

KINETICS OF ESTERIFICATION OF MONOISOPROPYLPHENOLS WITH PHOSPHORYL TRICHLORIDE

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The kinetics of liquid-phase isothermal esterification of POCl_3 with 2-isopropylphenol and 4-isopropylphenol have been studied within the temperature intervals of 110 to 130 and 90 to 110°C, respectively. The rate constants and activation energies of the individual steps of this three-step reaction have been calculated from the values measured. The reaction rates of the two isomers markedly differ: at 110°C 4-isopropylphenol reacts faster by the factors of about 7 and 20 for k_1 and k_3 , respectively. This finding can be utilized in preparation of mixed triaryl phosphates, since the alkylation mixture after reaction of phenol with propene contains an excess of 2-isopropylphenol over 4-isopropylphenol.

The mixed triaryl phosphates produced by reactions of monoisopropylphenols with POCl_3 are used as plasticizers and burning retarders in polymers, particularly PVC. Recently they have been increasingly applied in industry as incombustible lubricants, hydraulic liquids, and heat-transfer media.

2-And 4-isopropylphenols are prepared by the alkylation of phenol with propene; the alkylation mixture contains the unreacted phenol, monoisopropylphenols, diisopropylphenols, and — with excess of the alkylation agent — also triisopropylphenols¹⁻⁵. Reactivity of the mixture was followed by the reaction kinetics of phenol⁶ and monoisopropylphenols, so that a suitable proportion of the individual isomers might be suggested. The esterification produces the phosphates with desirable properties. Literature provides information on reactions of formation of trialkylphenyl phosphates^{7,8} but kinetic data about the process are currently not given due to complexity of the consecutive reactions of formation of triaryl phosphates.

For preparation of triaryl phosphates from the above-mentioned alkylation mixture it is important to know the esterification rates of POCl_3 with the alkylphenols and phenol itself. Our previous communication⁶ dealt with the esterification of POCl_3 with phenol. The aim of this present paper was to measure the rates of reactions of 2-isopropylphenol and 4-isopropylphenol with POCl_3 at the same conditions as in ref.⁶, because the comparison of esterification rate constants of phenol and both the alkylphenols can significantly contribute to proper control of the

production process of triaryl phosphates, as the two monoalkylphenols represent the most important components of the alkylation mixture from phenol and propene.

EXPERIMENTAL

The main reaction components used were 2-isopropylphenol (2-IPP), 4-isopropylphenol (4-IPP), and POCl_3 whose physical constants are given in Table I. The other chemicals used included *o*-xylene p.a., 2-ethylhexanol p.a., octadecane p.a. (Labora, Bratislava).

Apparatus and procedures. The alkylation of phenol with propene was carried out in a three-necked flask equipped with a reflux condenser, inlet of propene and outlet of gases and placed in a thermostat. The isolation of 2- and 4-isopropylphenols was carried out on a vacuum rectification column of 2 m length and 3 cm inner diameter packed with ceramic Rashig rings 5×5 mm, the overall pressure at the column head was 400 Pa, reflux ratio 3 : 1, total number of theoretical plates about 25 TP. The esterification apparatus was the same as that in ref.⁶, i.e. an isothermal three-necked reactor placed in a thermostat with oil bath and equipped with a magnetic stirrer and outlet tube to remove gaseous hydrogen chloride from the reaction mixture. Samples taken at definite time intervals were rapidly cooled to -18°C and treated and analyzed as in ref.⁶.

Analytical methods. The reaction mixture was analyzed on a gas chromatograph Chrom 5 (Laboratorní přístroje, Prague) with a flame-ionization detector. Quantitative evaluations were carried out with an automatic integrator Computing CI-100. Conditions of analyses: 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 250°C with a gradient of 5°C min^{-1} and from 150 to 270°C with a gradient of $20^\circ\text{C min}^{-1}$. Carrier gas — nitrogen at the flow rate of $30 \text{ cm}^3 \text{ min}^{-1}$, auxiliary gases — hydrogen $27 \text{ cm}^3 \text{ min}^{-1}$ and air $500 \text{ cm}^3 \text{ min}^{-1}$. Quantitative determinations were carried out by the method of internal standard (octadecane)⁹. Additional analytical methods: argentometry (determination of chlorides) and colourimetry (determination of phosphorus).

RESULTS AND DISCUSSION

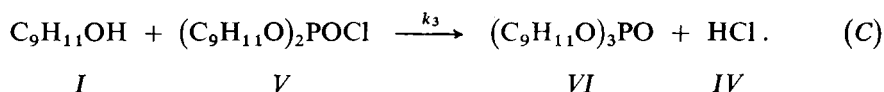
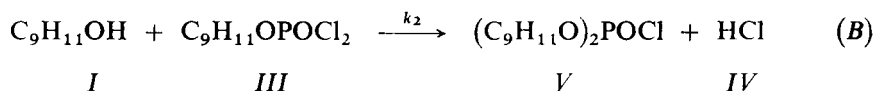
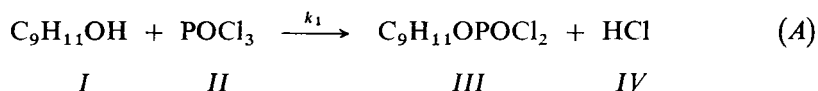
The time dependence of composition of the esterification mixture was measured at the temperatures of 110, 115, 125, and 130°C for POCl_3 + 2-isopropylphenol and

TABLE I
Physico-chemical properties of the chemicals used

Compound	Boiling point $^\circ\text{C}$	Melting point $^\circ\text{C}$	n_{D}^{20}	ρ_4^{20} kg m^{-3}	Chromatographical purity, %
2-Isopropylphenol	21.45	15.8	1.5285	1 012	9.98
4-Isopropylphenol	225	62	1.5228 ^a	955.6	99.6
Phosphoryl trichloride	128	1.18	1.4600	1 675	99.2

^a. At 70°C .

90, 100, 105, and 110°C for POCl₃ + 4-isopropylphenol. In both the cases the esterification kinetics was measured in the homogeneous system, open with regard to the hydrogen chloride released in the reaction. The esterification was realized as the following system of consecutive reactions:



Presuming that the reaction is of the first order with respect to each of the reacting components, this system of consecutive reactions can be described by the following set of 5 differential equations:

$$-dC_I/dt = k_1C_1C_{II} + k_2C_1C_{III} + k_3C_1C_V \quad (1)$$

$$-dC_{II}/dt = k_1C_1C_{II} \quad (2)$$

$$dC_{III}/dt = k_1C_1C_{II} - k_2C_1C_{III} \quad (3)$$

$$dC_V/dt = k_2C_1C_{III} - k_3C_1C_V \quad (4)$$

$$dC_{VI}/dt = k_3C_1C_V, \quad (5)$$

where *I* means alkylphenol (2- and 4-isopropylphenols), *III* means monoalkylphenyl dichlorophosphate, *V* is di(alkylphenyl) monochlorophosphate, and *VI* is tri(alkylphenyl) phosphate.

In the previous paper⁶ it was shown that the system is best described by this set of differential equations if the coefficients at the concentration terms in Eqs (1) through (5) are equal to 1, i.e., all the equations are of the second order. These data valid for phenol were now tested also for the monoalkylphenols by means of the values of dispersion and mean deviations. The results are presented in Table II.

From Table II it can be seen that the values of dispersion concentrations and mean deviations are even more convincing than in the case of phenol as the evidence that the values of exponents at the concentration terms in Eqs (1) through (5) are equal to 1.

TABLE II

Values of dispersion and mean deviations of the calculated and experimental values for various exponents at the concentration terms in Eqs (I)–(J) at the temperature of 110°C

Exponents	Dispersion		Mean deviation	
	2-IPP	4-IPP	2-IPP	4-IPP
$C_I^0 C_{II}^1$	0.124	0.028	0.353	0.169
$C_I^1 C_{II}^1$	0.006	0.017	0.080	0.131
$C_I^1 C_{II}^2$	0.071	0.027	0.266	0.166
$C_I^2 C_{II}^1$	0.076	0.031	0.277	0.177

TABLE III

Rate constant values of esterification of 2-isopropylphenol with $POCl_3$

Temperature °C	Rate constants, $dm^3 mol^{-1} s^{-1}$		
	$k_1 \cdot 10^{-6}$	$k_2 \cdot 10^{-6}$	$k_3 \cdot 10^{-6}$
110	8.61	3.88	2.22
115	15.6	8.58	3.05
125	20.8	13.6	10.3
160	24.2	20.8	19.4

TABLE IV

Rate constant values of esterification of 4-isopropylphenol with $POCl_3$

Temperature °C	Rate constants, $dm^3 mol^{-1} s^{-1}$		
	$k_1 \cdot 10^{-5}$	$k_2 \cdot 10^{-5}$	$k_3 \cdot 10^{-5}$
90	2.88	1.86	0.55
100	4.44	3.36	1.66
105	4.83	4.75	3.36
110	6.00	5.30	4.16

The rate constants were calculated by solving the system in the form (1)–(5) and are presented in Tables III and IV for 2- and 4-isopropylphenols, respectively. These tables show that the esterification rates of POCl_3 with 2- and 4-isopropylphenols are distinctly different. They are best compared at the temperature of 110°C at which

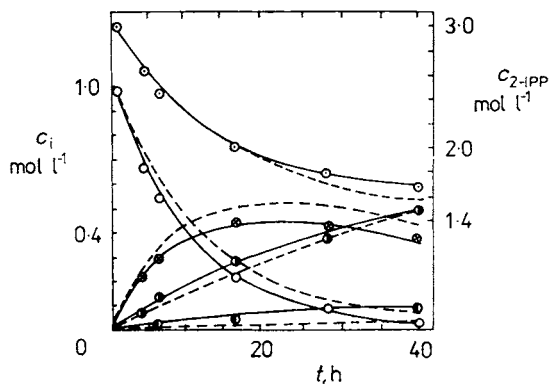


FIG. 1

Composition of reaction mixture during esterification of 2-isopropylphenol with POCl_3 at the temperature of 110°C . Points and solid curves represent experimental values, dashed curves represent the values calculated. 1, 1' \circ 2-IPP, 2, 2' \circ POCl_3 , 3, 3' \otimes POCl_2 (2-IPP), 4, 4' \bullet POCl (2-IPP) $_2$, 5, 5' \bullet PO (2-IPP) $_3$

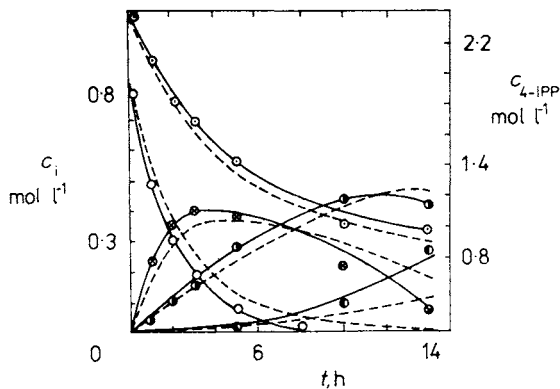


FIG. 2

Composition of reaction mixture during esterification of 4-isopropylphenol with POCl_3 at the temperature of 110°C . Points and solid curves represent experimental values, dashed curves represent the values calculated. 1, 1' \circ 4-IPP, 2, 2' \circ POCl_3 , 3, 3' \otimes POCl_2 (4-IPP), 4, 4' \bullet POCl (4-IPP) $_2$, 5, 5' \bullet PO (4-IPP) $_3$

the esterification kinetics was measured for both the isomers. Whereas k_1 (i.e. the rate of replacement of the first chlorine in POCl_3) is approximately seven times greater with 4-isopropylphenol, k_3 (the replacement of the last chlorine in POCl_3 to give triaryl phosphate) is 20 times greater with this isomer.

These results agree well with theoretical predictions, since the esterification is affected by steric hindrance and the substitution of chlorine by 2-isopropylphenol is substantially retarded as compared with the reaction of unsubstituted phenol. The steric hindrance cannot operate in the esterification with 4-isopropylphenol, on the contrary, this reaction is accelerated (as compared with that of phenol) by the inductive effect of alkyl substituent in accordance with the correlation theory (LFER) by Hammett¹⁰.

TABLE V
Activation energies of esterification of 2- and 4-isopropylphenols with POCl_3

Rate constant	Activation energy, kJ mol^{-1}	
	2-IPP	4-IPP
k_1	60.53	40.96
k_2	96.3	62.7
k_3	142.49	119.25

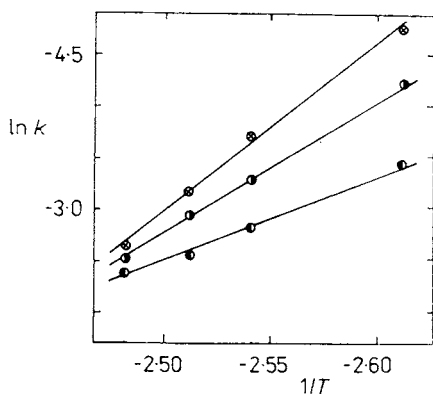


FIG. 3

Temperature dependence of esterification rate constants of 2-isopropylphenol with POCl_3 . \circ k_1 , \bullet k_2 , \ominus k_3

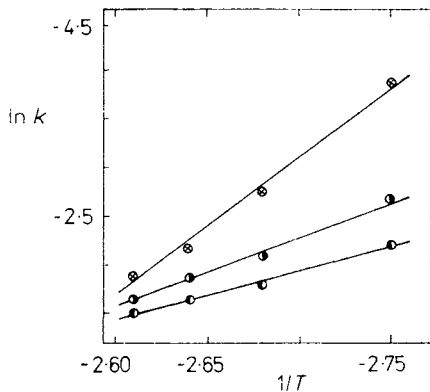


FIG. 4

Temperature dependence of esterification rate constants of 4-isopropylphenol with POCl_3 . \circ k_1 , \bullet k_2 , \ominus k_3

Figure 1 presents the dependence of composition of the esterification mixture ($\text{POCl}_3 + 2\text{-isopropylphenol}$) experimentally found at 110°C along with that calculated by solving the set of differential equations (1)–(5). The differences between these theoretical and experimental values are due to experimental error (relatively complicated analytical methods), non-ideality of the system (a diffusion process due to the hydrogen chloride released), and the approximation of the relations (1)–(5) to a real system. Obviously, zero concentrations of all components of the reaction mixture according to the relations (1)–(5) are not attained until after infinite time interval, nevertheless, it can be stated that the set of differential equations given describes the reaction system relatively well.

Figure 2 presents the time course of the esterification with POCl_3 and 4-isopropylphenol; it can be seen that this reaction is much faster than that with 2-isopropylphenol.

The temperature dependences of the rate constants measured are given in Figs 3 and 4. These dependences were treated by the least squares treatment to estimate the activation energies for the individual rate constants given in Table V. From the activation energy values obtained it follows that they gradually increase in the consecutive reactions (A)–(B)–(C), which agrees with theory.

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