

REACTIVITY OF AROMATIC OLIGOAMINES AND OLIGOCHLORIDES ON POLYCONDENSATION IN AQUEOUS-ORGANIC MEDIA*

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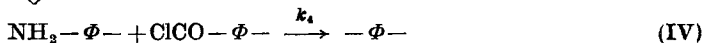
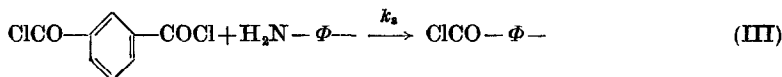
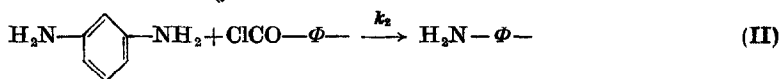
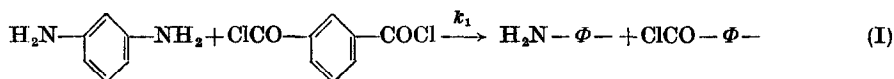
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(Received 20 November 1980)

The rate constants of the interaction of aromatic oligoamines with isophthalic acid dichloride and with oligoproducts having ClCO endgroups in the systems THF-water and cyclohexanone-water have been calculated with the aid of correlation equations and determined by a slow measuring (replenishment) method. A significant increase in the rates of the respective reactions was observed on increasing the H₂O concentration in the reaction system, and good agreement exists between calculated and experimental data.

SEVERAL authors (their work is summarized in [1], p. 222) have reported that water has a favourable effect on the preparation of high molecular polyamides obtained by reacting aliphatic and aromatic diamines with dichlorides of dicarboxylic acids. It was found that the presence of water in the reaction zone results in higher molecular weight polyamides both in homogeneous [1] (p. 142) and heterogeneous ([1] p. 176, 192) systems. In an earlier paper it was proposed that this influence of water is due to a considerable acceleration of polyamidation reactions in water-containing media. However there has been a lack of direct data on the increased reactivity of diamines, dichlorides and the corresponding oligomers in aqueous-organic media.

Determinations of the reactivity of the monomeric and oligomeric diamines and dichlorides were carried out by taking as an example the polycondensation of *m*-phenylenediamine with isophthalic acid dichloride taking place by the reactions[†]:



* Vysokomol. soyed. A24: No. 3, 606-610, 1982.

[†] The letter Φ in eqns. (I)-(IV) denotes fragments of the oligomer or polymer molecule that are responsible for the reactivity of NH₂ or COCl endgroups.

The most interesting and important of these reactions is reaction (IV), firstly, since it is the rate of (IV) that determines the MW of the resulting polymer during the main, completing stage of the polycondensation, and secondly, because for these reactions (between two oligomers) it is hardly possible to use direct methods of reactivity determination that were developed for monomeric compounds.

TABLE 1. RATE CONSTANTS OF *m*-NITROANILINE ACYLATION WITH BENZOYL CHLORIDE AND VALUES OF *S* IN AQUEOUS-ORGANIC SYSTEM; 298.16 K

Composition of the aqueous-organic system, vol. %	Rate constant, m ³ /mole·sec	<i>S</i>
THF	—	1.83
THF (95.5)–water (4.5)	0.195	2.23
THF (64.8)–water (35.2)	1.200	2.96
Cyclohexanone	0.064	1.78
Cyclohexanone (95.2)–water (4.8)	0.200	2.24

The reaction media in the investigation were the homogeneous systems THF–water and cyclohexanone–water, as well as the organic phases of the heterogeneous aqueous–organic systems (organic solvent–water–salting out agent) of like composition.

Constants k_1 , k_2 , k_3 and k_4 are the rates of stages (I–IV) of the polycondensation and may be obtained through the respective constants of interaction of the functional groups k'_1 , k'_2 , k'_3 and k'_4 [3], where $k_1=4k'_1$, $k_2=2k'_2$, $k_3=2k'_3$ and $k_4=k'_4$.

To find constants k'_1 – k'_4 we used the multiparameter correlation eqn. [3]

$$\log k' = \log k_{00} + \rho\sigma + \rho'\sigma^+ + RS + g(1 + \sigma^+S) + \frac{E_{00} - 5730[\rho\sigma^- + \rho'\sigma^+ + RS + g(1 + \sigma^+S)]}{19.1} \cdot \left(\frac{1}{298} - \frac{1}{T} \right),$$

where k_{00} is the rate constant* of aniline acylation with benzoyl chloride in benzene at 298°K; σ^- and σ^+ are constants for substituents in the mono-substituted aniline and monosubstituted benzoyl chloride respectively; S is a parameter of the solvent, $S = \log(k_{0j}/k_{00})$; k_{0j} is the rate constant of aniline acylation with benzoyl chloride in a j -solvent at 298°K; ρ , ρ' and R are constants taking account of the sensitivity of the reaction to the influence of the substituent in the mono-substituted aniline, that in the monosubstituted benzoyl chloride and that of the solvent, respectively; g is a cross term, T is temperature and E_{00} is the activation

* Subscript 00 means that there is no substituent, and the solvent is benzene.

energy for aniline with benzoyl chloride in benzene. The following are the numerical values of the parameters: $\log k_{00} = -4.17$; $\rho = -2.75$; $\rho' = 0.98$; $R = 1.08$ $g = 0.2$; $E_{00} = 31,300$ J/mole.

The main difficulty lies in determining parameter $S = \log k_0/k_{00}$ for the aqueous-organic media. Our determination of S was based on the rate constants of interaction of a most convenient pair (*m*-nitroaniline + benzoyl chloride) in media containing differing amounts of water. The value of S was given by the formula

$$S = \frac{\log (k/k_{00})\rho\sigma^-}{R},$$

where k is the acylation rate of *m*-nitroaniline with benzoyl chloride at 298°K $\log k_{00} = -4.17$; $\rho = -2.75$; $\sigma = 0.71$ for substituent $m = \text{NO}_2$, $R = 1.08$.

It is seen from Table 1 that the acylation rate constant and parameter S increase with increasing concentration of H_2O in the system.

Using the tabulated data on S (Table 1) for the aqueous-organic media, along with the σ^- and σ^+ values of the substituents and fragments responsible for reactivities of amino and acid chloride groups in the oligomers [3], we obtained data on the rates of all the reactions involved in the polycondensation process (Table 2).

TABLE 2. CALCULATED VALUES OF THE RATE CONSTANTS OF REACTIONS INVOLVED IN THE POLYCONDENSATION OF *m*-PHENYLENEDIAMINE WITH ISOPHTHALIC ACID DICHLORIDE IN AQUEOUS-ORGANIC SYSTEMS (2981.16 K)

Composition of aqueous-organic system, vol., %	Rate constants $\text{m}^3/\text{mole} \cdot \text{sec}$			
	k_1	k_2	k_3	k_4
THF	0.87	0.541	0.26	0.16
THF (95.8)–water (4.5)	2.65	1.66	0.80	0.50
THF (64.8)–water (35.2)	20.30	13.20	6.16	3.95
Cyclohexanone	0.748	0.48	0.29	0.14
Cyclohexanone (95.2)–water (4.8)	2.72	1.72	0.82	0.52

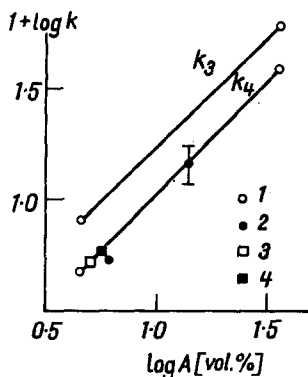
It is clear from the data in Table 2 that water added to the organic solvents significantly increases the constants of all the reactions involved in the process of polycondensation by the above scheme: the values of k_1 , k_2 , k_3 and k_4 in THF containing 35 vol. % water exceed values of the same constants in dry THF* by a factor of 25. Ratios of the constants, e.g. k_1/k_2 , on increasing the H_2O concentration in the system remain practically constant, which accords with results reported earlier [1, p. 25] regarding the constancy of k_1/k_2 in a number of solvents.

* Reasons why H_2O accelerates reactions of acylation of amines by acid halides are analyzed in some detail in [2] and [4].

It is also noteworthy that the absolute values of rate constants of reactions (I)–(IV) in solvents containing considerable amounts of water, including constants k_4 which largely determines the level of MW of the resulting polymer, are very large (3–20 m³ mole·sec). These values are commensurate with those previously reported [5] for interphase polycondensation processes, which makes one think that water present in interphase layers of two-phase systems has a considerable influence on the kinetics and mechanism of interphase polycondensation.

Comparing values of k_1 and k_4 in Table 2 it is apparent that these differ markedly for all the media examined. This means that it is not possible to determine the reactivity of aromatic oligomeric products from data on their monomeric analogues.

Experimental determination of the rate of formation of an aromatic polyamide with a structure similar to that indicated in the scheme was carried out by a method of slow measuring (replenishment) proposed in ref. [6] and used for the first time for a similar purpose in [7]. The rates of polycondensation in different (in respect to the H₂O concentration in the organic phase) emulsion systems of the type: organic solvent (THF, cyclohexanone)–water–salting out agent (acceptor) were determined under conditions of replenishment of a previously synthesized aromatic oligomeric diamine with isophthalic acid dichloride (see the experimental part of this paper).



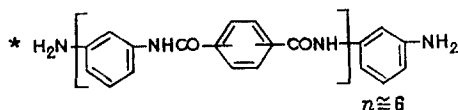
Plot of logarithm of rate constants of polycondensation reactions of *m*-phenylenediamine with isophthalic acid dichloride vs. logarithm of H₂O concentration in the reaction medium: 1, 2—THF–water; 3, 4—cyclohexanone–water. 1, 3—calculated data; 2, 4—experimental data for organic phase of the emulsion system.

The polyamidation rate constants obtained in this way are listed in Table 3. The tabulated data (comparing the 2nd and 3rd columns in Table 3 also give a clear idea of the extent to which the polyamidation process with the participation of aromatic acid chloride groups is accelerated on account of a higher H₂O concentration in the reaction phase.

It is of major importance to investigate the physical significance of the experimentally determined rate constant since the polycondensation process with replenishment is described by two constants k_3 and k_4 (in the case under consideration reactions (1) and (2) are ruled out since the oligodiamine ($-\Phi-\text{NH}_2$) had been synthesized beforehand). To shed light on this problem we compared the experimentally found polycondensation rate constant with the values calculated for the various aqueous-organic media (see Figure). It is seen from the Figure that the rate constant obtained by experiment is closest to constant k_4 . This is understandable as the replenishment method is "sensitive" solely to reactions that lead to higher MW of the polymer. Since the main MW increment takes place through reaction (IV), the latter method is the best for determining k_4 , i.e. the constant of mutual interaction of the oligomers. The "replenishment" method is practically insensitive to the rate constants of reactions (I)–(III).

TABLE 3. EXPERIMENTAL VALUES OF THE RATE CONSTANT OF POLYCONDENSATION OF THE AROMATIC OLIGO-DIAMINE* WITH ISOPHTHALIC ACID DICHLORIDE IN HETEROGENEOUS SYSTEMS OF TYPE; ORGANIC SOLVENT-WATER-SALTING OUT AGENT

Organic phase	H ₂ O concentration in organic phase, vol. %	Rate constant, m ³ /mole-sec
Cyclohexanone	5.5	0.58
THF	6.0	0.56
"	13.0	1.40



Experimentally found values of the polycondensation reactions determined for organic phases of heterogeneous (emulsion) systems are in agreement with calculated values for the homogeneous systems, which proves that in the case of the former (systems) the polyamidation process is limited by kinetic factors and takes place in an internal kinetic region.

It is also clear from this agreement that the assumption that the polyamidation reaction in aqueous-organic media is accelerated at the expense of catalysis by carboxylic acids formed via hydrolysis of acid chlorides does not hold, or at any rate is untenable as far as the cases examined by us are concerned.

Materials used in the investigation were in line with State Standards (GOST) or were purified by methods described in [7, 8]. Kinetic experiments involving *m*-nitroaniline acylation with benzoyl chloride were performed in the manner outlined in [9].

The method described in [7] was used to synthesize the polymers. The method used to synthesis the oligomeric diamines was as follows. To a water-soda solution of *m*-phenylene-

diamine taken with a predetermined excess was added, whilst stirring, a solution of a mixture of iso- and terephthalic acid chlorides (80:20). The H_2O concentration in the organic (reaction) phase was varied by altering the concentration of NaCl used as a salting out agent.

The rate constant of the polyamidation reaction taking place in emulsion systems was determined correct to $\pm 0.1 \text{ m}^3/\text{mole} \cdot \text{sec}$ in media containing $\approx 5\%$ water, and correct to $\pm 0.3 \text{ m}^3/\text{mole} \cdot \text{sec}$ in media containing $> 10\%$ water.

Translated by R. J. A. HENDRY

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Polymer Science U.S.S.R. Vol. 24, No. 3, pp. 678-686, 1982
Printed in Poland

0032-3950/83/030678-09\$07.50/0
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STUDY OF COMPLEX-FORMATION OF COPPER(II) WITH AMPHOLYTES CONTAINING NITROGEN-PHOSPHORUS*

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(Received 23 November 1980)

ESR was used to examine special features of complex formation of copper (II) in aminophosphorus-containing ampholytes. It was shown in the resin phase, according to the pH value of the equilibrium solution, degree of hydration, phosphorylation

* Vysokomol. soyed. **A24**: No. 3, 611-617, 1982.