THE EFFECT OF ACID ADDITIVES ON THE KINETICS OF THE ACYLATION REACTION OF AN AROMATIC AMINE IN AN INERT SOLVENT

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THE EFFECT OF ACID ADDITIVES ON THE KINETICS OF THE ACYLATION REACTION OF AN AROMATIC AMINE IN AN INERT SOLVENT

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The study by one of the authors of the present work of the kinetics of the acylation reaction of a series of aromatic amines, undertaken in order to elucidate the nature of the influence of steric factors on their reactivity ([1–5]), also showed that this reaction is sensitive to the medium. Taking into account that the latter circumstance is of interest for the theory and practice of organic chemistry, and bearing in mind that from this point of view the acylation reaction, as far as we know, has not yet been studied, we undertook an investigation of this question. The present communication sets forth the results of studying the effect of small additions of benzoic acid on the rate of the acylation reaction of aniline with benzoyl chloride and benzoic anhydride in benzene solution. The experimental method is described in work ([1]).

It has been established that the acylation reaction of aromatic amines with acid chlorides and anhydrides of organic acids proceeds according to the following two schemes:

$$\mathrm{RCOCl} + 2\mathrm{ArNH_2} \longrightarrow \mathrm{RCONHAr} + \mathrm{ArNH_2 \cdot HCl} \qquad \text{(A)}$$

$$(\mathrm{RCO})_2\mathrm{O} + \mathrm{ArNH_2} \longrightarrow \mathrm{RCONHAr} + \mathrm{RCOOH}. \qquad \text{(B)}$$

If the acylation by an acid chloride of aniline and its simplest derivatives is carried out in an inert solvent, then, as shown by Ebel ([6]) and Hinshelwood et al. ([7–10]), the HCl molecule liberated in the initial stage of the reaction is immediately bound by a second molecule of amine, with formation of a salt completely insoluble and entirely unreactive toward the acylating agent. In order to make certain that only

Fig. 1. Kinetic curves of the reaction of aniline with benzoyl chloride at different m: 0 (1); 0.0025 (2); 0.005 (3); 0.025 (4); 0.05 (5); 0.1 (6). $a = b = 0.00125$; $t = 25^\circ$.

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Figure 2. Kinetic curves of the reaction of aniline with benzoic anhydride at different m: 0 (1); 0.001 (2); 0.0025 (3); 0.005 (4); 0.01 (5); 0.05 (6); 0.1 (7). $a = b = 0.01$; $t = 25°$.

Figure 2: Figure 2. Kinetic curves of the reaction of aniline with benzoic anhydride at different m: 0 (1); 0.001 (2); 0.0025 (3); 0.005 (4); 0.01 (5); 0.05 (6); 0.1 (7). $a = b = 0.01$; $t = 25°$.

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by salt formation, and not by poor solubility of the salt in benzene, loss of reactivity is involved here, we studied the kinetics of acylation of 4-amino-4′-nitro-2,2′-diisopropoxybiphenyl (^4) and of its hydrochloride, which is readily soluble in benzene. It turned out that the rate constant for acylation (with *p*-nitrobenzoyl chloride) of the salt is approximately 20 times smaller than that of the amine itself (k_{25} equal to 0.0024 and 0.0451 l/mol · sec). Thus, hydrochloric acid has a deactivating effect on the ability of an aromatic amine to undergo acylation.

In Figs. 1 and 2 it is shown*, that in the acylation of aniline both with benzoyl chloride and with benzoic anhydride the reaction rate increases appreciably under the influence of additions of benzoic acid. From scheme B it follows that benzoic acid is liberated in the course of the very process of acylation by benzoic anhydride. Thus, in pure benzene this reaction should be autocatalytic. And indeed, curve 1 in Fig. 2 has an S-shaped form, which is characteristic of autocatalysis. The presence, even of small amounts, of benzoic acid in the initial stage of the acylation process leads to suppression of autocatalysis**; this is clearly illustrated by the other curves in Fig. 2.

The reason for such different effects of hydrochloric and benzoic acids on the rate of acylation, in our opinion, most probably lies in the fact that the indicated acids interact differently with the amine in benzene solution. Whereas hydrochloric acid converts the amine into a cation of low reactivity toward acylating agents, benzoic acid does not give an ionic compound with the aromatic amine, as a result of which the nitrogen of the amino group in the latter case does not pass into a tetracovalent positive state, which accounts here for the high reactivity of the amine. Confirmation that aromatic amines form compounds

of fundamentally different types with hydrochloric acid and with organic carboxylic acids may be found in the work of P. P. Shorygin and A. Kh. Khalilov (⁀11) (cf. (⁀12)).

It is of interest to determine in what quantitative dependence the rate of the acylation reaction stands with respect to the concentration of the acid catalyst present in the solvent. For the case of acylation with benzoyl chloride it is simplest to assume that the rate of the reaction in benzene containing benzoic acid is described by the following equation:

$$-\frac{d[\mathrm{ArCOCl}]}{dt} = k_0[\mathrm{ArCOCl}][\mathrm{ArNH_2}] + k_c[\mathrm{ArCOCl}][\mathrm{ArNH_2}][\mathrm{ArCOOH}], \quad (1)$$

where k_0 and k_c are the rate constants, respectively, of the noncatalytic and of the actual catalytic reactions. It follows from this that the observed rate constant of the overall process is equal to:

$$k = k_0 + k_c m, \quad (2)$$

where m is the analytical concentration of benzoic acid. It is clear that expression (2) will also be valid for the case of acylation with benzoic anhydride, when the value m becomes sufficiently large.

According to (2), a linear dependence should be observed between the acylation rate constant and the concentration of benzoic acid; this, however, was not confirmed by experiment. There is every reason to believe that the reason for the failure to observe a linear dependence in the present case lies in the fact that carboxylic acids possess the property of associating into dimers. Assuming that benzoic acid exhibits its catalytic effect chiefly–

* In Figs. 1-4 the following notation is used: a, b, and m are the initial concentrations, respectively, of the acylating agent, the amine, and benzoic acid, in mol/l; t is the temperature in °C.

** The rate of acylation with benzoyl chloride both in pure benzene and in the presence of benzoic acid dissolved in it obeys the bimolecular law well. The same holds for acylation with benzoic anhydride after autocatalysis has been suppressed by a sufficient amount of benzoic acid (approximately after its concentration becomes equal to 0.005 mol/l).

at the expense of its monomeric form, in Fig. 3 we have plotted the dependence of the acylation rate constants, both with benzoyl chloride and with benzoic anhydride, on the concentration of monomers present in the benzene solution, equal to $m\alpha$, where α is the degree of dissociation of the dimers into monomers*.

Now in both cases the experimental points fall quite satisfactorily on a straight line. Consequently, in order for relation (2) to hold for the acylation of aniline

with benzoyl chloride and benzoic anhydride, it is necessary in it to replace the analytical concentration of benzoic acid by the concentration of its monomeric form, i.e.

$$k = k_0 + k_c m\alpha. \tag{3}$$

The lengths of the segments cut off by the straight lines on the ordinate axis in Fig. 3 must numerically coincide with the value of the rate constant of the noncatalytic reaction. This is well illustrated by the data for the acylation reaction with benzoyl chloride (curve 1), since here the rate constant of the noncatalytic reaction is measured directly ($k_{25^\circ} = 0.0700$ l/mol · sec). Because of autocatalysis, the rate constant of the noncatalytic reaction for acylation with benzoic anhydride cannot be determined directly, but it is readily found with the aid of curve 2 and is equal to 0.000816 l/mol · sec. From the tangents of the angles of inclination of the straight lines in the same Fig. 3 one can calculate the value of the rate constant of the reaction that is catalyzed proper. The values of this quantity for acylation with benzoyl chloride and benzoic anhydride are, respectively, 22.3 and 9.86 $\left(\text{l}^2 \cdot \text{mol}^{-2} \cdot \text{sec}\right)$.

Fig. 3. Dependence of k on $m\alpha$ in the acylation of aniline with benzoyl chloride (1) and benzoic anhydride (2), $t = 25^\circ$. On the left along the ordinate axis are the values of k for 1, on the right—for 2.

Fig. 4. Dependence of $\log k$ on $1/T$ in the acylation of aniline with benzoyl chloride (a) and benzoic anhydride (b) at different m : 0 (1); 0.025 (2); 0.1 (3)

It is seen from Fig. 4 that, in the acylation of aniline with benzoyl chloride, the temperature dependence of the rate constant strictly obeys the Arrhenius equation if the reaction proceeds in pure benzene**. When, however, the solvent contains benzoic acid, there is no linear relationship between $\log k$ and $1/T$. The latter is not difficult to explain. Let us write expression (3) in a somewhat different form:

$$k = A_0 e^{-E_0/RT} + \left(A_c e^{-E_c/RT}\right) m\alpha, \tag{4}$$

where A_0, E_0 and A_c, E_c are the Arrhenius parameters, respectively, for the noncatalytic and catalytic reactions. Since the right-hand side of equation (4) cannot be represented in the form of one simple function $Ae^{-E/RT}$, a linear dependence of $\log k$ on $1/T$ should be observed only when one of the terms on the right-hand side of (4) can be neglected. In this case the following two limiting cases are possible: 1) the value of $m\alpha$ is so small that the value of k is predominantly determined by the first term, and the experimentally found value of the activation energy will be close to E_0; 2) the value of $m\alpha$ is sufficiently large, and k is determined mainly by the second term; consequently, the experimental

* The values of α were calculated from the dissociation constants of benzoic acid dimers into monomers in benzene solution ([13]).

** The activation energy, frequency factor, and activation entropy for the reaction of acylation of aniline with benzoyl chloride in pure benzene are, respectively: 7700 cal/mol, $3.0 \cdot 10^4$ l/mol · sec, and −40.2 cal/deg · mol. Our value of E_0 agrees well with the value determined by Hinshelwood et al. (7350 ([8]) or 7600 ([10])).

the activation energy will approach E_c. Naturally, those limiting values of $m\alpha$ after which one of the indicated terms becomes negligibly small in comparison with the other depend also on the ratio between the magnitudes k_0 and k_c. The absence of a linear relationship between the values of $\log k$ and $1/T$ in the acylation of aniline with benzoyl chloride indicates that the rate was measured in the region of such concentrations of benzoic acid where both terms of equation (4) are comparable with one another. As was to be expected, with an increase in the concentration of benzoic acid the temperature curve for the rate constant here shows a greater tendency to approach a straight line. At higher acid concentrations, rate measurements were not carried out because of the difficult solubility of the acid in benzene. However, for the acylation of aniline with benzoic anhydride at the same concentrations of benzoic acid, in Fig. 4 we already observe straight lines. Taking into account what has been said above, this is easy to understand, since in the latter case the value of k_0, in comparison with k_c, is very small. The experimental value of the activation energy here is close to 4000 cal/mol and does not depend substantially on the change in the concentration of benzoic acid within the range 0.005–0.1 mol/l.

We hope to express our judgment on the mechanism of the effect of acids on the kinetics of aniline acylation somewhat later, after obtaining some additional experimental data.

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REFERENCES CITED

1. L. M. Litvinenko, A. P. Grekov, ZhOKh, **26**, 3391 (1956).

2. L. M. Litvinenko, A. P. Grekov, ZhOKh, **27**, 234 (1957).

3. L. M. Litvinenko, R. S. Cheshko, A. D. Gofman, ZhOKh, **27**, 758 (1957).

4. L. M. Litvinenko, S. V. Tsukerman, A. P. Grekov, E. A. Slobodkina, Ukr. khim. zhurn., **23**, 223 (1957).

5. L. M. Litvinenko, A. P. Grekov, Ukr. khim. zhurn., **23**, 228 (1957).

6. F. Ebel, Ber., **60**, 2079 (1927).

7. G. Grant, C. Hinshelwood, J. Chem. Soc., **1933**, 1351.

8. E. Williams, C. Hinshelwood, J. Chem. Soc., **1934**, 1079.

9. V. Newling, L. Staveley, C. Hinshelwood, Trans. Farad. Soc., **30**, 597 (1934).

10. F. Stubbs, C. Hinshelwood, J. Chem. Soc., Suppl. Issue, No. 1, 71 (1949).

11. P. P. Shorygin, A. Kh. Khalilov, ZhFKh, **25**, 1475 (1951).

12. G. Barrow, J. Am. Chem. Soc., **78**, 5802 (1956).

13. F. Wall, F. Banes, J. Am. Chem. Soc., **67**, 898 (1945).

Note: Figure translations are in progress. See original paper for figures.