Investigation of polyimide formation from the complexes of the diester of benzophenonetetracarboxylic acid with diamines
7.* Role of the *o*-carboxylic group of acid diester in the formation and imidization of H-complexes

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The kinetics of thermal imidization of various H-complexes of semiesters of bis(*o*-phthalic) acids with diamines was studied. The activation energy of the imidization was shown to increase with increasing pK_a value of the diamine and E_a value of the dianhydride and with decreasing nucleophilicity of the alcohol used for the synthesis of H-complexes. The experimental kinetic data and the results of quantum chemical calculations of the heats of formation of the initial H-complexes and transition states made it possible to propose a mechanism for the imidization reaction. This mechanism takes into account the catalytic effect of the carboxylic group of the semiester in the *o*-position with respect to the ester group.

Key words: H-complex, polyimide, diester of 3,3′,4,4′-benzophenonetetracarboxylic acid, diamine.

The acylation of diamines by semiesters of tetracarboxylic acids is industrially used for the production of polyimides — highly thermostable polymers.[1] In this process, the semiesters of bis-*o*-phthalic acids are commonly obtained by the dissolution of the corresponding aromatic dianhydrides in boiling alcohols.[2] When the alcoholic solutions obtained are treated with diamines, the H-complexes,[3] in which the functional groups of the semiester and those of amine are bound by hydrogen bonds,[4] are spontaneously formed. The heat treatment of the H-complexes results in the elimination of water and alcohol to form imide cycles (acylation of amines by semiesters).

The present report deals with an investigation of the kinetics of the thermal imidization of H-complexes of various chemical compositions that were obtained from various dianhydrides, alcohols, and diamines. This allowed one to reveal a rather weak dependence of the activation parameters of the imidization of H-complexes on their chemical structure, which is probably related to the intramolecular transfer of the proton of the *o*-carboxylic group to the ester group within the H-complex.

* For report 6, see *Izv. Akad. Nauk, Ser. Khim.*, 1993, 300 [*Russ. Chem. Bull.*, 1993, **42**, 255 (Engl. Transl.)].

Experimental

H-complexes were obtained from commercially available reagents. Pyromellitic (PM) acid dianhydride (of TU (Technical Specification) OEZ 59-65 grade) was purified by sublimation, m.p. 285 °C; 3,3′,4,4′-benzophenonetetracarboxylic (BZP) acid dianhydride (of TU TSR 2159-69 grade) was purified by boiling in acetone, m.p. 225 °C; 3,3′,4,4′-diphenyloxidetetracarboxylic (DPO) acid dianhydride (obtained at Latvian branch of Institute of Rure Reagents (IREA) in 1985) was purified by distillation, m.p. 226 °C; 1,6-hexamethylenediamine (HMDA) (of TU 6-09-36-70 grade) was purified by distillation, m.p. 42 °C; 2,6-diaminopyridine (DAP) (Fluka) was purified by sublimation, m.p. 121 °C; 4,4′-diaminodiphenyl methane (DADPM) (of MRTU (Interrepublican Technical Specification) 6-09-2322-65 grade) was purified by sublimation, m.p. 92 °C; 4,4′-diaminodiphenyl sulfone (DADPS) (Fluka) was purified by recrystallization from methanol, m.p. 180 °C.

The alcohols for esterification of the dianhydrides were used without additional purification: MeOH (of GOST (All-Union State Standard) 6995-77 grade), m.p. 64 °C; EtOH (of GOST 5962-67 grade), m.p. 78 °C; Pr^iOH (of TU 7P-24-68 grade), m.p. 82 °C; Bu^nOH (of GOST 6000-78), m.p. 117 °C. To obtain dimethyl, diethyl, and dibutyl esters of BZP acid (BZPMe, BZPEt, and BZPBu, respectively) and diethyl esters of PM and DPO acids (PMEt and DPOEt, respectively), the starting dianhydrides were stirred with reflux in the corresponding alcohols till complete dissolution.[2] Diisopropyl ester of BZP ($BZPPr^i$) was obtained by stirring BZP dianhydride in boiling Pr^iOH in the presence of 5 wt % (relative to BZP dianhydride) of benzimidazole till complete dissolution.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 6, pp. 1060—1065, June, 1995.

1066-5285/95/4406-1021 $12.50

Table 1. Characteristics of thermal imidization of H-complexes of various structures

Entry	Composition of H-complex	T_{im} /°C	$k \cdot 10^4$ /s^{-1}	E_A /kJ mol^{-1}	A /s^{-1}
1	BZPMe · HMDA	125	0.3	114	$2 \cdot 10^{10}$
		150	0.8		
		180	9.6		
		220	195.0		
2	BZPMe · DAP	125	0.2	93	$4 \cdot 10^7$
		150	1.5		
		180	6.7		
		220	49.0		
3	BZPMe · DADPM	125	0.5	82	$3 \cdot 10^6$
		150	2.4		
		180	19.0		
		220	45.0		
4	BZPMe · DADPS	125	0.7	45	$8 \cdot 10^1$
		150	2.4		
		180	5.3		
		220	14.0		
5	BZPEt · HMDA	125	0.03	92	$1 \cdot 10^7$
		150	0.1		
		180	4.3		
		220	12.2		
6	BZPEt · DAP	125	0.3	66	$1 \cdot 10^4$
		150	1.1		
		180	1.8		
		220	8.3		
7	BZPEt · DADPM	125	0.1	60	$2 \cdot 10^3$
		150	1.3		
		180	2.7		
		220	6.1		
8	BZPBu · DADPM	125	1.8	59	$8 \cdot 10^3$
		150	5.4		
		180	7.4		
		220	25.3		
9	BZPPr^i · DADPM	125	1.3	52	$8 \cdot 10^2$
		150	3.2		
		180	12.8		
		220	22.0		
10	PMEt · DADPM	125	2.1	69	$2 \cdot 10^5$
		150	5.7		
		180	11.5		
		220	15.0		
11	DPOEt · DADPM	125	2.9	37	$3 \cdot 10^1$
		150	10.9		
		180	15.0		
		220	27.3		

H-complexes (Table 1) were obtained by dissolution of diamines in solutions of diesters in the corresponding alcohols. H-complexes were isolated from solutions by the removal of the alcohols *in vacuo* at 40 °C. The structure of H-complexes was studied by us previously[3] using spectral methods.

The kinetics of imidization of the H-complexes was investigated by IR spectroscopy under isothermal conditions at 125, 150, 180, and 220 °C. IR spectra were recorded on an UR-20 infrared spectrometer in KBr pellets. Prior to heating, the pellets were always ground and pressed again. The process of thermoimidization was monitored by the changing intensity of the band at 1780 cm^{-1} (see Ref. 5). The band at 1500 cm^{-1} was used as the reference band since its intensity was independent of heating. At each temperature the degree of imidization (i) was determined as the ratio

$$i = D_{1780/1500}/D^{220}_{1780/1500},$$

where $D_{1780/1500}$ is the ratio of the optical densities of the bands after thermal treatment and $D^{220}_{1780/1500}$ is their ratio after heating for 30 min at 220 °C. It was conditionally believed that the heating at 220 °C results in complete cyclization ($i = 1$).

The rate constants (k) of the imidization of H-complexes were determined by processing the obtained kinetic curves using a first-order equation.[5–7] The induction period caused by heating of the sample was not taken into account. Calculations were done with the formula known for thermal imidization of polyamidoacids [8]:

$$k = 2.303 \cdot \tau^{-1} \cdot \log 1/(1 - i),$$

where τ is the time of the reaction.

The activation energy E_A and preexponential factor A were calculated with the Arrhenius equation:

$$k = A \cdot \exp(-E_A/RT),$$

where R/J · (K mol)$^{-1}$ is the gas constant (8.31434) and T/K is the temperature of imidization.

The quantum chemical investigation was carried out by the AM1 method.[9] The acylation of amines by semiesters was calculated using an ammonium—monomethyl ester of maleic acid as the model system.

Results and Discussion

The compositions of the H-complexes and the kinetics of thermal imidization are given in Table 1. As an example, Figure 1 shows the kinetic curves of thermal imidization of the H-complex BZPMe · DADPS at different temperatures. The semilogarithmic anamorphoses of the kinetic curves (Fig. 1, *b*) are straight lines corresponding to the first order of the reaction. The kinetic curves and their anamorphoses for the other H-complexes given in Table 1 have an analogous form. The first order of the imidization reaction allows us to consider it as an intramolecular conversion of H-complexes.

The rate constants of imidization of the H-complexes are given in Table 1 along with the energies of activation E_A and preexponential factors A calculated on the basis of these constants.

The dependence of the activation parameters of imidization on the reactivity of the molecules included in the H-complexes. It is known that the value of pK_a is a measure of the reactivity of amines in acylation reactions.[10] The data of Table 1 show that the greater the pK_a value of amine, the higher the E_A of imidization. The highest value of E_A is observed in the acylation reactions of the semiester of aliphatic diamine (HMDA), whose pK_a is 10.9 (see Table 1, entries *1*, *5*). The lowest value of E_A is observed in the acylation of DADPS (pK_a 2.0, entry *4*), while an intermediate value of E_A is observed for DADPM (pK_a 4.7, entries *3*, *7*).

The values of the electron affinity (E_a) are believed to determine the reactivity of the derivatives of carboxy-

lic acids.[11] We do not know the E_a values of the semiesters, but the E_a values for the corresponding anhydrides are known,[12] *viz.*, 1.90 eV (PM), 1.55 eV (BZP), 1.30 eV (DPO). The data of Table 1 show that the energies of activation E_A of the imidization of H-complexes decrease in the same order.

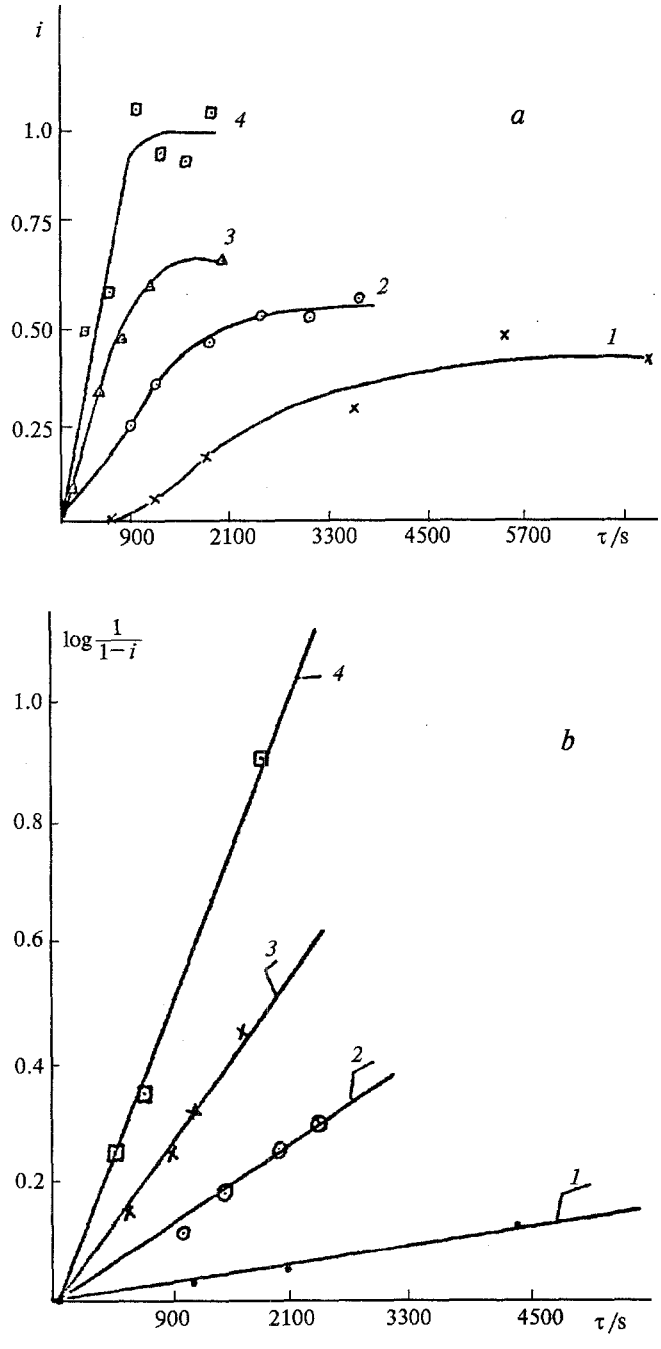


Fig. 1. Kinetic curves of thermal imidization of H-complex BZPMe · DADPS (*a*) at temperatures (°C) of 125 (*1*), 150 (*2*), 180 (*3*), and 220 (*4*) and their semilogarithmic anamorphoses (*b*).

It is known[13] that the rate of acylation of amines with carboxylates decreases in the following order of the alkoxy groups:

$$MeO- > EtO- > Pr^iO-$$

For the imidization of the H-complexes, the highest values of E_A (see Table 1) are observed for the complexes of methyl semiesters (entries *1*—*4*). In the case of ethyl semiesters (entries *5*—*7*), E_A is lower. If the ethyl ester is replaced by *n*-butyl ester, the E_A value of imidization of the H-complexes virtually does not change (entry *8*), whereas the use of isopropyl semiester results in an additional decrease in E_A (entry *9*). Thus, according to the kinetic experiment (see Table 1), in the case of thermocyclization of the H-complexes, the values of E_A decrease with decreasing basicity of the diamine and electron affinity of the semiester and with increasing nucleophilicity and spatial volume of the leaving alcohol group. The reactions of the acylation of amines with various derivatives of carboxylic acids not complicated by complex formation proceed, according to the Ingold classification, *via* a $B_{Ac}2$ mechanism (*cf.* Ref. 13). In these reactions there is the reverse dependence of the reactivity of the reagents, *viz.*, the increase in the acylation rate with increasing pK_a of an amine and with increasing E_a of the acylating reagent.[12]

This particular feature of the imidization reaction can be easily understood with the assumption that the rate limiting stage is the first step of the intramolecular proton transfer from the carboxyl moiety to the carbonyl oxygen atom of the ester group, rather than the stage of nucleophilic attack of the nitrogen atom at the carbonyl carbon atom of the ester group.

Structure of the H-complexes. Earlier it was shown by spectral methods that, in complexes formed when semiesters are mixed with amines in aqueous alcoholic solutions, both the carboxyl and ester groups of the semiester participate in the formation of the H-bond with the amino group.[3,4] Not only molecular H-complexes, but also salt structures[3,14] were detected in these processes. It was also shown that the content of the salt structures in the reaction products increases with in-

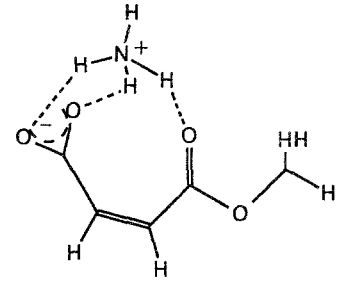
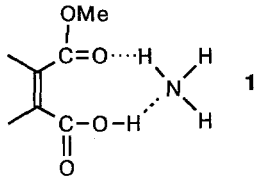
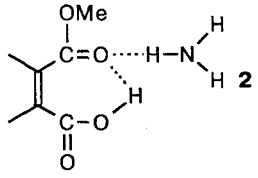
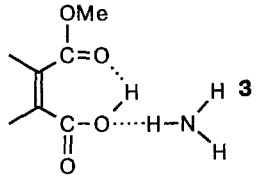
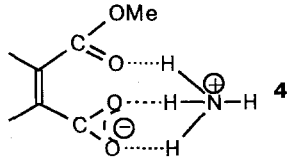
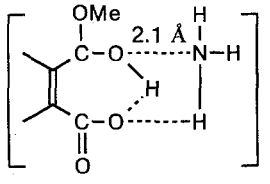
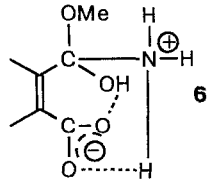
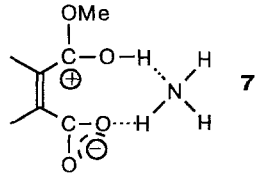


Fig. 2. Geometry of structure **4** (see Table 2) of the salt H-complex based on ammonium and the monomethyl ester of maleic acid optimized by the AM1 method.

Table 2. Heats of formation ($\Delta_f H$) and dipole moments (μ) of the structures obtained from ammonia and the monomethyl ester of maleic acid calculated by the AM1 method

Structure	$\Delta_f H$ /kJ mol^{-1}	μ /D
 **1**	*	*
 **2**	−691.74	4.6
 **3**	−692.33	3.7
 **4**	−642.25	6.9
 **5**	−519.00	9.8
 **6**	−567.76	10.8
 **7**	*	*

* Does not correspond to the local minimum on the surface of the potential energy.

creasing basicity of the amines. Several possible structures of H-complexes were proposed on the basis of the experimental data.[3,4]

In the present work, a quantum chemical calculation of the possible structures of H-complexes for the model compounds, *viz.*, monomethyl ester of maleic acid and ammonia, was carried out by the AM1 method (Table 2). We selected the structures with the minimum calculated heat of formation. It was found that the formation of chelate-like structures with intramolecular H-bonds of nonlinear geometry (structure **1**) is energetically unfavorable. No local minimum corresponding to structure **1** could be found on the curve of potential energy. The data of Table 2 indicate that the lowest heats of formation ($\Delta_f H$) are characteristic of structures where one of the H-bonds that participate in the formation of H-complexes is intramolecular and is formed between the proton of the carboxyl group and the carbonyl oxygen atom of the ester group (structures **2** and **3**). Another H-bond is intermolecular and is formed between the proton of ammonia and the carbonyl oxygen atom of the ester (structure **2**) or the carboxyl (structure **3**) group. These intermolecular H-bonds are nearly linear.

It is reasonable to describe the salt structure of H-complexes, which was detected by spectral and dielectric methods,[3,14] by structure **4** (see Table 2). The geometry of structure **4** calculated by the method of complete optimization (Fig. 2) attests that there are three H-bonds: two protons of the ammonium cation form H-bonds with the oxygen atoms of carboxylate anion, while the third proton is bonded with the carbonyl oxygen atom of the ester group.

Figure 2 shows that the plane of the ester group virtually coincides with the plane of the C=O bond, whereas the angle between the latter and the plane of the carboxylate group is about 90°. We believe that the H-bonds in structure **4** are much stronger than those in structures **2** and **3** and are therefore less sensitive to geometrical factors. Using quantum chemical calculations, a local minimum corresponding to salt structure **4** was found on the surface of the potential energy. The data given in Fig. 2 show that the heat of formation of structure **4**, $\Delta_f H$, is ~50 kJ mol^{-1} higher than that of H-complexes **2** and **3**. However, in real systems, the formation of H-complexes occurs in a highly polar aqueous-alcoholic medium, whose influence was not taken into account in the quantum chemical calculations. Therefore, the difference between the energy levels of **4** and **2**, **3** can be much less or may even favor structure **4**, because the dipole moment of salt structure **4** (6.9 D) is, according to our calculations, much greater than that of H-complex **2** (4.6 D) and, moreover, of H-complex **3** (3.7 D) (see Table 2).

Probable mechanism of the conversion of H-complexes to polyamide. An intramolecular H-bond is present in H-complexes that form spontaneously on mixing semiesters with amines (see Table 2, structures **2**, **3**). It is reasonable to propose that, in the case of H-com-

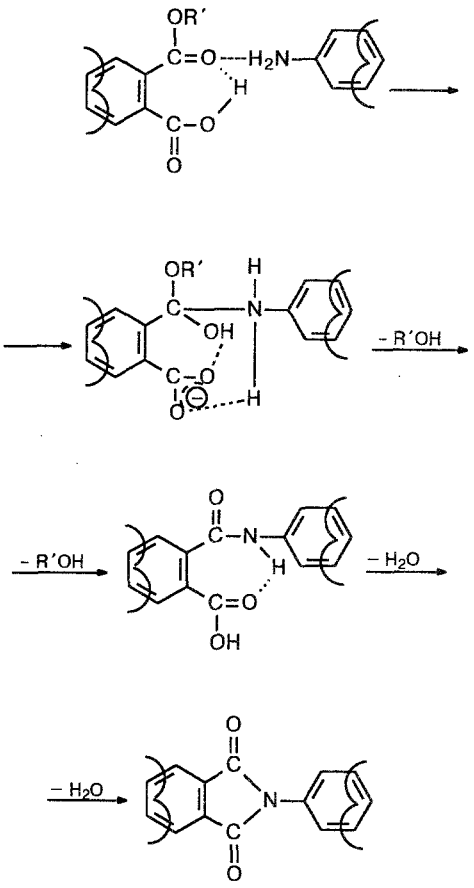
plexes with the intramolecular H-bond, the first stage of the imidization should be the intramolecular transfer of the proton from the carboxyl group to the carbonyl oxygen atom of the ester group. To confirm this suggestion, a quantum chemical calculation of the heat of formation of the imidization transition state (see Table 2, structure **5**) was carried out based on the model system of ammonium and monomethyl ester of maleic acid. In this transition state, the transfer of the proton of the *ortho*-carboxyl moiety to the oxygen atom of the ester group occurs somewhat prior to the nucleophilic attack of the nitrogen atom of ammonia on the carbonyl carbon atom of the ester. An optimized geometry of the transition state was calculated, which almost exactly corresponds to the completed transfer of the carboxyl group proton to the carbonyl oxygen atom of the ester. The N—C bond between the nitrogen atom of NH_3 and the carbon atom of the ester group is in the stage of formation. The N—C distance determined for structure **5** (see Table 2) is 2.1 Å and the heat of formation is $\Delta_f H = -519$ kJ mol^{-1}. This value is 170 kJ mol^{-1} higher than the heats of the formation of the starting H-complexes (Table 2, structures **2**, **3**). The high value of activation barriers makes it necessary to increase the temperatures for the imidization of H-complexes, even taking into account the inaccuracy of the calculation.

On the completion of the intramolecular proton transfer and the formation of the bond between the nitrogen atom of ammonia and the carbon atom of the ester, the intermediate product of the thermoimidization of H-complexes is formed. Quantum chemical calculations showed that there is a local minimum on the potential energy profile of the system, and completely optimized geometry of this minimum exactly corresponds to structure **6** (see Table 2). This structure is characterized by the fact that each oxygen atoms of the carboxylate group COO^- participates in the formation of H-bonds with the proton of the $\geq C\text{-}OH$ group and with the proton of the $-\overset{\oplus}{N}H_3$ group, respectively.

The formation of intermediate product **6** (see Table 2) from salt structure **4** seems, at first glance, to be possible as a result of the transfer of one of the protons of the ammonia cation to the ester group followed by the attack of the nitrogen atom of the positively charged carbonyl carbon atom on the protonated ester group. However, the transition state in such a process should be described by structure **7** (see Table 2), which, according to the quantum chemical calculations, can not be formed with view of the energetical barriers. On the curve of the potential energy, a local minimum corresponding to structure **7** is absent. Probably, the conversion of structure **4** to structure **6** is possible only via its transformation to structure **2** or **3** followed by the formation of transition state **5**.

Previously[14] it was shown by a dielectric method that salt structures of H-complexes enter the imidization at higher temperatures than molecular H-complexes, which

Scheme 1



was not explained thereafter. Possibly, additional energy is required for the transformation of the salt structure of a H-complex (Table 2, structure **4**) to molecular structures **2** and **3**. In view of this, the high values of the activation energy of the imidization of H-complexes can be explained by an increase in the pK_a of the diamines involved in these complexes. The mechanism, which we propose for the formation of imides from H-complexes of the semidiesters of tetracarboxylic acids and diamines, is shown in Scheme 1.

The salient feature of this mechanism is the intramolecular H-bond in semidiester, which facilitates the intramolecular transfer of the proton of the carboxyl group to the carbonyl oxygen atom of the ester group when heating H-complexes. The subsequent nucleophilic attack of amine on the carbonyl carbon atom results in an intermediate, which undergoes further conversion to amidoacid with elimination of alcohol. The thermal imidization of amidoacids has been described in the literature.[15]

The experimentally observed dependences of E_A of the imidization of H-complexes on the reactivity of the reagents that form these complexes are in good agree-

ment with the concepts on the influence of the chemical structure on the electron density on the carbonyl oxygen atom of the ester group. Therefore, the specific features of the thermal imidization of H-complexes should be taken into account in the synthesis of polyimides by the acylation of diamines with semiesters.

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Received December 30, 1993;
in revised form March 13, 1995