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ESTERIFICATION OF PHTHALIC ANHYDRIDE BY ALCOHOLS IN THE PRESENCE OF TITANIUM BIS(β-DIKETONATES)

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UDC 541.128:542.951.3:
547.584:547.266

Alkyl orthotitanates have been widely studied as catalysts for esterification reactions used, in particular, in the industrial manufacture of phthalic anhydride-based plasticizers [1-5]. The use of titanium chelates for this purpose is known [6-8], but there is practically no information on the kinetics in relation to various factors and on the reaction mechanism.

Previously we investigated the esterification of phthalic anhydride by 2-ethylhexanol in a dioctyl phthalate medium using a wide range of titanium chelates as catalysts [9]. The present paper is devoted to a study of the kinetics of reaction of phthalic anhydride with excess 2-ethylhexanol and normal C_6-C_9 alcohols in a medium of the corresponding ester in the presence of titanium bis(β-diketonates).

EXPERIMENTAL

Phthalic anhydride of analytical purity and distilled 2-ethylhexanol and normal C_6-C_9 alcohols were used. Bis(β-diketonato)dialkyoxytitaniums were synthesized from butyl orthotitanate and the corresponding chelating agents according to [10], and the hydrolysis products were synthesized according to [11].

The esterification was carried out at 185°C either in excess alcohol or in a medium of the resulting ester with a stoichiometric reagent ratio. The concentrations of phthalic anhydride and the catalyst were 0.2 and $4.35 \cdot 10^{-4}$ mole/liter, respectively. The reaction and the calculation of the rate constants were carried out similarly to [9].

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Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1247-1250, June, 1989. Original article submitted May 4, 1987.

0568-5230/89/3806-1133$12.50

TABLE 1. Rate Constants of Esterification of Phthalic Anhydride by 2-Ethylhexanol

Catalyst (ligand)	Formula	Esterification rate constant, $k\cdot10^5$, liters/(mole·sec)	
		in excess 2-ethylhexanol	in bis(2-ethylhexyl) phthalate medium
Bis(dibenzoylmethanato)dibutoxytitanium (bzbz)	$(bzbz)_2Ti(OBu)_2$	2,3±0,2	5,5±0,3
Bis(benozylacetonato) dibutoxytitanium (bzac)	$(bzac)_2Ti(OBu)_2$	2,8±0,2	8,5±0,5
Bis(acetylacetonato) dibutoxytitanium (acac)	$(acac)_2Ti(OBu)_2$	5,2±0,3	14,1±0,7
Butyl orthotitanate	$Ti(OBu)_4$	4,0±0,2	40,8±2,0
Bis(acetylacetonato) dibutoxytitanium: acetylacetone = 1:3	$(acac)_2Ti(OBu)_2 : acacH$	3,5±0,3	4,7±0,2

TABLE 2. Rate Constants of Esterification of Phthalic Anhydride by Normal Alcohols in a Medium of the Corresponding Diester

Alcohol	Rate constant $k\cdot10^5$, liters/(mole·sec)	
	butyl orthotitanate	bis(acetylacetonato) dibutoxytitanium
$C_6H_{13}OH$	5,8±0,5	12,2±0,8
$C_7H_{15}OH$	9,7±0,7	13,8±0,8
$C_8H_{17}OH$	20,3±1,5	10,2±0,8
$C_9H_{19}OH$	6,7±0,5	5,0±0,5

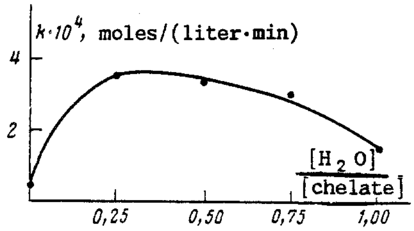


Fig. 1. Relation of the rate constants of esterification of phthalic anhydride by 2-ethylhexanol in the presence of hydrolyzed (acetylacetonato)triethoxytitanium to the degree of its hydrolysis.

RESULTS AND DISCUSSION

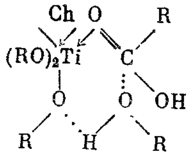
As was assumed previously [9], the catalytic activity of bis(chelate) derivatives of titanium is apparently due to the fact that in solutions they are in equilibrium with the monochelate and the titanate [12]

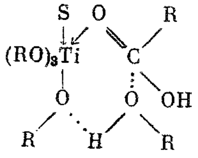
$$Ti(OR)_2Ch_2 \underset{-ChH}{\overset{+ROH}{\rightleftarrows}} Ti(OR)_3Ch \underset{-ChH}{\overset{+ROH}{\rightleftarrows}} Ti(OR)_4 \qquad (1)$$

able, because of their coordination unsaturation (unlike in the case of bis(chelates)), to form intermediate complexes of various structures, with whose participation, in the opinion of a number of authors [3, 5], esterification occurs in the presence of alkyl orthotitanates. Factors contributing to shifting of the equilibrium of (1) to the right, i.e., toward the formation of catalytically active species, should lead to an increase of the catalytic activity of the chelate and vice versa. Indeed, from Table 1, it is evident that, just as in the dioctyl phthalate medium, the rate constants of esterification, in excess 2-ethylhexanol increase in the series: bzbz < bzac < acac, which corresponds to a decrease of the stability of the bis(chelates) in the solution [13]. When a free chelating agent is added to the system, the rate constant decreases.

If the catalytic activity of the chelates were determined only by their stability in solution, it would always be lower than in the case of alkyl orthotitanate, similarly to esterification in the dioctyl phthalate medium [9]. However, when the reaction is carried out in excess 2-ethylhexanol in the presence of bis(acetylacetonato)dibutoxytitanium, the rate constant is higher than for butyl orthotitanate (Table 1). On the whole, the reaction occurs at a lower rate in the ester than in the alcohol.

The effect of the composition of the reaction medium on the catalytic activity of the Ti chelates can be explained on the basis of the reaction mechanism. By analogy with the esterification mechanism for butyl orthotitanate [3], we can assume that in the case of bis(chelate) dialkoxytitaniums, inner-sphere complexes of the monochelate and the titanate with the alcohol are formed initially, and the monoester is bonded in an outer-sphere manner


(IIa)


(IIb)

S = A and D, where A is alcohol, and D is diester.

Such an intermediate complex seems to us to be preferable to that considered in [5], where the monoester molecule is coordinated with the Ti atom and the alcohol enters the outer sphere. The structure of the transition state (IIa and b) explains well the liberation of water and the ester and the regeneration of the catalyst. Inner-sphere complexes of a titanate with an alcohol are known [14]. As regards complexes with a monoester, they apparently afford titanium acylates, whose formation during heating of phthalic anhydride with chelates we confirmed by IR spectroscopy. Data on the inhibiting effect of the monoester on esterification correspond to this [5]. Depending on the composition of the medium, in complex (IIb), predominantly the alcohol (A) or diester (D) molecule can be additionally coordinated to the Ti atom, which explains the different catalytic activity of the Ti compounds in the alcohol and the diester. For complex (IIa), there is no such possibility because the Ti atom in it is coordination-saturated. Therefore, in the case of catalysis by bis(chelates), the effect of the medium should be less than for alkyl orthotitanates. Indeed, in going from the aclohol to the diester, the esterification rate constant increases approximately three-fold in the case of bis(acetylacetonato)dibutoxytitanium and approximately ten-fold in the case of butyl orthotitanate.

Table 2 gives the rate constants of esterification of phthalic anhydride by normal C_6-C_9 alcohols in a medium of the corresponding esters in the presence of the most active chelate, the acetylacetonato one, and butyl orthotitanate. The relation of the rate constant to the length of the alkyl group of the alcohol is extremal in nature.

This is possibly due to the different degree of hydrolysis of the catalyst, which, in its turn, is due to the nature of the alcohol used in esterification. Because of transesterification in the reaction medium, the Ti derivatives contain alkoxy groups corresponding to the alcohol participating in the reaction. During esterification, the titanium-containing catalyst can be partially hydrolyzed by the water liberated in the reaction. The hydrolytic stability of the Ti alkoxides increases with increasing length of the alkoxy radical [10]. Therefore, with other conditions being equal, the degree of hydrolysis of the titanium-containing catalyst will decrease with increasing length of the alkyl radical of the alcohol. We have shown (Fig. 1) that the rate constants of esterification of phthalic anhydride by 2-ethylhexanol in the presence of the hydrolyzed chelate depend extremally on the degree of its hydrolysis, which agrees with the data of [15] on the catalytic activity of hydrolyzed butyl orthotitanate.

CONCLUSIONS

In the esterification of phthalic anhydride by 2-ethylhexanol in the presence of titanium bis(β-diketonates), the rate constants of the reaction increase with decreasing stability of the chelate. The relation of the rate constant of the reaction of phthalic anhydride with normal C_6-C_9 alcohols catalyzed by bis(acetylacetonato)dibutoxytitanium and butyl orthotitanate in a medium of the corresponding diesters is extremal in nature because of the different degree of hydrolysis of the catalyst during esterification.

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