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DISCUSSION

On the Effect of Solvation Factors on the Homogeneous Base Catalysis in Acylation Reactions

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The rate constant of aniline reaction with 3-nitrobenzenesulfonyl chloride is increased by bases, but this increase is not proportional to the concentration of the additive. With several catalysts, the increase depends on the combined effect both of their basicity and of their polarizability, implying a complex character of the catalysis. Kustova and Kuritsyn [1] found that the rate of acylation of aniline with 3-nitrobenzenesulfonyl chloride in ethyl methyl ketone medium is appreciably increased by base additives. The second-order rate constants k, l mol^{-1} s^{-1}, at the catalyst concentration c_{cat} of 0.01 M are as follows: Et_3N 2.149, Bu_3N 1.412, $(PhCH_2)_3N$ 0.746, Py 0.630, $(Me_2N)_3PO$ 0.023, DMSO 0.012, and $CH_3CON(CH_3)_2$ 0.007 (with no catalyst, $k_0 = 6.4 \times 10^{-3}$). Based on the opinion of Savelova and Oleinik [2], the referees come to a conclusion that the reaction involves formation of molecular complexes either with aniline or with 3-nitrobenzenesulfonyl chloride, which are more reactive that the starting reactants, thus implying base or nucleophilic catalysis in the system. However, they found no linear dependence between the pK of the bases and their catalytic activity constants $k_{cat} = (k - k_0)/c_{cat}$ and explained this result by steric reasons.

The dependence of k on the concentration of the DMSO additive fits the linear equation $k = k_0 + k_{cat} c_{cat}$, which is commonly accepted for homogeneous catalysis, at relatively low DMSO concentrations (0.01–0.5 M) comparable with aniline concentrations (10^{-3}–10^{-2} M) and gets increasingly nonlinear at increasing DMSO concentrations. The same trend is characteristic of the corresponding logarithmic dependence. At the same time, the linearity of the rate of homogeneous catalytic reactions in catalyst concentration is fulfilled to a certain limit, above which the sensitivity to increasing catalyst concentration recedes (as, for instance, in the amine-catalyzed Mannich condensation [3]).

We found that even though the k, log k, or log k_{cat} values tend to increase with increasing basicity of additives (B after Pal'm [4]), no linearity is observed here: Py and $(Me_2N)_3PO$ have close B value (472 and 471, respectively) but the corresponding k values differ 30 times. Similarly, at the close B values for DMSO (352) and $CH_3CON(CH_3)_2$ (343), the k values differ almost two times and the k_{cat} values, ten times. The observed catalytic effect of bases is also inconsistent with data of Kuritsyn [5] on the effect of solvents on aniline reaction with benzenesulfonyl chloride and similar data of Arcoria *et al.* [6] for aniline acylation with thiophenesulfonyl chloride.

We found that the rate constants of the reactions in study increase with solvent basicities B and Reichardt electrophilicities E_t. Therewith, the latter dependence is close to linear: the pair correlation coefficients r between log k and E_t are within 0.89–0.98 [7]. However, it should be noted that most solvents used in [5, 6] are alcohols with fairly high E_t values and, therefore, the systems studied may involve more intricate solvation interactions than simply aniline–base complex formation.

We found in [3] that the effect of physicochemical parameters of the catalyst (amine) on the rate of formaldehyde condensation with ethyl cyanoacetate can fairly be described by the Koppel–Pal'm four-parameter equation [4]. Physicochemical analysis showed that amines form with ethyl cyanoacetate donor–acceptor complexes, most commonly congruently melting, which is probably responsible for the catalytic properties of amines [8]. Therefore, it was interesting

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to find out if the catalytic activity of amines in the reaction in study can be generalized in terms of such multiparameter equations that take into account various solvation factors. However, since for Bu_3N and $(PhCH_2)_3N$ no B and E_t values which relate to specific solvation have been available in the literature, we could deal in our analysis with as little as five compounds. The pair correlation coefficients between k_{cat} and individual solvation factors $f(n^2) = (n^2 - 1)/(n^2 + 2)$, $f(\varepsilon) = (\varepsilon - 1)/(2\varepsilon + 1)$, B, E_t, equal to 0.071, 0.778, 0.886, and 0.822, fail to provide reliable information on the combined effect of these factors on k_{cat}. At the same time, regardless of the very poor correlation coefficient r with the polarizability factor $f(n^2)$, the combination of the latter with B leads to a two-parameter equation that fairly describes the effect of these two properties of bases on their catalytic activity (R is the multiple correlation coefficient and s is the standard deviation):

$$\log k_{cat} = -14.55 + (33.0 \pm 8.2)f(n^2)$$
$$+ (13.4 \pm 1.4)\times 10^{-3}B;\ R\ 0.979,\ s\ 0.300.$$

Reasonable correlation can also be obtained with two nonspecific solvation factors: polarity and polarizability (R 0.976), but the resulting equation takes no account of the possible catalytic effect of basicity. At the same time, simultaneous account for $f(\varepsilon)$ and B is unfruitful, resulting in unfair correlation (R 0.890).

The different effect of individual solvation factors, noted in [1, 5–7], is probably explained by that in the first case the solvent was methyl ethyl ketone which is an n-electron donor and thus a basic compound, and in the second, primarily alcohols which are H-bond donors but with appreciable B values. Sulfonyl chlorides are electon acceptors and can form complexes both with methyl ethyl ketone and with catalysts (bases); on the other hand, aniline, too, is an H-bond donor and can form complexes with n-electron donors, such as Et_3N, acetone, etc. [9]. Taking into account that aniline (B 346) is close in basicity to most catalysts used, we can propose occurrence in the system of various competing solvation processes whose equilibrium depends on the relative basicities and concentrations of the reagents. This is a probable reason for the nonlinearity of the rate–catalyst concentration dependence at large catalyst excesses, when such factors as solvation of the reaction complex in itself and binding of the HCl molecule evolved take force. The effect of polarizability, which is included in the above equation, suggests some contribution of nonspecific solvation of the aromatic reagents.

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