ESTERIFICATION KINETICS OF PHENOL WITH PHOSPHORYL TRICHLORIDE

Miroslav MAGURA[a], Ján VOJTKO[b], Eva ZEMANOVÁ[a], Alexander KASZONYI[b] and Ján ILAVSKÝ[b]

[a]*Chemko, 072 22 Strážske and*
[b] *Department of Organic Technology,*
Slovak Technical University, 812 37 Bratislava

Received March 24, 1988
Accepted May 16, 1988

The liquid-phase esterification kinetics of phenol with $POCl_3$ has been studied at isothermal conditions within the temperature interval from 90 to 110°C. The esterification rate constants of the first, second, and third esterification steps and the activation energies of these steps have been calculated. The given system of competitive consecutive reactions can be described by a system of differential equations which has been solved by the Gauss–Newton optimization method of non-linear regression in the Marquardt modification. In the sequence of the first, second, and third step the esterification rate constants have been found to gradually decrease, whereas the activation energies increase in the same sequence.

Triphenyl phosphate is used commercially as an incombustible plasticizer and combustion retarder for polymers, especially PVC. The formation of triphenyl phosphate from phenol and phosphorus or phosphoryl chlorides has been long known[1–3]. On the other hand, data about the kinetics of this process are not available because of the relative complexity of the consecutive reactions of formation of triphenyl phosphate.

At present, triphenyl phosphate is produced usually by the reaction of phenol with phosphoryl trichloride according to the summary reaction[4]

$$3\,C_6H_5OH + POCl_3 \rightarrow (C_6H_5O)_3PO + 3\,HCl \qquad (A)$$

however, instead of pure phenol its mixture with alkylphenols is used for the esterification.

The aim of this present communication was the kinetic measurement of the esterification of pure phenol to give triphenyl phosphate in liqud phase at the conditions of the open system with respect to hydrogen chloride. The intermediates (i.e. monophenyl- and diphenyl-derivatives $C_6H_5OPOCl_2$ and $(C_6H_5O)_2POCl$) were determined by a method developed for this purpose and described elsewhere[5]. The esterification rate constants were calculated by means of the Gauss–Newton method of non-linear regression in the Marquardt modification.

EXPERIMENTAL

Reagents

Phenol of p.a. purity grade, $POCl_3$ prepared in Chemko Strážske by oxidation of PCl_3 (Chemie-Kombinat, Bitterfeld, G.D.R.), *o*-xylene of p.a. purity grade, 2-ethylhexanol of p.a. purity grade, octadecane of p.a. purity grade (Lachema Bratislava).

Apparatus and Methods

The esterification reactor consisted of a three-necked flask equipped with a thermometer, reflux condenser, and inlet of nitrogen gas. The reflux condenser consisted of two parts, the upper part serving for the removal of gaseous hydrogen chloride which passed through a system of washing bottles filled with NaOH.

The whole reactor was immersed in an oil thermostat which allowed to maintain the temperature chosen with the accuracy of $\pm 0{\cdot}2°C$. The reaction mixture was stirred by means of a magnetic stirrer.

Before the measurement the reactor was charged with phenol, catalyst ($MgCl_2$), and *o*-xylene as an inert solvent. This mixture was heated to the reaction temperature, and $POCl_3$ was rapidly added under the surface from a funnel. The composition of the mixture was followed by withdrawing 0·5 cm^3 samples of the reaction mixture at chosen time intervals. The samples were rapidly cooled to −18°C to practically stop the reaction. Before the analysis the reaction mixture was allowed to react with excess 2-ethylhexanol at 80°C for 2 h in a microreactor. The alcohol reacts substantially faster than phenol and converts the unreacted $POCl_3$ and the intermediate monochloride and dichloride into the corresponding ester or mixed esters:

$$POCl_3 + 3\,C_8H_{17}OH \rightarrow (C_8H_{17}O)_3PO + 3\,HCl \qquad (B)$$

$$C_6H_5OPOCl_2 + 2\,C_8H_{17}OH \rightarrow C_6H_5OPO(OC_8H_{17})_2 + 2\,HCl \qquad (C)$$

$$(C_6H_5O)_2POCl + C_8H_{17}OH \rightarrow (C_6H_5O)_2PO(OC_8H_{17}) + HCl \qquad (D)$$

The mixture modified in this way could be analyzed by means of gas chromatography using a CHROM 5 apparatus (Laboratorní přístroje, Prague) equipped with a flame ionization detector. The chromatography was evaluated quantitatively by means of an automatic integrator Computing CI-100. The chromatography was carried out in a glass column of 1·25 m length and 3 mm inner diameter, packed with 5% OV 225 on Chromosorb, the temperature was increased from 100 to 260°C at the rate of 6°C per min, and the following carrier gases were used (flow-rate in $cm^3\,min^{-1}$): nitrogen (20), hydrogen (30), air (500). The quantitative evaluation was carried out by the method of internal standard (octadecane).

The orientation measurements of the reaction course were based on determination of reactive chlorine atoms in the reaction mixture (argentometry).

A possible escape of $POCl_3$ from the reaction mixture was monitored by determination of phosphorus in the washing bottles by the colourimetric method after mineralization.

RESULTS AND DISCUSSION

The initial composition of the reaction mixture: phenol 2·6542 mol dm^{-3}, $POCl_3$ 0·8912 mol dm^{-3} (molar ratio phenol:$POCl_3$ = 3 : 1), $MgCl_2$ 0·0237 mol dm^{-3}, xylene 5·5072 mol dm^{-3}. The composition changes with time were followed at the temperatures of 90, 95, 100, and 110°C (Tables I–IV) by independent analyses of the individual components. The phenyl phosphates are formed by the following reactions:

$$C_6H_5OH + POCl_3 \xrightarrow{k_1} C_6H_5OPOCl_2 + HCl \tag{E}$$

$$C_6H_5OH + C_6H_5OPOCl_2 \xrightarrow{k_2} (C_6H_5O)_2POCl + HCl \tag{F}$$

$$C_6H_5OH + (C_6H_5O)_2POCl \xrightarrow{k_3} (C_6H_5O)_3PO + HCl \tag{G}$$

where k_1, k_2, and k_3 are the esterification rate constants of $POCl_3$ to the first, second and third degree, respectively.

For the conditions of a batch reactor, this system is described by a set of five differential kinetic equations:

$$r_1 = -dC_A/dt = k_1C_A^XC_B^Y + k_2C_A^XC_R^Y + k_3C_A^XC_S^Y \tag{1}$$

$$r_2 = -dC_B/dt = k_1C_A^XC_B^Y \tag{2}$$

$$r_3 = dC_R/dt = k_1C_A^XC_B^Y - k_2C_A^XC_R^Y \tag{3}$$

$$r_4 = dC_S/dt = k_2C_A^XC_R^Y - k_3C_A^XC_S^Y \tag{4}$$

$$r_5 = dC_T/dt = k_3C_A^XC_S^Y\,, \tag{5}$$

where C_A means the phenol concentration, C_B is $POCl_3$ concentration, and C_R, C_S, and C_T denote the concentrations of the esters $C_6H_5OPOCl_2$, $(C_6H_5O)_2POCl$, and $(C_6H_5O)_3PO$, respectively.

The equations (*1*) through (*5*) represent a simultaneous system of five differential equations with three unknowns and with two degrees of freedom which can serve for increasing the accuracy of the results and for their correlation.

Esterifications are generally known to be reversible reactions of the second order[6]. As, however, in the above-given arrangement hydrogen chloride escapes from the reaction mixture, the esterifications of $POCl_3$ with phenol become irreversible.

In order to confirm the presumed validity of the kinetic relations of the second order, the experimental results were evaluated for four versions of calculations, viz: (i) In Eqs (*1*) through (*5*) zero was introduced for X and 1 for Y (formally the first order equations), (ii) in Eqs (1)–(5) it was $X = 1$ and $Y = 1$ (formally the second order equations), (iii) in Eqs (*1*)–(*5*) it was $X = 1$ and $Y = 2$ (formally the third order equations), (iv) in Eqs (*1*)–(*5*) it was $X = 2$ and $Y = 1$ (formally the third order equations). The method of non-linear regression was used to find the dispersions of concetrations and the mean deviations of the measured and calculated values (Table V).

TABLE I

The concentration (mol dm^{-3}) changes of the individual reaction components during the esterification of $POCl_3$ with phenol at 90°C

Time h	C_6H_5OH	$POCl_3$	$C_6H_5OPOCl_2$	$(C_6H_5O)_2POCl$	$(C_6H_5O)_3PO$
0	2·654	0·891	0·000	0·000	0·000
1·5	2·610	0·668	0·150	0·024	0·000
2	2·507	0·535	0·248	0·058	0·000
3	2·467	0·488	0·276	0·077	0·000
4	2·386	0·392	0·346	0·095	0·009
5	2·236	0·223	0·445	0·161	0·013
6	2·142	0·148	0·463	0·165	0·036
7	2·073	0·111	0·427	0·263	0·040
10	1·968	0·079	0·365	0·307	0·090
12	1·886	0·048	0·298	0·400	0·095
16	1·671	0·011	0·187	0·380	0·264
20	1·589	0·000	0·144	0·364	0·334
24	1·499	0·000	0·094	0·316	0·432

TABLE II

The concentration (mol dm^{-3}) changes of the individual reaction components during the esterification of $POCl_3$ with phenol at 95°C

Time h	C_6H_5OH	$POCl_3$	$C_6H_5OPOCl_2$	$(C_6H_5O)_2POCl$	$(C_6H_5O)_3PO$
0	2·688	0·761	0·000	0·000	0·000
0·5	2·632	0·676	0·081	0·003	0·000
1	2·520	0·510	0·238	0·013	0·000
1·5	2·234	0·097	0·408	0·055	0·000
2	2·162	0·033	0·478	0·100	0·000
2·5	2·152	0·020	0·531	0·110	0·000
4	2·003	0·004	0·425	0·316	0·014
6	1·829	0·003	0·226	0·428	0·103
8	1·663	0·003	0·075	0·454	0·228
10	1·562	0·000	0·012	0·425	0·324
15	1·532	0·000	0·004	0·390	0·366

The smallest dispersion values as well as the smallest deviation of the measured and calculated values were obtained in the case where the exponents at the concentra-

TABLE III

The concentration (mol dm^{-3}) changes of the individual reaction components during the esterification of $POCl_3$ with phenol at 100°C

Time h	C_6H_5OH	$POCl_3$	$(C_6H_5O)POCl_2$	$(C_6H_5O)_2POCl$	$(C_6H_5O)_3PO$
0	2·654	0·890	0·000	0·000	0·000
1	2·400	0·543	0·265	0·065	0·011
1·5	2·213	0·292	0·480	0·104	0·011
2	2·114	0·139	0·612	0·123	0·013
4	1·878	0·049	0·406	0·409	0·019
5	1·666	0·006	0·192	0·618	0·068
6	1·544	0·004	0·062	0·694	0·128
7	1·473	0·000	0·023	0·654	0·208
8	1·416	0·000	0·007	0·593	0·285
9	1·334	0·000	0·005	0·457	0·422
10	1·245	0·000	0·001	0·324	0·559
15	1·131	0·000	0·000	0·140	0·745

TABLE IV

The concentration (mol dm^{-3}) changes of the individual reaction components during the esterification of $POCl_3$ with phenol at 110°C

Time h	C_6H_5OH	$POCl_3$	$C_6H_5OPOCl_2$	$(C_6H_5O)_2POCl$	$(C_6H_5O)_3PO$
0	2·469	0·919	0·000	0·000	0·000
0·5	2·172	0·545	0·271	0·103	0·000
1	2·095	0·457	0·355	0·113	0·012
1·5	1·895	0·274	0·402	0·206	0·036
2	1·847	0·197	0·481	0·202	0·037
2·5	1·756	0·098	0·551	0·215	0·055
3	1·694	0·037	0·576	0·245	0·060
4	1·481	0·016	0·275	0·554	0·072
5	1·275	0·013	0·105	0·560	0·240
6	1·216	0·006	0·085	0·523	0·304
7	1·035	0·004	0·022	0·357	0·535
8	0·931	0·000	0·000	0·246	0·672

tions of phenol and phosphoryl trichloride were equal to one, which confirms the presumption of the esterification being a second order reaction. Therefore, in the subsequent evaluation of the experimental results the set of differential equations (*1*) through (*5*) was solved for the value 1 in all the exponents at the concentration terms. Table VI gives the rate constants obtained by solving Eqs (*1*)—(*5*) by means of the Gauss–Newton method in the Marquardt modification using an SM 30 computer.

From the absolute values of the rate constants it is seen that the esterification to the first degree proceeds as the easiest step (the substitution of the first chlorine atom in the $POCl_3$ molecule is the easiest one also from the sterical point of view), the sub-

TABLE V

Determination of the minimum deviation of the measured concentratin data from the calculated ones in the esterification of $POCl_3$ with phenol

Values of exponents in Eqs (*1*) through (*5*)		Dispersions of concentrations	Mean differences between the measured and calculated concentration values, mol dm^{-3}
X	Y		
0	1	0·021	0·147
1	1	0·020	0·141
2	1	0·045	0·214
1	2	0·048	0·235

TABLE VI

The calculated rate constants and activation energies of the esterification of $POCl_3$ with phenol

Temperature °C	Rate constants, dm^3 mol^{-1} h^{-1}					
	k_1	error in k_1	k_2	error in k_2	k_3	error in k_3
90	0·055	0·005	0·035	0·003	0·013	0·002
95	0·092	0·003	0·058	0·001	0·015	0·001
100	0·135	0·011	0·083	0·004	0·048	0·001
110	0·240	0·030	0·167	0·020	0·087	0·015
Activation energy kJ mol^{-1}	84·1		89·3		119·6	

stituion of the second chlorine atom being slower and that of the third Cl atom (with formation of the triphenyl phosphate required) is the slowest.

Fig. 1 presents the values of the measured and calculated concentrations values of all components of the reaction mixture at the temperature of 95°C, and the agreement between these measured and calculated values can be denoted as acceptable, hence the equation set (*1*) through (*5*) approximately reflects the behaviour of the phenol–$POCl_3$ system during the esterification.

The deviation of the experimental values from the theoretical ones can be explained by the errors of the (exacting) analyses of the reaction mixture as well as by the fact that the reaction system represents an open system with respect to escape of hydrogen chloride (i.e. the kinetics of the liquid-phase process can be partially affected by the diffusion of the hydrogen chloride escaping from the reaction mixture). Another source of deviations of the measured values from the calculated ones consists in the fact that the values calculated theoretically from Eqs (*1*)–(*5*) reach zero concentration values only after an infinitely long time, whereas in the experimental measurements these values are reached after relatively short reaction time.

The values k_1, k_2, and k_3 given in Table VI were used for the calculation of the activation energies of the esterifications to the first, second, and third degrees by the method of linear regression; these activation energies are also presented in Table VI. The temperature dependence of the rate constants is given in Fig. 2.

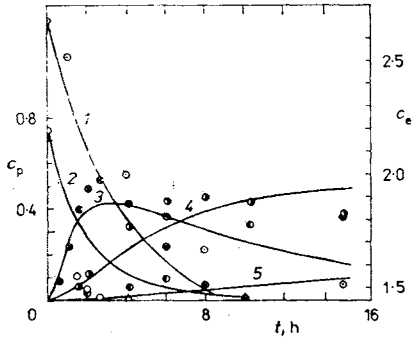

FIG. 1

Composition of reaction mixture in esterification of phenol with $POCl_3$ at 95°C. The points represent the experimental values, the curves give the calculated values. *1*, ⊙ phenol, *2*, ○ $POCl_3$, *3*, ⊗ $C_6H_5OPOCl_2$, *4*, ◑ $(C_6H_5O)_2POCl$, *5*, ◐ $(C_6H_5O)_3PO$. c_p the phenol concentration, c_e concentrations of the other components

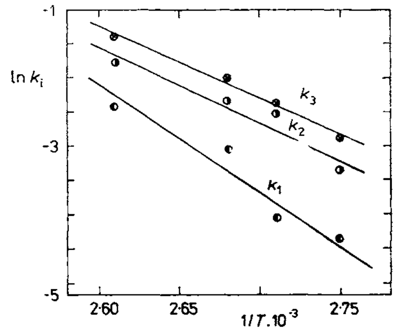

FIG. 2

Temperature dependence of rate constants

REFERENCES

1. Hempel A.: U.S. 1 840 335 (1932).
2. FMC Corp.: U.S. 3 077 491 (1963).
3. Genet R. M.: U.S. 3 553 155 (1971).
4. Perry J. H.: *Chemical Engineers Handbook*. McGraw-Hill, London 1963.
5. Magura M., Zemanová E., Vojtko J.: Chem. Prum. *38*, (1988).
6. Lebedev N. N.: *Chemia a technologia základných organických a petrochemických syntéz*, p. 227. Alfa, Bratislava 1979.

Translated by J. Panchartek.