PROTONATION OF REAGENTS AND ACID-BASE CATALYSIS
IN ACYLATION

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The kinetic characteristics of the model reaction of electron transfer and the reaction of acylation of aromatic amines by aromatic acid anhydrides were investigated as a function of the concentration of acid catalyst and a correlation was established between the type of this function and the characteristics of protonation of the amines. The rate constants of the catalytic and noncatalytic flows of the forward and reverse reactions in the phthalic anhydride-\( p \)-toluidine system were determined as a function of the molarity and proton-acceptor properties of the solvent. The mechanism of acid–base catalysis was examined as a sequence of proton and electron transfer processes.

Keywords: catalysis, kinetics, protonation.

According to the generally accepted opinion [1-3], there are stages with proton transfer in acid–base catalysis which cause the formation of protonated and deprotonated forms of the reagents and intermediates. The possibility of electron transfer (excitation) is not considered in this scheme. The question of the role of the protonated forms in catalytic reactions then arises, and the findings on slowing and stopping of the reaction on addition of strong acids must be taken into consideration in discussing it [4]. Some features of acid–base catalysis were investigated in the present study in the reaction of acylation of aromatic amines by aromatic carboxylic acid anhydrides, in which autocatalysis was investigated previously in [5]. The mechanism of acid–base catalysis is discussed within the framework of our scheme in [6] with quantum chemical calculations and experimental data on different flow rate constants of the reaction.

EXPERIMENTAL

The reagents – phthalic anhydride (1a), \( p \)-toluidine (1b), \( p \)-anisidine (1c), and \( N,N,N',N' \)-tetramethyl-\( p \)-phenylenediamine (2a) – were purified by sublimation. Chloroform was purified by passing through Al\(_2\)O\(_3\) calcined at 350°C, and MeCN was purified by the usual method. Dimethylacetamide was successively distilled over KOH and CaH\(_2\) (twice), and after preliminary purification THF was distilled over Na–K melt. The IR and UV spectra were obtained on UR-20 and Specord UV-VIS spectrophotometers. The kinetics of acylation were followed spectrophotometrically by absorption of 1a (1777 cm\(^{-1}\)) and the product of the reaction 1a + 1b (36,000 cm\(^{-1}\)). The electron transfer reaction was investigated based on the absorption of 2a\(^{+}\) (16,000 cm\(^{-1}\)). The kinetic constants were calculated on a DVK-3 computer. The quantum chemical calculations of the molecules and complexes were performed on an ES-1066 computer with the AMPAC program with AM1 (PM3) methods. The electron absorption spectra were calculated on a BESM-6 computer with the CNDO/S3 method with the program written by V. G. Maslov.

DISCUSSION OF THE RESULTS

In the reaction of an electron and proton donor (DH) and electron and proton acceptor (A), it was assumed that electron transfer in the elementary event of the reaction takes place in the specific electron-excited state of the complex of the reagents stabilized by a H bond according to [6]. In acid catalysis, the role of the proton donor HX consists of activation of acceptor A, resulting in an increase in its electron affinity and consequently stabilization of the excited level with charge transfer (CT):


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Fig. 1. Steric structure of the calculated model of the reaction complex in the phthalic anhydride–aniline–formic acid system.

For the case of (1a), protonation of the electron acceptor A is the first event and significantly facilitates the next stage of electron transfer. Protonation of phthalic anhydride at the carbonyl oxygen atom increases its electron affinity from 1.2 [7] to 6.6 eV (estimation with the energy of the higher occupied molecular orbital) and consequently decreases the energy of the CT triplet level of the reaction complex of 1a with aniline (2e) (Fig. 1) to thermal values in comparison to the corresponding value for a complex of neutral molecules of the reagents (Table 1). Formation of a H bond between the catalyst HX and acceptor A has a smaller, but still significant catalytic effect.

In basic catalysis, the catalyst base Y activates the DH donor electron by formation of a H bond [Eq. (2b)] or deprotonation of DH [Eq. (2a)]:

The potentiation of the electron-donor properties of DH caused by this increase the probability of thermal electron transfer. In this case, the question of the formation of excited levels with low energy (<1 eV) is of key significance, since these levels are accessible for thermal filling in ordinary conditions.

In the case of bifunctional catalysis in which deprotonation of DH and protonation of A occur synchronously, the electron donor–acceptor (EDA) properties of the reagents are significantly potentiated, and the conditions are created for virtually unactivated electron transfer. In the calculated model of reaction complex 1a/2b (Fig. 1), the aniline molecule reacts as an electron donor with the C\(^3\) carbon atom of the anhydride, and a bridging H bond with a length of approximately 2.5 \(\text{Å}\) is formed with a molecule of formic acid, which plays the role of a proton carrier. Table 1 shows that the catalytic effect of the H bond is relatively clearly manifested, but this effect is probably understated by the PM3 method of calculation. When proton transfer precedes electron transfer, spontaneous electron transfer should take place in the 1a–H\(^+\)/2b\(^-\) ion pair formed, as the negative charges of the energy of the triplet level indicate. In these conditions, electron and proton transfer take place together and are not separated by a measurable amount of time. The catalytic effect of acids and bases thus consists of stabilization of the excited level of the donor–acceptor complex (A...DH)*, which increases its filling and thus increases the reaction rate.

Addition of strong acids as catalysts causes protonation of the reagents. Since the basicity of the electron donor DH is always higher than the basicity of the acceptor A (for example, the \(pK_a\) of aromatic amines and anhydrides differ by 8–10 units), the concentration of AH\(^+\) forms, which have a higher electron affinity (5-7 eV [8]), is insignificant. Protonation of the donor DH significantly decreases its reactivity, since the ionization potential increases: the DH\(_2\)'X\(^-\) forms can be oxidized only by a protonated acceptor [9].