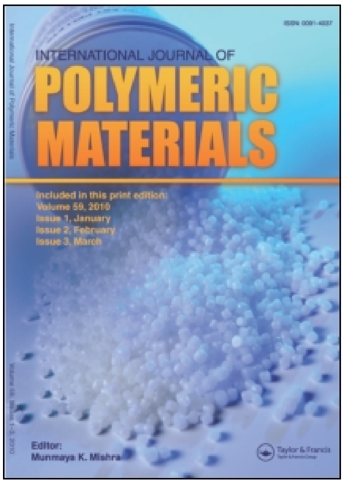

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Kinetics of the Reaction of 2,6-Di-*tert*-Butylphenol with Methyl Acrylate in the Presence of Potassium 2,6-Di-*tert*-Butylphenolate and the Effect of Proton Donor Components on the Reaction Mechanism

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To cite this Article Volod'kin, A. A. , Zaikov, G. E. and Deev, A. S.(1992) 'Kinetics of the Reaction of 2,6-Di-*tert*-Butylphenol with Methyl Acrylate in the Presence of Potassium 2,6-Di-*tert*-Butylphenolate and the Effect of Proton Donor Components on the Reaction Mechanism', International Journal of Polymeric Materials, 16: 1, 121 — 130
To link to this Article: DOI: 10.1080/00914039208035414
URL: http://dx.doi.org/10.1080/00914039208035414

Intern. J. Polymeric Mater., 1992, Vol. 16, pp. 121–130
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Printed in the United Kingdom

Kinetics of the Reaction of 2,6-Di-*tert*-Butylphenol with Methyl Acrylate in the Presence of Potassium 2,6-Di-*tert*-Butylphenolate and the Effect of Proton Donor Components on the Reaction Mechanism

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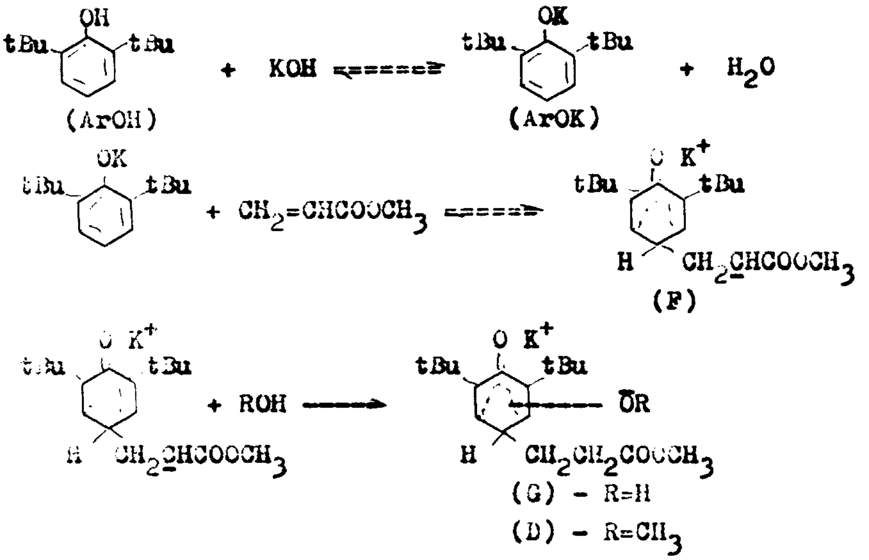
The kinetic scheme of the reaction of 2,6-di-*tert*-butylphenol (ArOH) with methyl acrylate (MA) in the presence of potassium 2,6-di-*tert*-butylphenolate (ArOK) is proposed and elementary constants are calculated for the catalytic steps and the influence of proton donor components ArOH, H_2O and CH_3OH on kinetic regularities is studied. The kinetic scheme contains 30 components and involves 62 rate constants of elementary steps which were computed by the mathematical simulation method of process kinetics using a computer. The comparison was carried out for the computed and experimental data relating to the consumption rate dependence of ArOH on ArOK concentration and the concentration of proton donor components.

KEY WORDS 2,6-di-*tert*-butylphenol, methyl acrylate reaction mechanism.

INTRODUCTION

It has been shown[1] that the kinetic scheme of the reaction of 2,6-di-*tert*-butylphenol (ArOH) with methyl acrylate (MA) in the presence of 2,6-di-*tert*-butylphenolate (ArOK) and an alkali (KOH) satisfactorily describes the mechanism of this reaction involving 14 components and 28 elementary steps. This mechanism is realized in the absence of the solvent (superconcentration solutions) with the participation of ionic pairs and the existence of an interaction step of ArOH with MS is supposed, the participation of water or methanol in stabilization of the intermediate ionic pairs:



Mathematical simulation of the process kinetics (direct task) leads to the set of constants of elementary steps based on data from a wide range of ArOH and KOH concentrations (more than 50%). But qualitative changes of the system's properties of this catalyst of high ArOH content are also revealed. Therefore the kinetic scheme described earlier should be added and changed, to take into account the peculiarities of the reaction between ArOH and MA in the presence of individual ArOK.

THEORETICAL COMPUTATIONS

Computations of the kinetic scheme are provided by a PC 1640HD20 computer using a program for the computation of reaction kinetics based on the solution of "the hard system" of familiar differential equations by Gear's method.[2]

The program involves the notation of the elementary steps, constants, reaction components and their initial concentrations. This allows us to change operatively the number of elementary steps, the rate constants of these steps and the initial concentrations by file reduction (in Norton Commander Programme). Computed data are fixed in the form of the plot expressed kinetics of the consumption of ArOH, MA and accumulation of the methyl ester of β-(4-hydroxy-3,5-di-*tert*-butylphenol) propionic acid (ArAlkOMe). The principle used in the mathematical simulation is "block" optimization of the set of reactions affecting the process kinetics at fixed values of concentration and the content of the catalyst, taking into account data on optimization of the constants of the elementary steps given in Reference 1.

The improved kinetic scheme consists of 30 components and 62 elementary steps which describe the mechanism of the reaction that forms in the process of reagent interaction for the main product and by-products of the reaction: ArOMe, the

TABLE I

The rate constants of the elementary stages of the reaction of 2,6-di-*tert*-butylphenol with methyl acrylate at 116°C (calculated)

Reaction	*k*
1. ArOH + KOH → ArOK + H_2O	3.10^2
2. ArOK + H_2O → ArOH + KOH	10^3
3. ArOK + MA → F	2.5
4. F → ArOK + MA	1
5. F + H_2O → G	40
6. G → ArAlkOME + KOH	5.10^{-2}
7. G + H_2O → ArAlkOMe + KOH.H_2O	6
8. G + KOH → ArAlkOMe + CH_3OK + H_2O	3.10^{-3}
9. KOH.H_2O → KOH + H_2O	10^6
10. KOH + H_2O → KOH.H_2O	6.10^5
11. CH_3OK + H_2O → CH_3OH + KOH	10^6
12. CH_3OH + KOH → CH_3OK + H_2O	10^5
13. ArOH + CH_3OK → ArOK + CH_3OH	5.10^3
14. ArOK + CH_3OH → ArOH + CH_3OK	10^4
15. F + CH_3OH → D	70
16. D + H_2O → ArAlkOMe + KOH + CH_3OH	6.10^{-1}
17. D + CH_3OH → ArAlkOMe + $CH_3OH.CH_3OK$	6.10^{-1}
18. D + CH_3OH + CH_3OH → ArAlkOMe + $CH_3OH.CH_3OH.CH_3OK$	10^5
19. D + $CH_3OH.CH_3OH.CH_3OK$ → ArAlkOMe + 2.$CH_3OH.CH_3OK$	2.10^{-2}
20. $CH_3OH.CH_3OH.CH_3OK$ → $CH_3OH.CH_3OK$ + CH_3OH	7.10^{-3}
21. $CH_3OH.CH_3OK$ → CH_3OK + CH_3OH	10^{-3}
22. CH_3OK + CH_3OH → $CH_3OH.CH_3OK$	50
23. D → ArAlkOMe + CH_3OK	10^{-1}
24. F + $CH_3OH.CH_3OH.CH_3OK$ → ArAlkOMe + CH_3OK + $CH_3OH.CH_3OK$	10^{-4}
25. KOH.H_2O + H_2O → KOH.2H_2O	5.10^4
26. KOH.2H_2O → KOH.H_2O + H_2O	10^4
27. KOH.2H_2O + H_2O → KOH.3H_2O	7.10^4
28. KOH.3H_2O → KOH.2H_2O + H_2O	10^4
29. MA + KOH → $CH_2{=}CHCOOK$ (MAK) + CH_3OH	10^{-1}
30. MA + KOH.H_2O → MAK + CH_3OH + H_2O	10^{-1}
31. MA + KOH.2H_2O → MAK + CH_3OH + 2.H_2O	1.5
32. MA + KOH.3H_2O → MAK + CH_3OH + 3.H_2O	50
33. 2.H_2O → H_2O +H_2O	10^7
34. H_2O + H_2O → 2.H_2O	10^7
35. 3.H_2O → 2.H_2O + H_2O	10^7
36. 2.H_2O + H_2O → 3.H_2O	10^7
37. ArAlkOMe + KOH → ArAlkOK + CH_3OH	10^{-1}
38. ArAlkOMe + KOH.H_2O → ArAlkOK + CH_3OH + H_2O	1
39. ArAlkOMe + KOH.2H_2O → ArAlkOK + CH_3OH + 2.H_2O	2
40. ArAlkOMe + KOH.3H_2O → ArAlkOK + CH_3OH + 3.H_2O	10^2
41. F + MA → F.MA	2.10^{-1}
42. F.MA → F + MA	4.10^{-2}
43. F.MA + ArOH → ArAlk$(OMe)_2$ + ArOK	3.10^{-4}
44. F + ArOH → GG	8.10^{-2}
45. GG → F + ArOH	10^{-3}
46. GG → ArAlkOMe + ArOK	4.10^{-2}
47. GG → ArOCH_3 + ArAlkOK	5.10^{-5}
48. ArOK + ArOK → D.ArOK	10^2
49. D.ArOK → ArOK + ArOK	10^2
50. D.ArOK → ArOK.ArO—K + ArOK	15
51. ArOK.ArO—K → D.ArOK	5

TABLE I (*continued*)

Reaction	*k*
52. $ArOK.ArO{-}K \rightarrow ArOK.ArO^- + K^+$	5.10^{-2}
53. $MA + MA + K^+ \rightarrow MA.MA.K^+$	2.10^3
54. $D.ArOK + ArOK \rightarrow T.ArOK$	10^3
55. $T.ArOK \rightarrow D.ArOK + ArOK$	10^{-5}
56. $MA.MA.K^+ + MA + H_2O \rightarrow$ polymer	10^5
57. $D.ArOK + H_2O \rightarrow ArOK + KOH + ArOH$	10^{-1}
58. $T.ArOK + H_2O \rightarrow D.ArOK + KOH + ArOH$	10^{-1}
59. $D.ArOK + CH_3OH \rightarrow ArOK + CH_3OK + ArOH$	10^{-1}
60. $T.ArOK + CH_3OH \rightarrow D.ArOK + CH_3OK + ArOH$	10
61. $T.ArOK + CH_3OH + CH_3OH \rightarrow D.ArOK + ArOH + CH_3OH.CH_3OK$	10^4
62. $CH_3OH.CH_3OK + CH_3OH \rightarrow CH_3OH.CH_3OH.CH_3OK$	10^3

product of the condensation by the Michaelis reaction $ARAlk(OMe)_2$, β-(4-hydroxy-3,5-di-*tert*-butyl) potassium propionate (ArAlkOK), potassium acrylate (MAK) and also the intermediate complexes that form as a result of the interaction of the complex F with ArOH (GG), the interaction of the complex F with MA (F, MA) and the interaction of the complex F with methanol (D) (see Table I).

As compared with the proceeding scheme,[1] the kinetic scheme proposed is added by the step of ArAlkOMe formation in reaction of the complex F with ArOH which is the determining one at the conditions of catalysis of the reaction ArOH with MA by individual ArOK. But it should be taken into account that the individual 2,6-di-*tert*-butyl potassium phenolate is only partially soluble in the reagents' mixture and can exist in the form of the dimer D.ArOK. It should also be noted that the fact that the hindered phenols' salts are dimerized is known in the literature.[3]

There is some information showing the inequality of the cations in corresponding dimers.[4] The latter appears to be a reason for the initiation of polymerization of MA, for example, as a result of the formation of loose cation pairs of the potassium 2,6-di-*tert*-butylphenolate dimer (ArOK, ArO + K) and potassium cation interaction with MA.

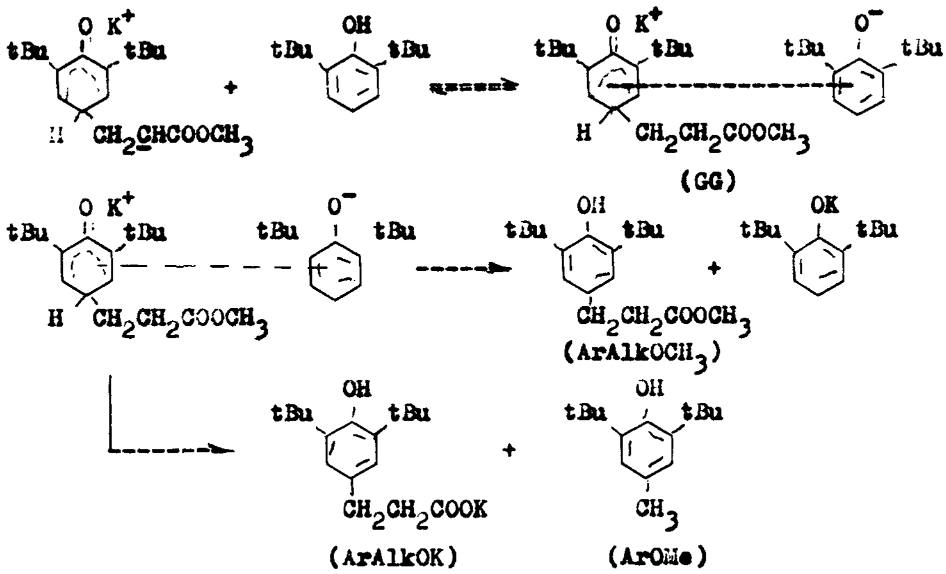
Limited solubility of potassium, 2,6-di-*tert*-butylphenolate can be expressed at the first approximation through the formation of the potassium, 2,6-di-*tert*-butylphenolate trimer (T.ArOK). Dimers and trimers can interact with water and methanol resulting in the formation of monomeric ArOK, and also of KOH and potassium methylate, as is expressed in the following kinetic scheme:

$$\begin{aligned}
&T.ArOK \rightarrow D.ArOK + ArOK\\
&D.ArOK \rightarrow ArOK + ArOK\\
&D.ArOK + H_2O \rightarrow ArOK + KOH + ArOH\\
&T.ArOK + H_2O \rightarrow D.ArOK + KOH + ArOH\\
&D.ArOK + CH_3OH \rightarrow ArOK + CH_3OK + ArOH\\
&T.ArOK + CH_3OH \rightarrow D.ArOK + CH_3OK + ArOH\\
&T.ArOK + 2.CH_3OH \rightarrow D.ArOK + ArOH + CH_3OK.CH_3OH
\end{aligned}$$

Finally, this scheme is taken into account in the influence of CH_3OH-CH_3OK associates in the stage of ArAlkOMe formation. The role of these associates becomes a remarkable one in the process of alkylation of 2,6-di-*tert*-butylphenol by methyl acrylate in presence of ArOK and CH_3OH. The inhibitory effect of alkali metal alcoholate associates with alcohols on the alcoholate reactions is well known.[5]

Therefore in correspondence with the proposed kinetic scheme ArAlkOMe formation can proceed as a result of cationic exchange of the GG complex consisting of two phenolic fragments which is followed by ArOK production.

In parallel with this reaction the cleavage of the GG complex proceeds resulting in the formation of ArAlkOK and ArOMe, but the rate of this reaction should be 3 orders less than the complex GG cleavage rate with ArAlkOMe formation:



ArOMe was discovered by the GLC method.

EXPERIMENTAL

Kinetic and analytical measurements were carried out using the method described in Reference 1. ArOK was obtained as a result to the addition of *tert*-BuOK (in *tert*-BuOH) (equivalent quantity) to ArOK followed by filtration and purification by hexane and washing of the crystalline product.

DISCUSSION

The results on the reaction of alkylation of ArOH by methyl acrylate (MA) in the presence of ArOK differ from the results on the reaction catalyzed by ArOK and H_2O. These differences are especially remarkable in the presence of the catalyst with high H_2O content and were expressed in reaction rates, process selectivity and degree of conversion of ArOH.

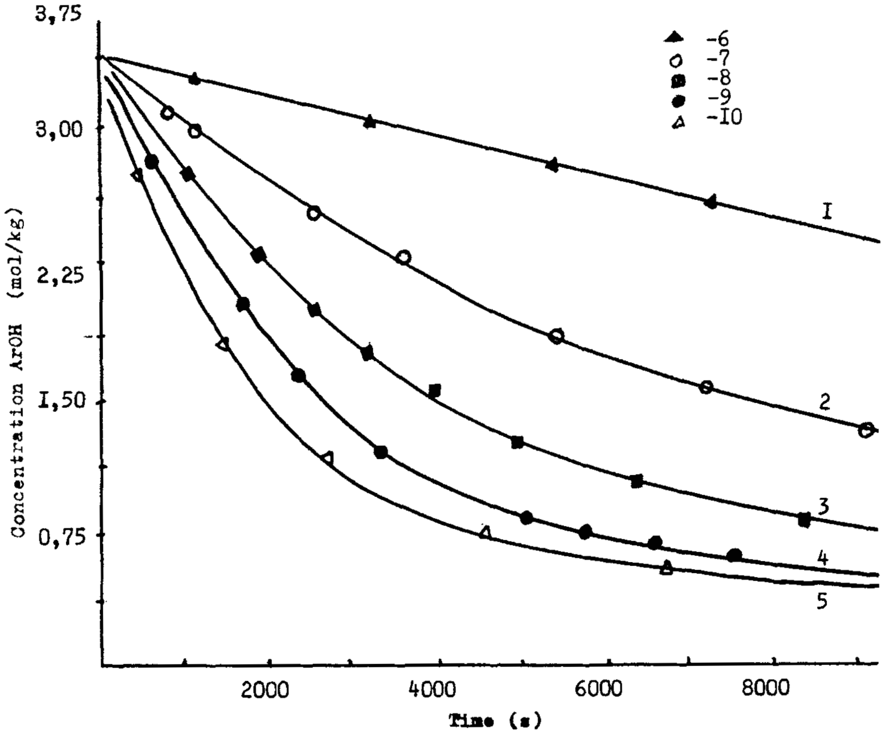


FIGURE 1 Computed (1)–(5) and experimental (6)–(10) data on ArOH consumption kinetics (116°C, $[ArOH]_0$ = 3.29; $[MA]_0$ = 3.75 mol/kg). [ArOK], mol/kg: (1) 0.01; (2) 0.03; (3) 0.06; (4) 0.118; (5) 0.20. △ 6; ● 7; □ 8; ○ 9; ▲ 10.

However other regularities are observed when the catalyst contains a small quantity of water. In that case ArOH consumption kinetics fits in with other regularities which are consequences of the kinetic scheme discussed. The selection of elementary constants in the proposed scheme allows us to achieve a satisfactory coincidence between computed and experimental data in the wide range of ArOK and H_2O concentrations and the ArOK/H_2O ratio.

Figure 1 shows the dependence of ArOH consumption kinetics in the process of the interaction with MA on ArOK concentrations in the presence of individual ArOK. It follows from these data that experimental results and computations carried out in the kinetic scheme solution using constants of the elementary steps actually coincide. This is a case for computation and experimental data on the accumulation of the by-product $ArAlk(OMe)_2$ in the process of ArOH alkylation reaction by methyl acrylate.

Good coincidence of experimental and computational data is observed when we consider the reaction kinetics of ArOH and MA in the presence of ArOK and H_2O. In Figure 2, the kinetics is presented for ArOH consumption as calculated from the proposed and computed scheme of the reaction. In this instance catalyst ArOK containing 15% mol. H_2O is used. It follows from this instance that good coincidence between experimental and computational data can be achieved, when

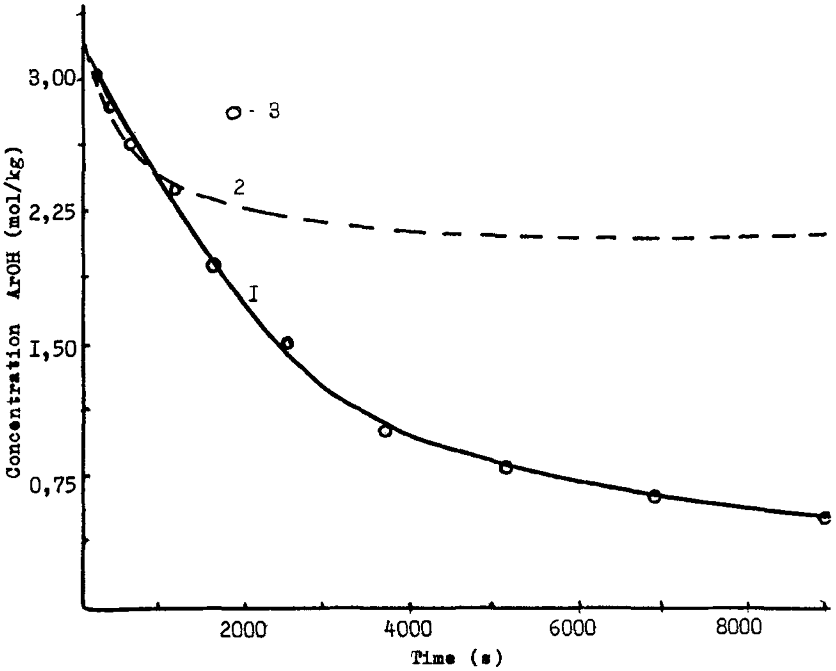


FIGURE 2 Computed (1)–(2) and experimental (3) data on ArOH consumption kinetics (116°C, $[ArOH]_0 = 3.29$; $[MA]_0 = 3.75$; $[ArOK]_0 = 0.118$; $[H_2O]_0 = 0.018$ mol/kg: (1) Computation by scheme with the constants of the elementary steps shown in Table I. (2) Computation by data of reference 1.

we take into account the additions and changes brought to the above-mentioned kinetic scheme of the reaction of 2,6-di-*tert*-butylphenol with methyl acrylate.

In Figure 3 the kinetics is give of ArOH consumption in the reaction with MA in the presence of ArOK containing 30, 40, 80, 100 and 135% mol. H_2O, respectively. This dependence is specific and shows the influence of H_2O concentration on ArOK activity in a wide range of H_2O concentrations. The regularity discovered therein is near to that related to KOH in the catalytic system ArOK-KOH.

Figure 4 shows the dependence of the consumption rate change W (relatively on ArOH, time 160 s) on H_2O content. The characteristic shape of the curve with the maximum ArOH consumption rate at H_2O content 80% is in good correlation with the proposed scheme of the reaction and earlier published data.[1] Regression analysis of this nonlinear dependence gives the following analytical expression:

$$W(160\ s) = 8{,}5.10^{-4} + 2{,}104.10^{-3}[H_2O] + 7{,}406.10^{-2}[H_2O]^2 - 0{,}1902.[H_2O]^3 + 0{,}1096.[H_2O].^4$$

Figure 5 demonstrates experimental and computational data related with (to) the dependence of reaction time W (at 160 s) on concentration of ArOK (curve 1) and ArOK and H_2O (curve 2). At small concentrations of ArOK, H_2O has an inhibitory effect and appears to relate to the existence of the critical concentration

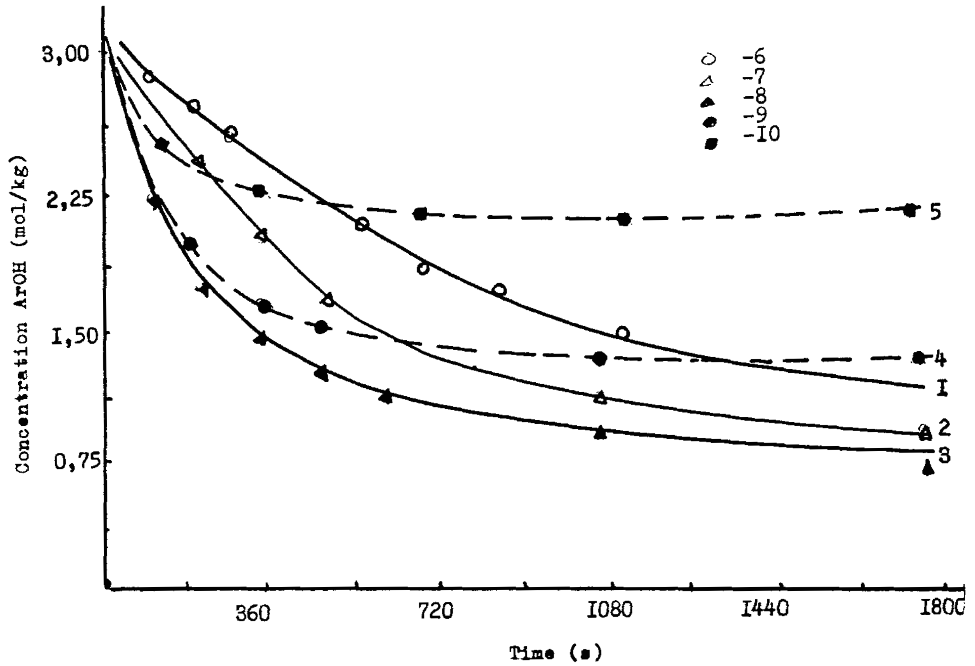


FIGURE 3 Computed (1)–(5) and experimental (6)–(10) data on kinetics of ArOH consumption (116°C, $[ArOH]_0 = 3.29$; $[MA]_0 = 3.75$; $[ArOK]_0 = 0.118$ mol/kg, H_2O, mol/kg): (1) 0.032; (2) 0.052; (3) 0.092; (4) 0.118; (5) 0.165. ○ 6; △ 7; ▲ 8; ● 9; □ 10.

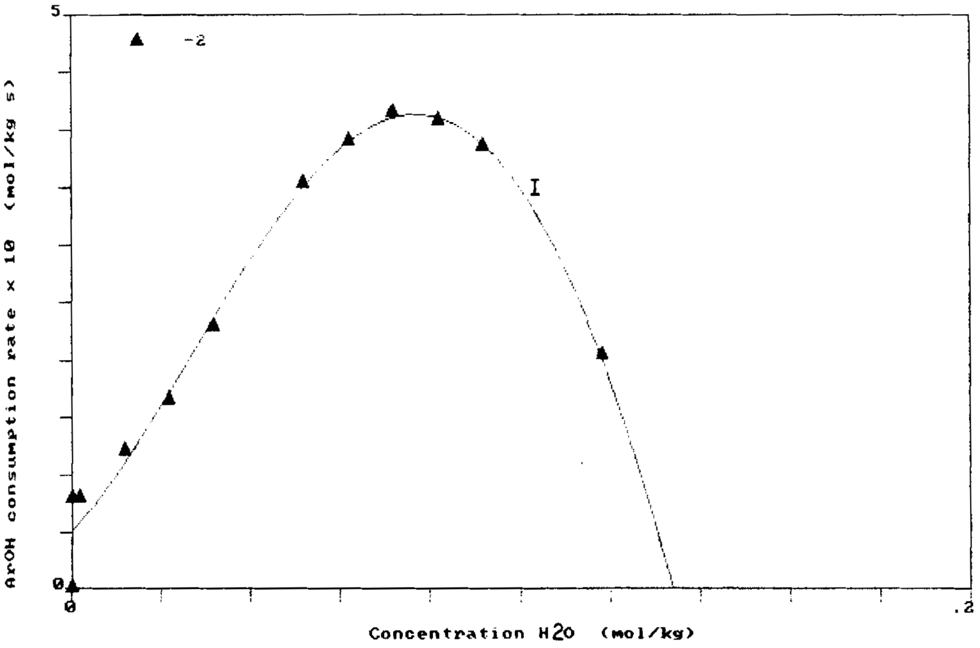


FIGURE 4 Computed and experimental dependencies of the ArOH consumption rate (W 160 s) on H_2O concentration (116°C, $[ArOH]_0 = 3.29$; $[MA]_0 = 3.75$; $[ArOK]_0 = 0.118$ mol/kg). (1) Computation; (2) Experimental.

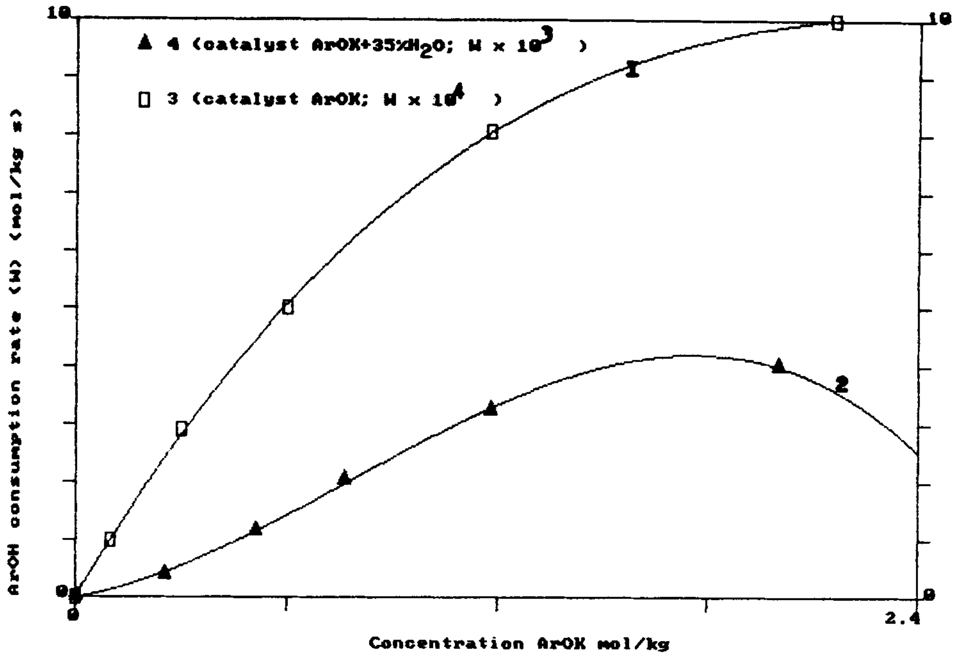


FIGURE 5 Computed (1)–(2) and experimental (3)–(4) dependencies of the ArOH consumption rate (W 160 s) on catalyst concentration (116°C, $[ArOH]_0 = 3.29$; $[MA]_0 = 3.75$ mol/kg): (1) $[ArOK]_0 = 0.118$ mol/kg; (2) $[ArOK]_0 = 0.118$; $[H_2O]_0 = 0.0415$ mol/kg.

on ArOK in the presence of H_2O. It should be mentioned that dependencies above differ considerably from each other at small ArOK concentrations. Regression analysis gives the following results:

$$W^{*}_{*} = 1{,}457.10^{-5} + 2{,}483.10^{-2}.[ArOK] - 1{,}975.10^{-2}.[ArOK]^2 + 4{,}987.10^{-3}.[ArOK]^3$$

for reaction rate of ArOH with MA in presence of ArOK and 35% mol. H_2O and

$$W^{**} = 1{,}571.10^{-6} + 2{,}838.10^{-4}.[ArOK] + 1{,}575.10^{-3}.[ArOK]^2 - 1{,}606.10^{-3}.[ArOK]^3.$$

In the investigation of the influence of CH_3OH on kinetics of the reaction under study a good coincidence is also obtained. Furthermore, it is shown that CH_3OH does not influence the ArOH consumption kinetics at concentrations comparable with those of ArOK.

Therefore a sum of the results obtained gives a base for interpreting the mechanism of the alkylation reaction of 2,6-di-*tert*-butylphenol with MA from the earlier expounded positions (catalytical chain mechanism), taking into account the peculiarities of ArOK catalysis in the presence of these substances of different nature and having proton donor properties: ArOH, H_2O, CH_3OH and the influence of compounds on the reaction kinetics at all.

CONCLUSIONS

As a result of mathematical stimulation of the reaction kinetics of 2,6-di-*tert*-butylphenol with methyl acrylate the kinetic scheme is proposed which thoroughly describes the physical and chemical process that proceeds during the formation of methyl ester of β-(4-hydroxy-3,5-*tert*-butylphenol) propionic acid and other accompanied products of the reaction.

The mechanism is suggested for 2,6-di-*tert*-butylphenol reaction with methyl acrylate. The mechanism is founded on the participation of proton donor compounds: 2,6-di-*tert*-butylphenol, water and alcohols, in the interaction process of the reagents, intermediate species with the catalyst.

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