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Concerning the Solvent Effect on the Rate of the Reaction between Picryl Chloride and Diphenylphosphinic Hydrazide

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Abstract—The solvent effect on the rate constant of the reaction of picryl chloride with diphenylphosphinic hydrazide can be quantitatively described by a two-parameter equation considering the basicity and polarity of the medium. The reaction proceeds via formation of a charge-transfer complex between the reagents. Its nucleophilic solvation facilitates formation of the final products.

Recently Yanchuk [1] published the results of studying the solvent effect on the rate of the reaction of picryl chloride **I** with diphenylphosphinic hydrazide **II**. It was established that the process considerably accelerates with the increase in the basicity (nucleophilicity) of the medium, though the correlation of the experimental rate constants $\log k_0$ with such characteristics as the Gutmann donor number (*DN*) and the Palm basicity (*B*) [2] is moderate: The pair correlation coefficients *r* are 0.965 and 0.957, respectively. At the same time, any linear correlations with the parameters of polarity or polarizability of solvents are lacking. Based on these observations and also on the fact that the rate of the reaction in relatively inert benzene considerably increases on addition of electron-donating solvents, Yanchuk suggested the possibility of nucleophilic catalysis of this reaction. That is, compound **II** is specifically solvated by such solvents through the formation of a hydrogen bond, which should facilitate formation of the tetrahedral transition state **I**–**II**–solvent, as well as the elimination of a hydrogen chloride molecule. However, the correlation of the rate constants of the suggested concurrent catalytic process $\log k_b$ with the basicity of the medium is even worse than for the rate constants of the overall process: *r* is 0.954 with *DN* and 0.926 with *B*. This fact suggests that, although nucleophilic solvation plays the leading role in the reaction under study, its catalytic effect is doubtful. Furthermore, the probable effect of other solvation processes cannot be neglected. First of all, it concerns the nonspecific solvation. The difference in the reaction rates in the solvents with low basicity counts in favor of this fact. Hence, the rates of the reaction in benzonitrile and nitrobenzene are almost equal (k_0 0.116 and 0.105 $\mathrm{l\,mol^{-1}\,s^{-1}}$, respectively), whereas the basicities *B* differ by a factor of more than two: 155 and 67. At the same time, the reaction rates in nitrobenzene and benzene differ by a factor of 2.5 (k_0 0.105 and 0.0418 $\mathrm{l\,mol^{-1}\,s^{-1}}$, respectively), despite close values of *B*: 67 and 48, respectively. Finally, though the basicities of methyl and ethyl acetates are almost equal (170 and 181), the rate constants of reactions in them differ by a factor of almost two (0.143 and 0.250 $\mathrm{l\,mol^{-1}\,s^{-1}}$).

These facts stimulated us to check the possibility of generalizing $\log k_0$ data from [1] by means of the four-parameter Koppel–Palm equation, which was successfully used for generalization of the influence of physicochemical properties of solvents on the rate of reactions in them [3]. This equation was supplemented by the fifth parameter considering the effect of cohesion pressure (δ^2) and reflecting the probable consumption of energy for cavity formation in the solvent structure to accommodate the reaction complex.

$$\log k = a_0 + a_1 \frac{n^2 - 1}{n^2 + 2} + a_2 \frac{\varepsilon - 1}{2\varepsilon + 1} + a_3 B + a_4 E_T + a_5 \delta^2. \tag{1}$$

Experimental data were taken from [1], and physicochemical properties of solvents, from the review [4]. The calculations were carried out by the procedure recommended by CAC IUPAC [5]. Thus, a five-parametric regression equation was obtained which generalizes the experimental data for all the 15 solvents under study. However, in spite of the sufficiently high coefficient of multiple correlation ($R = 0.976$), considerable standard errors of many regression coefficients for some parameters indicate their little influence on the process. According to recommendations in [5], the effect of separate factors was established by successively excluding summands with these factors and establishing the greatest effect of each of the factors by the minimum value of R for the rest parameters. By this procedure we found that the correlation between physicochemical parameters of solvents and their effect on the reaction rate may be with the acceptable accuracy described by two-parameter equation (2) considering the basicity and polarity of solvents.

$$\log k_0 = -1.84 + (1.03 \pm 0.51)f(\varepsilon) + (3.70 \pm 0.34) \times 10^{-3}B. \quad (2)$$

Here R is 0.972, and the root-mean-square error s is ±0.134. The obtained two-parameter equation is characterized by the higher degree of coupling than the monoparametric dependence on B (r_{0B} is 0.957 in [1] and 0.964 with refined B values according to our calculations). This equation adequately describes the experimantal data according to the Fisher test ($F_{\text{ad}} = 27.46 > F^{\text{t}}_{(0.95;\,14;\,12)} = 2.64$) with the significant coefficient of multiple correlation ($F_{\text{m}} = 88.1 > F^{\text{t}}_{(0.95;\,12;\,2)} = 19.4$) at the confidence probability of 0.95.

Thus, the experimental values of the logarithms of the second-order rate constants of the reaction of **I** with **II** may be satisfactorily generalized directly without the hypothetical subdivision into the catalytic and noncatalytic reaction. Note that generalization of the catalytic rate constants k_b calculated in [1] by Eq. (2) as well as by the monoparametric dependence on B is worse as compared with k_0.

Considering the obtained correlation dependences, let us try to evaluate the correctness of the conclusion made in [1] about the selective solvation of hydrazide **II** with donor solvents in the initial stage. In general, the solvation of the starting substances decreases the reaction rate owing to complications in formation of the intermediate reaction complex and transition state, but in the case under consideration the positive sign of the regression coefficient at the basicity parameter shows that solvation is preferential just in formation of the transition state. Here it is timely to remember that the similar reaction of dinitrochlorobenzene with aniline is a classic example of a process passing through the stage of formation of the charge-transfer complex, which is proved by kinetic and spectral studies [6, 7]. Considering that picryl chloride is the stronger electrophile than dinitrochlorobenzene and is capable of formation of charge-transfer complexes even with aromatic hydrocarbons [8], and that the basicity B of aliphatic amines similar in the properties to **I** is about 660 [2], and that of hydrazine is 560 [9], which is considerably larger than the basicity of solvents used in [1] (the largest value for hexamethylphosphoramide is 470), it is possible to conclude with confidence that in the reactions under study the first stage should be formation of a charge-transfer complex between the reagents **I** and **II**, followed by its conversion to the transition state. Subsequent solvation in this stage with the less basic solvents should facilitate the charge redistribution in it and the evolution of hydrogen chloride. The increase in the polarity of the medium is favorable for this process. For example, in polar nitrobenzene the rate of the reaction is considerably higher than in benzene.

It can be noted that the similar effect of solvation was revealed by Pytela [10] who generalized the data [11] on the kinetics of the reaction of dinitrochlorobenzene with piperidine in various solvents.

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