

KINETICS OF ESTERIFICATION OF DIISOPROPYLPHENOLS WITH PHOSPHORYL TRICHLORIDE

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The title liquid-phase isothermal esterification kinetics have been measured in the temperature intervals of 110–125 and 110–160°C for 2,4- and 2,6-diisopropylphenols, resp. The values measured have been used to calculate the rate constants of the respective three steps and to determine the activation energies. 2,6-Diisopropylphenol has been found to react only to the first degree, and the rate constants of the other two reaction steps (k_2 , k_3) were only calculated from the differential equations given by means of a computer.

The synthesis of isopropylphenols by alkylation of phenol with propene produces a mixture containing phenol and its mono-, di-, and triisopropyl derivatives^{1–3}. This reaction mixture is submitted to esterification with phosphoryl tri-chloride to give a mixture of triaryl phosphates which is used commercially as a combustion retarder, PVC plasticizer, hydraulic and heat-transfer liquid. The properties of the diisopropylphenols present in the alkylation mixture are little described. It is stated that in the industrial production of mixed triaryl phosphates 2,6-diisopropylphenol, due to its low reaction rate, behaves as a ballast and accumulates in the process. According to literature data^{4–7} the unreacted alkylphenols are distilled from the raw phosphate and recycled in the process. If the concentration of 2,6-diisopropylphenol is increased in the recycled material, this component is separated and removed from the process. With regard to the relatively complex analysis and low reaction rates, the esterification kinetics of diisopropylphenols have not been described in literature so far.

Analytical methods for such mixtures were published⁸ and proved useful also for investigation of the esterification course of diisopropylphenols. The rates of reactions of phenol and 2- and 4-isopropylphenols were dealt with in our previous papers^{9,10}. In order to understand the kinetic relations in the alkylation mixture, it was necessary to measure the values of rate constants of diisopropylphenols. The aim of this present communication, therefore, is to measure the esterification rates of 2,4-diisopropylphenol (2,4-di-IPP) and 2,6-diisopropylphenol (2,6-di-IPP) with POCl_3 under the same conditions.

EXPERIMENTAL

Reagents: The principal reaction components used were 2,4-diisopropylphenol (b.p. 249°C, m.p. 22.5°C, n_D^{20} 1.512, d_4^{20} 0.947 g cm⁻³, chromatographical purity 99.5%), 2,6-diisopropylphenol (b.p. 236°C, m.p. 18°C, n_D^{20} 1.511, d_4^{20} 0.957 g cm⁻³, chromatographical purity 98.2%), and POCl₃ (b.p. 107.7°C, m.p. 1.20°C, d_4^{20} 1.46 g cm⁻³, chromatographical purity 99.2%). The other chemicals used included *o*-xylene p.a. (as a solvent for 2,4-di-IPP), isopropylbiphenyl (as a solvent for 2,6-di-IPP), 2-ethylhexanol p.a., octadecane, pentadecane p.a., compressed nitrogen and air.

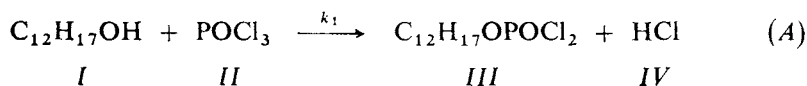
Apparatus and procedure: The alkylation of phenol with propene was carried out in a reactor consisting of a three-necked flask with reflux condenser, propylene inlet, and relief gas outlet, immersed in a thermostat (110°C); 2,4- and 2,6-diisopropylphenols were isolated by rectification on a column of 2 m height and 3 cm inner diameter packed with 5 × 5 mm Raschig rings, the overall pressure at the column head was 400 Pa, reflux ratio 3 : 1, number of theoretical plates 25. The rectification gave relatively pure 2,4-diisopropylphenol, but the 2,6-diisopropylphenol of desired concentration was only obtained by repeated rectification. The samples taken at definite time intervals were cooled to a temperature of c. -18°C and analyzed after the treatment described elsewhere⁸.

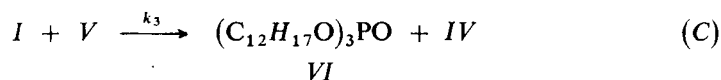
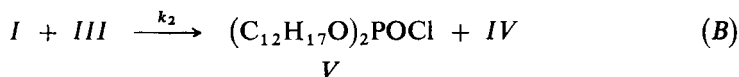
Analytical methods: The reaction mixture was analyzed by means of a gas chromatograph Chrom 5 (Laboratorní přístroje, n.p., Prague) with a flame ionization detector. Quantitative evaluations were made with the help of an automatic integrator Computing CI-100. Conditions of the analysis: glass column of 1.25 m length and 3 mm inner diameter, packed with 5% OV 225 on Chromosorb, programmed temperature control from 100 to 150°C with a gradient of 5°C per min and from 150 to 270°C with a gradient of 20° per min; carrier gas — nitrogen at a flow rate of 30 cm³ min⁻¹, auxiliary gases — hydrogen (27 cm³ min⁻¹) and air (500 cm³ min⁻¹). Quantitative evaluation was made by the method of internal standard — octadecane and pentadecane for 2,4- and 2,6-diisopropylphenols, respectively. Argentometry and colourimetry were used as complementary methods for determination of chlorides and phosphorus, respectively.

RESULTS AND DISCUSSION

The composition of reaction mixture was measured for the esterification of 2,4-diisopropylphenol with POCl₃ at the temperatures of 110, 115, 120, and 125°C and for that of 2,6-diisopropylphenol with POCl₃ at 110, 120, 130, and 160°C. Thus the esterification kinetics of 2,4- and 2,5-diisopropylphenols with POCl₃ was measured in a homogeneous phase under the conditions of open system with respect to the hydrogen chloride released during the reaction.

The esterification reaction of diisopropylphenol with POCl₃ consists in a system of consecutive reactions which can be described by a system of five differential equations in a similar way as in our previous papers^{9,10} presuming the first order in each of the components:





$$-dC_I/dt = k_1 C_I C_{II} + k_2 C_I C_{III} + k_3 C_I C_V \quad (1)$$

$$-dC_{II}/dt = k_1 C_I C_{II} \quad (2)$$

$$dC_{III}/dt = k_1 C_I C_{II} - k_2 C_I C_{III} \quad (3)$$

$$dC_V/dt = k_2 C_I C_{III} - k_3 C_I C_V \quad (4)$$

$$dC_{VI}/dt = k_3 C_I C_V, \quad (5)$$

where *I* means 2,4- and/or 2,6-diisopropylphenol, *III* is the mono(dialkylphenyl) dichlorophosphate, *V* is the bis(dialkylphenyl) monochlorophosphate, and *VI* is the tris(dialkylphenyl) phosphate.

When following the esterification kinetics of phenol and monoisopropylphenols we found that the rate equations are of the second order. These data were tested by means of the values of dispersion and average deviations for 2,4-diisopropylphenol (Table I). These tests were not realized in the case of 2,6-diisopropylphenol, since tris(2,6-diisopropylphenyl) phosphate is not practically formed under the conditions given.

On the basis of the earlier measurements^{9,10} of phenol, 2- and 4-isopropylphenols and the present measurement of 2,4-diisopropylphenol it can be presumed that the reactions with 2,6-diisopropylphenol are of the second order, too.

TABLE I

Values of dispersions and mean deviations for 2,4-diisopropylphenol and various values of exponents at the temperature of 110°C

Exponents at the concentration terms	Dispersion	Mean deviation
$C_I^0 C_{II}^1$	0.026	0.162
$C_I^1 C_{II}^1$	0.002	0.041
$C_I^1 C_{II}^2$	0.131	0.362
C_I^2	0.028	0.168

The exponents at the concentration terms being known, it was possible to calculate the rate constants for 2,4-diisopropylphenol (Table II) and 2,6-isomer (Table III). From the tables it can be seen that the rates of reactions of POCl_3 with 2,4-diisopropylphenol and the 2,6-isomer differ in order of magnitude. The reaction rates of the isomeric dialkylphenols were compared at the temperature of 110°C , and it was found that 2,6-diisopropylphenol only reacts to the first degree even after a very long period of time (see Fig. 2), i.e. only the first chlorine of POCl_3 is replaced.

For the kinetic measurements of esterification of 2,6-diisopropylphenol we had to adopt a new solvent – isopropylbiphenyl – whose higher boiling point allowed the reaction rate to be followed at higher temperatures. But even after 80 h at 160°C the reaction mixture did not contain any tris(2,6-diisopropylphenyl) phosphate, and the constants k_2 and k_3 given in Table III are those calculated by the computer and have only orientational meaning. The reaction rate of 2,6-diisopropylphenol is decreased because of the presence of two alkyl groups ortho to the phenolic OH group¹¹, hence it can be stated that in the technological procedure this dialkylphenol

TABLE II

Values of rate constants of esterification of 2,4-diisopropylphenol with POCl_3

Temperature $^\circ\text{C}$	Rate constants, $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$		
	$k_1 \cdot 10_3$	$k_2 \cdot 10_3$	$k_3 \cdot 10^3$
110	125	98	65
115	131	111	72
120	142	117	88
125	146	133	96

TABLE III

Values of rate constants of esterification of 2,6-diisopropylphenol with POCl_3

Temperature $^\circ\text{C}$	Rate constants, $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$		
	$k_1 \cdot 10^3$	$k_2 \cdot 10^6$	$k_3 \cdot 10^9$
110	0.2	0.04	0.9
120	0.4	0.1	0.5
130	2.4	5.2	0.8
160	45.0	5.5	10.0

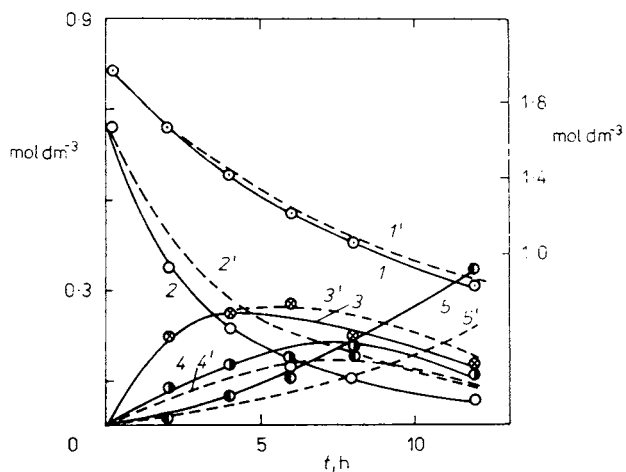


FIG. 1

The time course of the composition of reaction mixture of 2,4-diisopropylphenol (2,4-di-IPP) with POCl_3 at the temperature of 110°C . — The values measured, --- the values calculated. 1, 1' \circ 2,4-di-IPP, 2, 2' \circ POCl_3 , 3, 3' \otimes $(2,4\text{-di-IPP})\text{POCl}_2$, 4, 4' \bullet $(2,4\text{-di-IPP})_2\text{POCl}$, 5, 5' \bullet $(2,4\text{-di-IPP})_3\text{PO}$

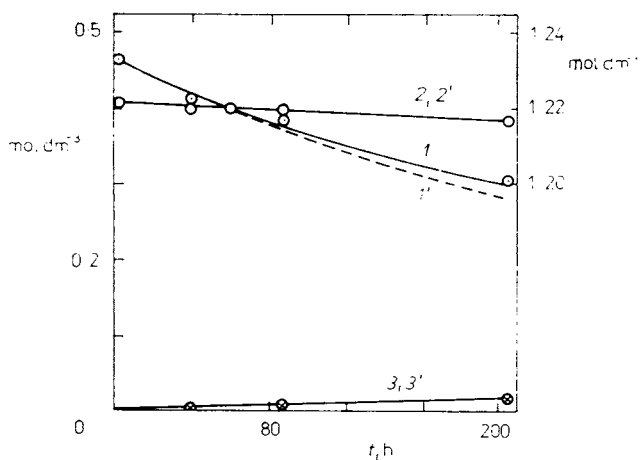


FIG. 2

The time course of the composition of reaction mixture of 2,6-diisopropylphenol (2,6-di-IPP) with POCl_3 at the temperature of 110°C . — The values measured, --- the values calculated. 1, 1' \circ 2,6-di-IPP, 2, 2' \circ POCl_3 , 3, 3' \otimes $(2,6\text{-di-IPP})\text{POCl}_2$

will be practically unreactive in the mixture with the other alkylphenols and will be accumulated in the distillate during the treatment of the final product. The results of kinetic treatment are loaded with a certain systematic error because of the escape of POCl_3 from the reaction mixture. In the measurements it was found that the initial ratio of 2,6-diisopropylphenol to POCl_3 , viz 3 : 1, changed during the reaction to the value of 5 : 1 due to the loss of POCl_3 during the long-term experiment. Therefore all the data about the rate constants of 2,6-diisopropylphenol have only semiquantitative meaning.

On the other hand, 2,4-diisopropylphenol is esterified more slowly than 4-isopropylphenol but almost comparably with phenol (due to the rate increase caused by the *para* substituent), which is a rather surprising finding with regard to the relatively small inductive effect of *para*-isopropyl group.

Figure 1 presents the time course of composition of the reaction mixture during the esterification of 2,4-diisopropylphenol with POCl_3 along with that found theoretically by simultaneous solution of the system of the differential equations (1) through (5) (at the temperature of 110°C).

In spite of the objective sources of errors, the reaction course is expressed relatively precisely by the system of differential equations (1) through (5), these results being more convincing with 2,4-diisopropylphenol than with phenol itself.

Figure 2 presents the time course of the esterification of 2,6-diisopropylphenol with POCl_3 , wherefrom it can be seen that the reaction is very slow in this case, the first step even being not complete (also at the temperature of 160°C). From technological standpoint it can be stated that this dialkylphenol (present in the mixture with the other alkyl derivatives of phenol) practically will not react and will be accumulated in the distillate during purification of the final product.

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