COMPLEX FORMATION BY PHENOLS WITH TERTIARY AMINES IN APROTIC MEDIA

M. L. Keshtov, S. V. Vinogradova, V. A. Vasnev, and V. V. Korshak

UDC 541.124:541.49:547.56:547.233.3

At the present time, the acceptor-catalytic polyesterification of diols with dicarboxylic acid dianhydrides in the presence of tertiary amines is used for the synthesis of polyesters and copolyesters with various structures. It has been established that the structure of the bisphenols, the nature of reaction medium, and the temperature of the reaction have a large influence on the nature and results of this process [1]. In particular, the acceptor-catalytic polyesterification of bisphenols and dicarboxylic acid dichlorides in the presence of strongly basic tertiary amines takes place via a stage of the interaction of a complex of the phenol and the tertiary amine with the dichloride, i.e., by the mechanism of general base catalysis [1].

In order to investigate the mechanism of the process and to describe its features, such as the complex dependence of the effective rate constant on the temperature, quantitatively, it was considered desirable to study the initial stage of the reaction — the stage of complex formation by the phenolic groups with the tertiary amines on the assumption of a rapid and equilibrium formation of an equimolar complex [2]

$$\underset{C_{ArOH}C_{R_3N}}{ArOH + R_3N} \overset{K_e}{\rightleftarrows} \underset{C_c}{ArOH \ldots NR_3} \quad (1)$$

In an excess of tertiary amine, the equilibrium constant

$$K_e = C_c/[(C^0_{ArOH} - C_c)\, C^0_{R_3N}] \quad (2)$$

where C_c, $C^0_{R_3N}$, and C^0_{ArOH} are the instantaneous concentration of the complex and the initial concentrations of the tertiary amine of the phenol, respectively. Then,

$$C_c = K_e C^0_{R_3N} C^0_{ArOH}/(1 + K_e C^0_{R_3N}) \quad (3)$$

If it is borne in mind that the optical density (D) of the solution of the complex and ArOH after the deduction of the optical density of R_3N at a given wavelength

$$D = [(C^0_{ArOH} - C_c)\varepsilon_{ArOH} + C_c\varepsilon_c]\, l,$$

where ε_{ArOH} and ε_c are the molar absorption coefficients of ArOH and of the complex, respectively, and l is the length of the cell, then, according to Eqs. (1)-(3)

$$(D - D_0)/C^0_{R_3N} = K_e C_{ArOH} l\,(\varepsilon_c - \varepsilon_{ArOH}) - K_e(D - D_0) \quad (4)$$

where $C^0_{R_3N} \simeq C_{R_3N}$ and $D_0 = C^0_{ArOH} l \varepsilon_{ArOH}$.

In the range of wavelengths of the absorption of phenols, the optical density of tertiary amines is practically equal to zero.

It can be seen from Eq. (4) that the relation $(D - D_0)/C^0_{R_3N}$ provides the possibility of calculating K_e. The values of K_e at various temperatures for the systems studied are given in Tables 1-3. The temperature dependence of K_e according to the equation [3]

$$\ln K_e = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (5)$$

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 12, pp. 2730-2734, December, 1980. Original article submitted January 7, 1980.

 0568-5230/80/2912-1906$07.50

TABLE 1. Thermodynamic Parameters of the Complex-Forming Reaction of Phenols with Triethylamine [$pK_\alpha(CH_3NO_2)$ = 18.35; E_N = 3.8]

ArOH	Solvent	T, °K	K_e, liter/mole	$-\Delta H$, kcal/mole
Phenol pK_a DMSO 13,7 [1]	n-Heptane	297	60,40±0,51	9,10±0,1
		303	49,00±0,51	
		308	34,00±0,50	
		313	29,00±0,50	
	Dichloroethane	298	28,00±0,05	7,30±0,1
		307	19,00±0,05	
		314	16,00±0,05	
		325	10,00±0,05	
	Dioxane	298	1,15±0,05	9,00±0,1
		305	0,76±0,05	
		313,5	0,51±0,05	
		323,5	0,31±0,05	
p-Chlorophenol pK_aDMSO 12,7 [1]	n-Heptane	298	185,0±0,51	10,50±0,1
		307	110,0±0,51	
		313	76,0±0,51	
		318	63,5±0,51	
	Dichloroethane	297	66,0±0,51	9,60±0,1
		303	48,0±0,51	
		313	32,0±0,51	
		321	20,0±0,51	
	Dioxane	297	5,00±0,03	10,00±0,1
		303	3,55±0,03	
		316	1,86±0,03	
o-Chlorophenol pK_a DMSO 12,5 [1]	n-Heptane	297	8,50±0,03	8,23±0,1
		307	6,00±0,03	
		317	3,50±0,03	
		332	2,05±0,03	
	Dichloroethane	295	13±0,05	7,30±0,1
		307	9,0±0,05	
		342	6,0±0,05	
		342,5	2,5±0,05	
	Dioxane	Small values		

permits the determination of the enthalpy of formation of hydrogen bonds ΔH (kcal/mole). The values of ΔH are also given in Table 1-3. As can be seen from Tables 1-3, the energy of a hydrogen bond between ArOH and R_3N in heptane is somewhat higher than in dichloroethane. One of the possible reasons for this difference in ΔH is a decrease in the energy of electrostatic interaction between the proton acceptor and donor with a rise in the dielectric constant of the solvent. However, the values of K_e and ΔH are affected not only by the polarity of the medium (physical solvation) but also by its capacity for participating in the specific (chemical) solvation of the reactants. The dielectric constants of n-heptane and dioxane are close but the values of K_e and of ΔH in dioxane are smaller, which can apparently be explained by the formation of complexes between the dioxane and phenol molecules.

It can be seen from Tables 1-3 that the replacement of the H in the para position of phenol by the electronegative Cl atom leads to increases in K_e and in the ΔH value of the hydrogen bond. In the case of o-chlorophenol the opposite pattern is observed. This is apparently due to the formation of a strong intramolecular H-bond in the o-chlorophenol molecule [4].

It appeared of interest to trace the influence of the basicity of the tertiary amine and the steric accessibility of the N atom on the process of complex formation. For this purpose we used various tertiary amines: triethylamine, tributylamine, and triallylamine. The first two tertiary amines possess fairly similar basicities but differ in the steric accessibility of the N atom (see Tables 1-3, where E_N is a constant characterizing the steric accessibility of an amine N atom [5]). At the same time, triethylamine and triallylamine have fairly close values of E_N but differ substantially in basicity (Table 1).

The value of K_e depends appreciably both on the steric accessibility of the N atom and on its basicity (see Table 2). Thus, triethylamine, the N atom of which is more sterically accessible than that of tributylamine has higher K_e values. Similarly, K_e for the less basic triallylamine is considerably smaller than for the more basic triethylamine. The results obtained permit the conclusion that an increase in the steric accessibility of the N atom of a tertiary amine and a rise in its basicity lead to an increase in K_e.

TABLE 2. Characteristics of the Hydrogen Bonds between Phenols and Triallylamine in Heptane [pK_α (CH_3NO_2) = 4.89, E_N = 3.5]

ArOH	Solvent	T, °K	K_e, liter/mole	$-\Delta H$, kcal/mole
p-Chlorophenol	n-Heptane	298	31,0±0,8	10,28±0,1
		305	18,8±0,8	
		314	13±0,8	
		324	8,0±0,8	
Phenol	»	298	12,5±0,3	10,0±0,1
		303	8,6±0,3	
		318	4,3±0,3	
		326	2,8±0,3	
o-Chlorophenol	»	298	4,0±0,2	8,68±0,1
		305	2,8±0,2	
		312	2,0±0,2	
		322	1,15±0,2	
p-Chlorophenol	Dichloroethane	296	7,3±0,2	10,5±0,1
		304	4,6±0,2	
		317	2,3±0,2	
		333	1,5±0,2	
Phenol	»	296	3,750±0,1	9,6±0,1
		305	2,5±0,1	
		314	1,5±0,1	
		318	0	
o-Chlorophenol	»	299	2,3±0,1	8,70±0,1
		306	1,550±0,1	
		312,5	1,2±0,1	

TABLE 3. Characteristics of the Hydrogen Bonds of Phenols with Tributylamine in Heptane and Dichloroethane [$pK_\alpha(CH_3NO_2)$ = 17.77, E_N = 4.5]

ArOH	Solvent	T, °K	K_e, liter/mole	$-\Delta H$, kcal/mole
p-Chlorophenol	n-Heptane	296	47,0±0,5	10,9±0,1
		305	25,0±0,5	
		317	12,5±0,5	
		325	8,5±0,5	
Phenol	»	296	22,0±0,5	10,5±0,1
		305	12,5±0,5	
		312	9,0±0,5	
		324	4,6±0,5	
o-Chlorophenol	»	293	3,00±0,03	7,3±0,1
		303	2,00±0,03	
p-Chlorophenol	Dichloroethane	293	20,0±0,05	8,3±0,1
		303	16,0±0,5	
		313	7,5±0,5	
		323	5,4±0,5	
Phenol	»	292	10,00±0,05	10,96±0,1
		300	6,10±0,05	
		308	3,80±0,05	
		320	2,50±0,05	
o-Chlorophenol	»	293	6,40±0,05	6,4±0,1
		303	3,3±0,05	
		312	2,50±0,05	

On the whole, according to the K_e values, the tertiary amines studied form the sequence $(C_2H_5)_3N > (C_4H_9)_3N > (CH_2{=}CHCH_2)_3N$. It may be assumed that under the conditions of general base catalysis the rate constant of the acceptor-catalytic esterification and of polyesterification will also increase in this sequence. The available literature information on the rate constants for the acylation of phenol and p-nitrophenol by benzoyl chloride in the presence of triethylamine and tributylamine confirm this conclusion [1].

EXPERIMENTAL

The equilibrium constants of the complex-forming processes were determined spectrophotometrically on a Specord UV-VIS spectrophotometer with a thermostating device. The mea-

surements were carried out in the 260-300 nm region. The concentration of the phenols was 10^{-4} M and the concentrations of triethylamine from 10^{-2} to 10^{-1} M; the absorption of the tertiary amines was negligibly small.

Solutions of triethylamine of various concentrations were added to solutions with identical concentrations of phenol in, for example, n-heptane. The equilibrium constant of the association of the phenol with the triethylamine was calculated from the concentration dependence of the optical densities of the solutions, the association of the phenol can be neglected. A shift of the UV absorption maxima in the long-wave direction took place as a result of the formation of a H-bond [1]. The formation of a H-bond is also indicated by the increase in the intensity of the UV absorption of the phenol in the presence of triethylamine. According to Mashkovskii and Odinokov [6], complete proton transfer in complexes with a H-bond is observed at $-\Delta H > 11$ kcal/mole. In order to show the constancy of K_e, it was calculated from the absorption at various wavelengths. For example, for the phenol–triethylamine–heptane system measurements were made at 274, 276, 278, 280, 284, and 286 nm. Then the values of ΔH were found graphically from Eq. (5). The mixtures were investigated in the range of temperatures from 20 to 60°C with an accuracy of ±0.5°C. All the substances investigated were subjected to careful purification, and their physicochemical constants corresponded to those given in the literature.

CONCLUSIONS

1. The equilibrium constants (K_e) and the enthalpies of formation of H-bonds in complex-formating reactions of phenols with tertiary amines in aprotic solvents fall with a rise in the polarity of the medium and in its capacity for specific solvation with the phenols.

2. The introduction of the electron-accepting substituent chlorine into the para position of phenol leads to a considerable rise in K_e, but in the case of o-chlorophenol, because of the strong intramolecular H-bond the value of K_e is somewhat lower than for unsubstituted phenol.

3. With an increase in the steric accessibility of the N-atom of a tertiary amine and a rise in its basicity, K_e increases. The tertiary amines studied form the following sequence of decreasing K_e values: $(C_2H_5)_3N > (C_4H_9)_3N > (CH_2=CHCH_2)_3N$.

LITERATURE CITED

1. A. I. Tarasov, Dissertation, Moscow (1973).
2. S. Nagakura and H. Baba, J. Am. Chem. Soc., 74, 5693 (1952).
3. E. I. Gur'yanova, I. P. Gol'dshtein, and T. P. Perepelkova, Usp. Khim., 45, 1568 (1976).
4. S. Nagakura, J. Am. Chem. Soc., 76, 3070 (1954).
5. S. V. Bogatkov, L. V. Bystrov, and R. I. Kruglikova, Reakts. Sposobn. Org. Soedin., 15, 180 (1978).
6. A. A. Mashkovskii and S. E. Odinokov, Dokl. Akad. Nauk SSSR, 204, 1165 (1973).