Chemistry

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1965

SovietRxiv

Abstract

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Investigation of the Kinetics of the Polycondensation of Bisphenols with Terephthaloyl Chloride

The present work had as its aim the elucidation of the influence of the nature of the substituents at the central carbon atom of bisphenols on their reactivity.

For this purpose we investigated the kinetics of the polycondensation of terephthaloyl chloride (TPC) with bis-(4-hydroxyphenyl)methane, 2,2-bis-(4-hydroxyphenyl)propane, 2,2-bis-(4-hydroxyphenyl)hexafluoropropane, bis-(4-hydroxyphenyl)phenylmethane, 2,2-bis-(4-hydroxyphenyl)-2-phenylethane, bis-(4-hydroxyphenyl)trifluoromethylphenylmethane, and bis-(4-hydroxyphenyl)diphenylmethane in the temperature range 160–200°. The reaction was carried out in a ditolylmethane solution in a stream of dry nitrogen purified of oxygen, the feed rate of which was controlled by a rheometer. For the reaction, 100 ml of ditolylmethane was taken, and the amount of the initial TPC and bisphenols corresponded to a solution concentration of 0.065 mole/liter.

Monitoring of the course of the reaction was carried out by determining the amount of hydrogen chloride liberated in the process of polycondensation.

Calculation of the rate constants of polycondensation of TPC with the bisphenols under study according to equations for reactions of the first, second, and third orders showed that the rate constants of the second-order reaction retained a constant value. At 200° in a number of cases a rather good constancy was observed for constants calculated according to equations for reactions of both second and first order. The experimental points on the plots of the dependence of $1/(a-x)$ (where x is the amount of hydrogen chloride liberated by a given moment of the reaction, a is the amount of hydrogen chloride that should be liberated at 100% completion of the reaction) on time lie satisfactorily on straight lines intersecting the ordinate axis at the point corresponding to $1/a$.

For constructing the plots, the experimental data were processed by us by the method of least squares. The tangent of the angle of inclination of such a straight line to the abscissa axis gives the rate constant of the reaction at the given temperature. In Fig. 1, as an example, graphical dependences of $1/(a-x)$ on the reaction duration are given for the case of the interaction of 2,2-bis-(4-hydroxyphenyl)hexafluoropropane with TPC.

Fig. 1. Dependence of $1/(a-x)$ on the duration of polycondensation of TPC with 2,2-bis-(4-hydroxyphenyl)hexafluoropropane

The reaction order, determined by the Van' t Hoff method (^{1}) for the interaction of TPC with 2,2-bis-(4-hydroxyphenyl)propane, proved to be 2.01. This is one more confirmation that the reaction between TPC and bisphenols proceeds by a bimolecular mechanism.

Table 1 gives the rate constants of the reaction of interaction of TPC with various bisphenols at temperatures from 160 to 200°. As can be seen from Table 1, the difference in the values of the rate constants for bis-(4-hydroxyphenyl)methane and 2,2-bis-(4-hydroxyphenyl)propane, and also 2,2-bis-(4-hydroxyphenyl)-2-phenylethane and bis-(4-hydroxyphenyl)phenylmethane, is small. Sig-

a considerable decrease in the reaction rate in comparison with the first two bisphenols (see Table 1) is observed for bis-(4-hydroxyphenyl)-diphenylmethane, bis-(4-hydroxyphenyl)-trifluoromethylphenylmethane, and 2,2-bis-(4-hydroxyphenyl)-hexafluoropropane, especially at temperatures of 160, 170, and 180°.

Table 1

Rate constants of the reaction of TPACl with various bisphenols

No.	Initial bisphenol	Rate constant, L/mol · s 10^{-5} at reaction temperature	Rate constant, L/mol · s 10^{-5} at reaction temperature	Rate constant, L/mol · s 10^{-5} at reaction temperature	Rate constant, L/mol · s 10^{-5} at reaction temperature
		160°	170°	180°	200°
1	$HOC_6H_4-CH_2-C_6H_4OH$	14,7	21,7	37,3	92,7
2	$HOC_6H_4-C(CH_3)_2-C_6H_4OH$	11,6	16,5	35,0	90,2
3	$HOC_6H_4-C(H)(C_6H_5)-C_6H_4OH$	12,6	18,3	26,3	57,5
4	$HOC_6H_4-C(CH_3)(C_6H_5)-C_6H_4OH$	10,0	16,7	25,4	55,1
5	$HOC_6H_4-C(C_6H_5)_2-C_6H_4OH$	7,5	14,8	24,9	71,6
6	$HOC_6H_4-C(CF_3)(C_6H_5)-C_6H_4OH$	6,9	12,7	20,5	57,4
7	$HOC_6H_4-C(CF_3)_2-C_6H_4OH$	5,9	9,2	14,4	35,6

In the acylation reaction of phenols with acid chlorides, proceeding by a bimolecular mechanism, nucleophilic attack on the carbonyl carbon of the carboxylic acid takes place, and a new bond is formed at the expense of the lone pair of electrons of the oxygen atom of the phenol, which can be represented by the following scheme:

$$X{-}C_6H_4{-}\overset{+}{C}({=}\,O){-}Cl \;+\; Y{-}C_6H_4{-}O{:}{-}H \longrightarrow \left[\begin{array}{c} Y{-}C_6H_4{-}O\cdots H \\ X{-}C_6H_4{-}\overset{\delta+}{C}({=}\,O)\cdots Cl \end{array}\right] \longrightarrow X{-}C_6H_4{-}C({=}\,O){-}O{-}C_6H$$

As a result of the action of the inductive effect of the substituents at the central carbon atom of the bisphenol, transmitted through two simple C–C bonds and the benzene ring, the lone electrons of the oxygen atoms of the bisphenols, depending on the nature of the substituents, will be displaced toward the ring to a greater or lesser extent:

$$H{-}\ddot{O}{-}C_6H_4{-}C(R_1)(R_2){-}C_6H_4{-}\ddot{O}{-}H$$

This displacement will be greater in the case of electron-acceptor substituents and smaller for electron-donor substituents.

Consequently, according to the above scheme of the reaction mechanism, one should expect that electron-donor substituents at the central carbon atom of the bisphenol will increase the rate of the reaction of the bisphenol with the dicarboxylic acid chloride, while electron-acceptor substituents will retard it.

The ability of substituents at the central carbon atom of the bisphenols under consideration to displace the lone electrons of the oxygen atoms toward the ring should increase in the following sequence:

$$-C(CF_3)_2- \;>\; -C(CF_3)(C_6H_5)- \;>\; -C(C_6H_5)_2- \;>\; -C(H)(C_6H_5)- \,; \quad -C(CH_3)(C_6H_5)- \;>\; -CH_2- \,;$$

and the rate of the reaction of TPA chloride with bisphenols bearing these substituents should, conversely, decrease.

The data on the reaction-rate constants given in Table 1 generally confirm this sequence. The slight difference in the values of the rate constants for dioxydiphenylmethane and Dian,

Figure 2

Fig. 2. Dependence of the degree of completion of the reaction on the duration of polycondensation of TPA chloride with bis-(4-hydroxyphenyl)-diphenylmethane

Figure 3

Fig. 3. Dependence of the rate constants on temperature for the reaction of TPA chloride with bis-(4-hydroxyphenyl)-methane

as well as dioxydiphenylphenylmethane and dioxydiphenylphenylethane, is explained by the small difference between the induction effects of H–and CH_3–, transmitted in this case through two simple σ-bonds and a benzene ring.

The replacement of the electron-donating methyl groups of Dian by strongly electron-accepting trifluoromethyl groups leads to the result that

Table 2

Arrhenius equations, activation energies, and probability factors for the reaction of TPA chloride with various bisphenols

No.	Initial bisphenol	Arrhenius equation	Activation energy, cal/mol	Probability factor, l/mol · sec
1	$HOC_6H_4-CH_2-C_6H_4OH$	$\lg K = 6.39 - \frac{4630}{T}$	21 100	$0.245 \cdot 10^7$
2	$HOC_6H_4-C(CH_3)_2-C_6H_4OH$	$\lg K = 4.51 - \frac{4861}{T}$	22 200	$0.327 \cdot 10^6$
3	$HOC_6H_4-C(H)(C_6H_5)-C_6H_4OH$	$\lg K = 3.74 - \frac{3263}{T}$	14 900	$0.556 \cdot 10^4$
4	$HOC_6H_4-C(CH_3)(C_6H_5)-C_6H_4OH$	$\lg K = 4.21 - \frac{3842}{T}$	17 500	$0.162 \cdot 10^5$
5	$HOC_6H_4-C(C_6H_5)_2-C_6H_4OH$	$\lg K = 6.71 - \frac{4907}{T}$	20 300	$0.513 \cdot 10^7$
6	$HOC_6H_4-C(CF_3)(C_6H_5)-C_6H_4OH$	$\lg K = 5.79 - \frac{4074}{T}$	18 600	$0.617 \cdot 10^6$
7	$HOC_6H_4-C(CF_3)_2-C_6H_4OH$	$\lg K = 5.55 - \frac{4027}{T}$	18 400	$0.355 \cdot 10^6$

the rate of the polycondensation reaction of hexafluoro-Dian with TPA chloride is 2–2.5 times lower than for Dian.

On the basis of these data it may be concluded that the polycondensation reaction of TPA chloride with the bisphenols studied proceeds by a bimolecular substitution mechanism, and that the reactivity of the bisphenols depends to a large extent on the induction effect of the substituents at the central carbon atom.

The temperature coefficients of the reaction of bisphenols with TPA chloride lie within the range from 1.4 to 2.1. The degree of completion of the studied

the reactions studied over the same time interval increases noticeably with increasing temperature. Thus, at a reaction temperature of 200° during the first

4 hours 50-70% of hydrogen chloride is evolved, whereas at 160° in the same time only 10-20% is evolved. Toward the end of the reaction the increase in the degree of completion gradually slows down (Fig. 2).

The change in the rate constants of the reactions of TPA chloride with bisphenols having different substituents at the central carbon atom as a function of temperature occurs in accordance with the Arrhenius equation: $K = Ae^{-E/RT}$, as can be seen from the example of the interaction of bis-(4-hydroxyphenyl)methane with TPA chloride (Fig. 3). The experimental data, treated by the method of least squares for these reactions, gave the Arrhenius equations presented in Table 2, from which the activation energies and probability factors were calculated (see Table 2). As is evident from Table 2, the apparent activation energy for the interaction of the bisphenols studied with TPA chloride lies within the range from 15,000 to 22,000 cal/mol, and the probability factor from 10^4 to 10^7 l/mol · sec. The probability factor in the Arrhenius equation characterizes the number of molecules colliding with one another per second. A bimolecular reaction has a normal rate if its constant is expressed by the equation: $K = 2.8 \cdot 10^{11} e^{-E/RT}$ (2).

From this it may be concluded that the reaction of TPA chloride with the bisphenols we used belongs to the group of reactions slower than most bimolecular reactions.

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Received
22 III 1965

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

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