

# The Synthesis of Alkyl Phosphates for fibres Antistatic Treatment. Mathematical Modelling of the Process

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## ABSTRACT

The alkyl phosphates synthesis for the realisation of fibres antistatic substances, is carried out by phosphatising fatty saturated alcohols (fraction  $C_{16}$ - $C_{18}$ ) with  $POCl_3$  or  $PCl_3$ . The reaction is conducted in a semicontinuous reactor. The non-isothermal thermokinetic method is used for the kinetic study. An original reaction cell and electronic dispositive are used for the kinetic curves registration. A second order reaction for the phosphatising process is established by thermokinetic curves processing. The activation energy and frequency factor are determined.

## Key Words

alkyl phosphates, fibres antistatic treatment, phosphatising reactor, process kinetic, activation energy, frequency factor.

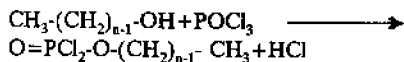
## INTRODUCTION

The preparation products which improve the mechanical, electrical and surface-active properties of fibres, are of great importance during the obtaining and processing of chemical yarns and fibres [1].

Good antistatic properties of the fibres are given by preparation products based on

phosphorus compounds [2-5]. Some of these products based on alkyl phosphates are obtained by phosphatising fatty natural alcohols (fraction  $C_{16}$ - $C_{18}$ ) with  $POCl_3$ , followed by the partial neutralisation of the generated hydrochloric acid and the neutralisation of the mono and diphosphoric esters.

The obtaining of alkyl phosphates is the most important stage from the kinetic point of view in the synthesis of preparation products:



In order to elaborate a mathematical model and to optimise the process, the kinetic parameters of the reaction are required.

Obtaining the kinetic curves and evaluating the rate constants at different temperatures by common kinetic methods are rather difficult for the present reaction. Thus, if the chemical method for analysing the reaction medium is adopted, it is necessary to work with large samples and conditions in which, because of the great reaction heat [6], the reaction temperature cannot be controlled, having a variation of decimal of degrees.

When the evaluation of the kinetic parameters is made from the measurements of the hydrochloric acid volume produced by the reaction, for constant volume and temperature conditions, working with small samples in order to control the temperature, the difficulties appear because of the great hydrochloric acid retention in the reaction mass due to the reaction products polarity and the reaction medium viscosity. In addition, because of the rapidity of the reaction (it is essentially completed in 3-4 minutes), the removal of the samples from the system and their analysis are not practical.

These are the reasons that, in order to evaluate the kinetic parameters, the thermokinetic methods are preferred, using the automatic recording of the kinetic curves.

## EXPERIMENTAL

A thermistor was used as temperature sensor and an automatic recorder y-t, was used for the automatic recording of the thermokinetic curves. When using a thermistor for temperature recording the advantages are the great precision (almost  $10^{-4}$  degrees) and a quick answer to the

temperature variations (because of the thermistor's very small heat capacity).

The reaction cell, (adiabatic reactor), presented in Figure 1, is made of glass. The thermistor is affixed to the bottom of the ampulla with the epoxy resin in which the aluminium powder was enclosed, in order to make possible a good thermic contact. The reaction cell was isolated from the external medium and enclosed in

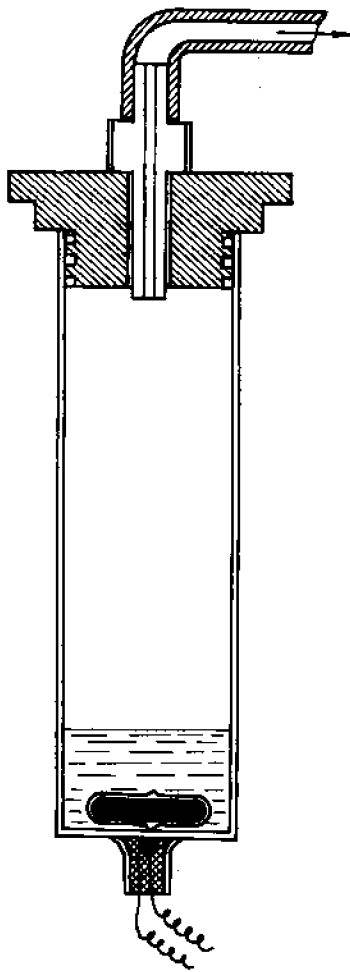


Fig 1. The reaction cell

a polyvinyl chloride recipient, both for the calibrating of the thermistor and for the thermokinetic curves registration.

The thermistor was installed in one of the bridge's branch having a parallel shunt with a resistor for the linearisation of the temperature scale. A stabilised current was supplied to the bridge, and the equilibrium bridge control was made with an electronic millivoltmeter.

The non-equilibrium current of the bridge due to the temperature variation in the reaction vessel was recorded as a function of time with a potentiometric recorder y-t, type ENDIM 621-02.

Using this electronic connection, temperature variations of  $2 \cdot 10^{-4}$  degrees can be approached, but for the given case the measurement precision of about  $\pm 10^{-2}$  degrees was sufficient, because the temperature range used in the kinetic studies was of 8-14 degrees.

For a temperature range of 20-35 degrees, the realised electronic thermometer presents a good linearity, the linearity deviations are under 1%.

The chart speed was of 24 mm/min, sufficient for a time evaluation within 1% precision.

## RESULTS AND DISCUSSION

From the practical point of view the phosphatising reaction of technical alcohols with  $\text{POCl}_3$  is interesting. A series of preliminary tests made with pure alcohols (ethanol, decyl-alcohol and dodecyl-alcohol) and with technical alcohols (fraction  $\text{C}_{12}\text{-C}_{18}$ ), have pointed out different kinetic behaviours, connected with the alcohol molecular weight. The same studies indicated that technical alcohols have almost the same kinetic behaviour with dodecyl alcohol in the phosphatising reaction with  $\text{POCl}_3$ . This is the reason why dodecyl alcohol was used when the reaction order was determined.

### The Reaction Order Evaluation

In order to determine the reaction order, the half-reaction time method was used, with

applicability in the case in which the kinetic equation of the reaction is:

$$V = - \frac{dC_R}{dt} = k C_R^n \quad (1)$$

Where:

$C_R$  - reaction concentration at the arbitrary time

$n$  - reaction order

$k$  - rate constant

Considering reactions with two reactants, for which the kinetic equation is:

$$V = - \frac{dC_{R1}}{dt} = k C_{R1}^a C_{R2}^b \quad (2)$$

If the concentrations of the two reactants are equal  $C_{R1} = C_{R2} = C_R$ , equation (2) is reduced to equation (1), and the reaction order is  $n = a+b$ .

Integration of equation (1) results in:

$$\frac{1}{n-1} \left( \frac{1}{C_R} \right)^{n-1} - \left( \frac{1}{C_{OR}} \right)^{n-1} = kt \quad (3)$$

where  $C_{OR}$  is reactant concentration at the initial time.

Considering the half-reaction time definition, we obtain from equation (3):

$$\tau_{1/2} = \frac{2^{n-1} - 1}{(n-1)k} \frac{1}{C_{OR}^{n-1}} \quad (4)$$

For a given reaction taking place at constant temperature the reaction order and the rate constant are constant and equation (4) can be simplified in the following form:

$$\tau_{1/2} = \frac{\text{const}}{C_{OR}^{n-1}} \quad (5)$$

The half time of reaction can be evaluated from the kinetic curve,  $C_R = f(\tau)$ , considering different reactant concentration values, and determining the time for which the half concentration value is obtained. Thus, the initial reactant concentration can be replaced by the momentary concentration in equation (5).

$$\tau_{1/2} = \frac{\text{const}}{C_R^{n-1}} \quad (6)$$

The thermokinetic curve  $T = f(\tau)$  can be

used instead the kinetic curve for the evaluation of the half time, because the reaction's medium temperature increase is proportional with the reactant's concentration decrease.

The reactant concentration at a given time can be expressed by the following relation, considering the direct proportionality between the reactant's concentration decrease and the reaction's medium temperature:

$$C_R = \frac{K}{V\Delta_R H} (T_\infty - T) \quad (7)$$

in which:

$\Delta_R H$  - reaction heat effect (J/mol)

$V$  - reaction mixture volume

$K$  - the heat capacity of reaction system

$T$  - time function of temperature

$T_\infty$  - the temperature at end of the reaction

The half time expression, considering equation (7), becomes:

$$\tau_{1/2} = \text{const.} \left( \frac{\Delta_R H \cdot V}{K} \right) \frac{1}{(T_\infty - T)^{n-1}} \quad (8)$$

$$\text{or: } \tau_{1/2} = \frac{\text{const.}}{(T_\infty - T)^{n-1}} \quad (9)$$

For the reaction order evaluation equation (9) is linearised by its logarithmic form:

$$\ln \tau_{1/2} = \text{const.} - (n-1) \ln(T_\infty - T) \quad (10)$$

The obtained data from the thermokinetic curve illustrated in Figure 2, are presented in co-ordinates in  $\tau_{1/2} - \ln(T_\infty - T)$  in Figure 3.

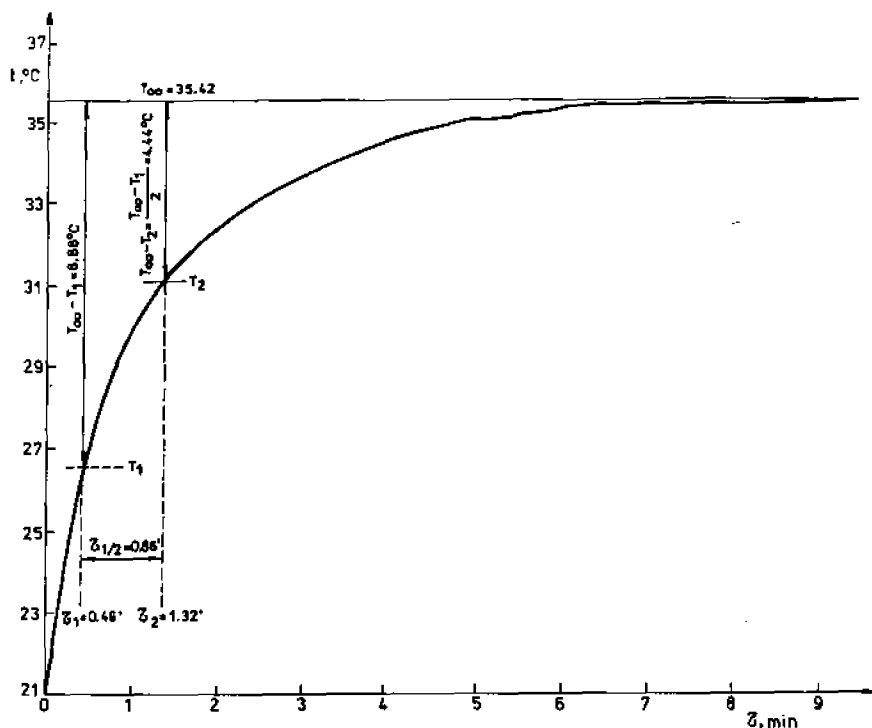


Fig 2. The thermokinetic curve and the half time evaluation for the dodecanol phosphatizing reaction;  $C_0$  ( $\text{POCl}_3$ ) = 3.145 mol/L

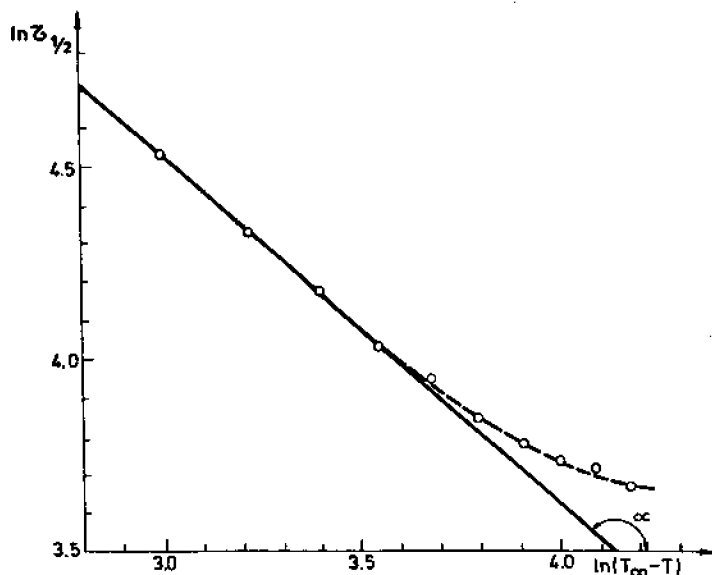


Fig 3. The evaluation of the reaction order

The experimental data do not satisfy equation (10) for the initial times, as it can be observed from the diagram. This probably appears as a consequence of the fact that in this period of time the alcohol is not solubilised and the reaction is heterogeneous.

Considering only the linear part of the curve shown in Figure.3, from the line's slope, the reaction order has the value 1.902. The phosphatising reaction of alcohols with  $\text{POCl}_3$  can be considered as a second order reaction.

#### The Temperature's Influence on the Rate Constant. The Activation Energy Evaluation

Admitting the second order reaction, the differential kinetic equation will be:

$$v = \frac{dx}{dt} = k (C_{0A} - x) (C_{0B} - x) \quad (11)$$

where:

$C_{0A}$  - initial concentration of  $\text{POCl}_3$

$C_{0B}$  - initial concentration of the alcohol

$x$  - number of moles which have reacted in the volume's unity until the arbitrary time

By integration of equation (11) the result is:

$$\ln \frac{C_{0A} - x}{C_{0B} - x} = \ln \frac{C_{0A}}{C_{0B}} + (C_{0A} - C_{0B}) kt \quad (12)$$

Because of the rate constant increase with temperature in nonisothermal conditions, in coordinates  $\ln [(C_{0A} - x)/(C_{0B} - x)]$  and  $t$  instead of a line, a curve with decreasing slope is obtained. By the differentiation of this curve (using the tangents' method), the rate constant can be evaluated at different moments of the reaction and at different temperatures.

By using the thermokinetic curves in order to calculate the temperature dependent rate constant, equation (12) is modified replacing concentration by relative temperatures according to the different moments of reaction. Admitting an excess of  $\text{POCl}_3$  in comparison with the alcohols ( $C_{0A}$ ,  $C_{0B}$ ) and knowing that:

$$C_{0A} = \frac{K(T_{\infty} - T_0)}{V\Delta_R H} \text{ and } C_A = \frac{K(T_{\infty} - T)}{V\Delta_R H} \quad (13)$$

equation (12) becomes:

$$f(T) = \ln \frac{a(T_n - T_0) - (T - T_0)}{T_n - T} = \ln a + C_{0B}(a-1)kr \quad (14)$$

where:

$$a = \frac{C_{0A}}{C_{0B}} = \frac{n_{0A}}{n_{0B}} \text{ represents the molar ratio between}$$

$\text{POCl}_3$  and alcohol at the initial moment of the reaction.

Owing to the variation of the reaction's medium temperature in diagram  $f(T) - \tau$  a curve with a slope which varies slowly with temperature is obtained. That is why the graphical differentiation is not adequate and the secant's method was used for the evaluation of the rate constant. According to this method, the rate constant's value at a given temperature is calculated as follows:

$$k(\bar{T}) = \frac{f(T_n) - f(T_{n-1})}{C_{0B}^{(a-1)} (\tau_n - \tau_{n-1})} \quad (15)$$

where:  $k(\bar{T})$  - is the average rate constant in the temperature range  $(T_n - T_{n-1})$ , and  $- T_n, T_{n-1}$  are the

temperatures of the reaction medium (in relative degrees) at the moment  $\tau_n$  and  $\tau_{n-1}$ , respectively.

Because the considered temperature ranges are very small, the variation of the rate constant with temperature can be approximated as linear. An excess of  $\text{POCl}_3$  was used in order to determine the rate constants depending on temperature. The most concordant results have been obtained by use of a molar ratio of 4:1 or 5:1  $\text{POCl}_3$ /alcohol; that's because the alcohol is solubilised in  $\text{POCl}_3$  in a few seconds, and because only the production of mono-ester is very probable. Data presented in Tables 1 and 2 have been calculated from the thermokinetic curves for these determinations. In these tables:

-  $T$  was calculated as:  $0.2218 N$ ,

-  $N$  - number of divisions read in graphic for the moment

-  $t_n = 20 + 0.2218 N$  is temperature expressed in degrees Celsius

-  $t = \frac{t_{n-1} + t_n}{2}$  is the average temperature's value

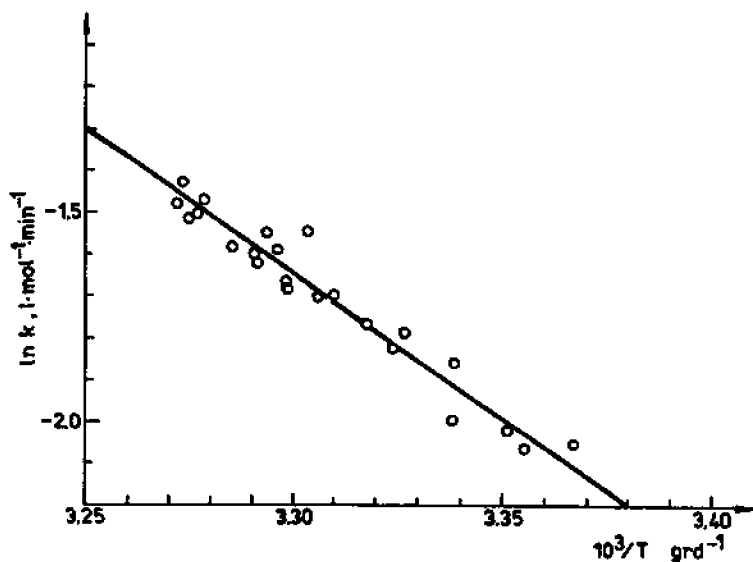
at which the constant is evaluated.

Table 1. The experimental results interpretation for  $a=4$  and  $C_{0B} = 1.509 \text{ mol/L}$

$\tau$ , min	N div.	T rel.deg.	t(°C)	f(T)	t(°C)	k(L.mol <sup>-1</sup> .min <sup>-1</sup> )
0	0	$T_0=0$	24.0	1.3863	-	-
0.25	6.95	1.545	25.54	1.5323	24.77	0.1284
0.50	13.6	3.018	27.02	1.8954	27.60	0.1572
0.75	18.9	4.186	28.19	1.8954	27.60	0.1620
1.00	25.35	5.623	29.62	2.2108	29.18	0.1830
1.25	28.45	6.310	30.31	2.4216	29.97	0.1863
1.50	31.0	6.876	30.88	2.6470	30.54	0.1992
1.75	33.2	7.364	31.36	2.9033	31.12	0.2264
2.00	34.9	7.737	31.74	3.1649	31.56	0.2300
2.25	36.2	8.029	32.03	3.4390	31.90	0.2233
2.50	37.1	8.229	32.23	3.6872	32.13	0.2193
2.75	37.85	8.395	32.34	3.9578	32.31	0.2389
3.0	38.4	8.516	32.52	4.2176	32.43	0.2284
-	40.2	8.916	32.92	-	-	-

**Table 2. The experimental results interpretation for the phosphatising reaction;  $n = 5$ ;  $C_{0B} = 1.326 \text{ mol/L}$**

$\tau$ , min	N div.	T rel.deg.	$t(^{\circ}\text{C})$	$f(T)$	$t(^{\circ}\text{C})$	$k(\text{L}\cdot\text{mol}^{-1}\cdot\text{min}^{-1})$
0	0	$T_0=0$	23.0	1.6094	-	-
0.25	7.05	1.563	24.56	1.7801	23.78	0.1287
0.50	14.70	2.816	25.82	1.9549	25.19	0.1318
0.75	17.3	3.835	26.84	2.1349	26.33	0.1358
1.00	21.7	4.813	27.82	2.3580	27.33	0.1682
1.25	25.1	5.567	28.58	2.5858	28.20	0.1718
1.50	27.9	6.194	29.19	2.8283	28.89	0.1829
1.75	30.3	6.721	29.73	3.1117	29.46	0.2138
2.00	32.0	7.097	30.09	3.3635	29.91	0.1899
2.25	33.25	7.375	30.45	3.6337	30.18	0.2037
2.50	33.60	7.453	30.60	3.9154	30.44	0.2125
2.75	34.25	7.597	30.60	4.1821	30.68	0.2011
	23.3	8.273	-	-	-	-



**Fig.4. The variation of the rate constant with temperature.**

The temperature's influence on the rate constant can be presented by means of Arrhenius' equation, which, linearised by its logarithmic form, is:

$$\ln k = \ln A - \frac{E_a}{R} \frac{1}{T} \quad (17)$$

Experimental data shown in Tables 1 and 2 have been graphically represented in logarithmic - hyperbolic coordinates in Figure 4.

A linear dependence of the experimental data appears in this diagram, within the limit of experimental errors.

Arrhenius equation's coefficients have been calculated by means of the data from Tables 1 and 2, using the smallest square method. The obtained values were:  $E_a = 56.35$  kJ/mol;  $A = 1.015 \times 10^9$  L mol<sup>-1</sup> min<sup>-1</sup>.

## CONCLUSIONS

- The non-isothermal kinetic method was used for the kinetic study of the phosphatising reaction of fatty alcohols with, POCl<sub>3</sub>. A reaction cell provided with a thermistor as temperature sensor and an electronic apparatus was used, making possible the obtaining of a linear dependence between temperature and the registered voltage.

- By data processing of the kinetic curves a second order reaction was found, using the half-time method.

- The optimal experimental conditions were established in order to obtain a good agreement; the best results have been obtained with a great excess of POCl<sub>3</sub>.

- The rate constants depending on temperature have been determined for a temperature range of 22-23 °C.

- Arrhenius equation's coefficients have been evaluated by the smallest squares method, the values  $E_0 = 56.35$  kJ/mol,  $A = 1.015 \times 10^9$  L mol<sup>-1</sup> min<sup>-1</sup> were obtained.

## REFERENCES

- 1 Ehrler P., Sprengmann W., *Chemiefasern Textilindustrie*, 656, Sept. (1981).
- 2 Romanian Patent 85368 (1984).
- 3 Romanian Patent 67013 (1979).
- 4 Romanian Patent 67019 (1979).
- 5 Romanian Patent 86369 (1984).
- 6 Beldie C., Aelenei N., Onu A., Nemtoi Gh., Sandescu F., *Rev.Roumaine Chim.*, 34, 445 (1989).