm (*B*) basicity parameters and the thermodynamic basicity scale of Gutmann (*DN*) reflect the same nucleophilic effects of organic bases in the reaction of hydrazine derivatives with isocyanates and, therefore, are interchangeable. This is also confirmed by the conclusion of Makitra *et al.* [19] about equivalence of *B* and *DN* values and their possible interchangeability in treatment kinetic data.

The aforesaid gives us grounds to suggest that the catalysis mechanism is preassociative (within the frames of the general base mechanism) and common for all the bases, even though the latter belong to different classes of organic compounds. On the first stage [scheme (6)] hydrazide **XIX** associates with base B (**I**–**XVIII**) to form complex **XXII** via hydrogen bonding. The association is a fast and an equilibrium process.

$$\underset{\textbf{XIX}}{(C_6H_5)_2(O)PNHNH_2} + \underset{\textbf{I–XVIII}}{B}$$
$$\rightleftarrows \underset{\textbf{XXII}}{(C_6H_5)_2(O)PNHHN\_H\cdots B}. \qquad (6)$$

The second stage [scheme (7)] is the rate-limiting reaction of associate **XXII** with phenyl isocyanate **XX**. Increased nucleophilicity of hydrazide facilitates formation of a new bond with the isocyanate carbon atom to form a cyclic transition state **XXIII** which

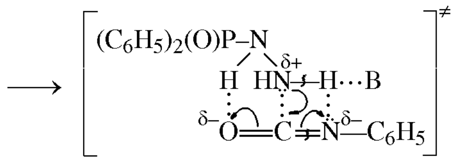
Table 2. Noncatalytic k_0 and catalytic k_b rate constants of the reactions of diphenylphosphinic hydrazide and *p*-toluidine with phenyl isocyanate and picryl chloride in benzene in the presence of catalysts at 25°C

Nucleophile	Catalyst	Phenyl isocyanate			Picryl chloride		
		k_0, l mol^{-1} s^{-1}	k_b, l^2 mol^{-2} s^{-1}	k_b/k_0, l mol^{-1}	k_0, l mol^{-1} s^{-1}	k_b, l^2 mol^{-2} s^{-1}	k_b/k_0, l mol^{-1}
$(C_6H_5)_2(O)PNHNH_2$	Pyridine	0.449 [3]	66.2 ± 4.1	147	0.0418 [20]	7.12 ± 0.28	170
	N,N-Dimethylformamide	0.449 [3]	23.0 ± 2.3	51.2	0.0418 [20]	2.77 ± 0.14	66.2
	Dioxane	0.449 [3]	12.5 ± 1.5	27.8	0.0418 [20]	0.880 ± 0.031	21.0
p-$CH_3C_6H_4NH_2$	Dimethyl sulfoxide	0.00386 [21]	0.196 [22]	49.4	0.745 [23]	0	0
	N,N-Dimethylformamide	0.00386 [21]	0.108 [22]	27.2	0.745 [23]	0	0
	Dioxane	0.00386 [21]	0.00800 ± 0.00037	2.07	0.745 [23]	0	0

then converts to the reaction product, semicarbazide **XXI**, with regeneration of catalyst **I**–**XVIII**.

$$\mathbf{XXII} + O{=}C{=}N{-}C_6H_5$$

XX



XXIII

$$\longrightarrow (C_6H_5)_2(O)PNHNHCONHC_6H_5 + B. \qquad (6)$$

XXI

The close catalytic activities of organic bases in the reactions of diphenylphosphinic hydrazide with phenyl isocyanate and picryl chloride (Table 2) suggest that activation of substrate molecules does not play a significant role, and the different effects of these bases are evidently explained by interaction with the starting hydrazide or the transition state. From this point of view it is interesting to compare the effect of these catalysts in the reactions of diphenylphosphinic hydrazide and *p*-toluidine with phenyl isocyanate and picryl chloride. The absence of accelerating effect of DMSO, DMF, and dioxane in the reaction of *p*-toluidine with picryl chloride can be explained, by analogy with the reactions of aromatic amines with *p*-nitrobenzenesulfonyl bromide and picryl chloride [24], by activation of the amino group in the transition state, since the contributions of activation of the starting amine into the rates of the reactions with phenyl isocyanate and picryl chloride should be the same. The fact that organic bases exhibit almost equal catalytic activities in the reactions of diphenylphosphinic hydrazide with phenyl isocyanate and picryl chloride suggests that the catalyst interacts with the hydrogen atom of the starting hydrazide.

Hence, the accelerating effect of organic bases on the rate of the reaction of diphenylphosphinic hydrazide with phenyl isocyanate is evidently explained by formation of a hydrogen bond involving the amino hydrogen atom of the starting hydrazide.

EXPERIMENTAL

Benzene for kinetic studies was prepared according to [25]. Diphenylphosphinic hydrazide was synthesized and purified according to the procedures described in [26, 27]. Phenyl isocyanate was distilled in a vacuum directly before use. Organic catalysts were purified by known procedures. The purity of the compounds used was determined by the coincidence of their physicochemical characteristics with published data and by the constancy of the kinetic parameters of a reaction involving a particular substance, measured after several consequtive cycles of purification.

The reaction progress was followed as described in [28]. The kinetic measurements were performed in benzene at 25 ± 0.05°C. The initial concentrations of diphenylphosphinic hydrazide and phenyl isocyanate were 0.625×10^{-3} M each, and the concentrations of catalysts were 0.0001–0.05 M. The accuracy of resulting data was evaluated by mathematical statistics methods (confidence level 0.95) [29].

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