The Reaction Mechanism of 2,6-di-Tert. Butyl Phenol Alkylation by Methyl Acrylate in the Presence of 2,6-di-Tert. Butyl Phenolate of Potassium and Alkali

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The reaction of 2,6-di-tert. butyl phenol alkylation in the conditions of alkali catalysis is used in the synthesis of antioxidants, inhibitors of radical reactions in the processes of polymer stabilizers production technology. The catalytic system consisting in 2,6-di-tert. butylphenolate of alkali metal and alkali metal hydroxide, is most efficient in the alkylation reaction of 2,6-di-tert. butyl phenol by methyl acrylate. For the investigation of the reaction mechanism of 2,6-di-tert. butyl phenol alkylation by methyl acrylate in the presence of 2,6-di-tert. butylphenolate of potassium (ArOK) and alkali (KOH) on the basis of consumption kinetics of 2,6-di-tert. butyl phenol (ArOH), the computer calculation procedure was used for the kinetic system containing 14 components with life times differing by a few magnitudes of order. The program was adapted for the operation in the operational system RT-60 of MINICOMPUTER (Model MERA-660). The kinetic scheme consists of 28 elementary stages which describe the formation mechanism of methylox compound, (4-hydroxy-3,5-di-tert. butyl phenol) potassium propionate as well as water, methyl alcohol, alkali monohydrate and ion pairs.

KEYWORDS: Kinetics, mechanism, 2,6-di-tret-butilphenol, elementary acts, absolute rate constants, energy of activation

Much attention is being given to the problems of inhibition of radical chain processes of organic compounds oxidation.[1] It is important both for the development of the theory of inhibited oxidation and for practical purposes. Sterically hindered phenols are often used as inhibitors of free-radical processes of oxidation.[2]

The reaction of 2,6-di-tert. butyl phenol alkylation in the conditions of alkali catalysis is used in the synthesis of antioxidants, inhibitors of radical reactions and in the processes of polymer stabilizers production technology. Acidity properties of 2,6-di-tert. butyl phenol ($pK_a = 11.5$) are less than those of unsubstituted phenol and, as a result, phenolates are not formed due to the action of alkalis on the sterically hindered phenol in aqueous or water–alcohol solution.[3] These data
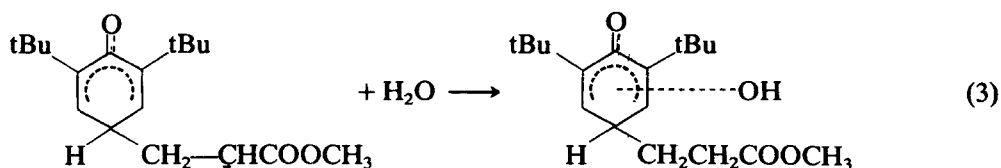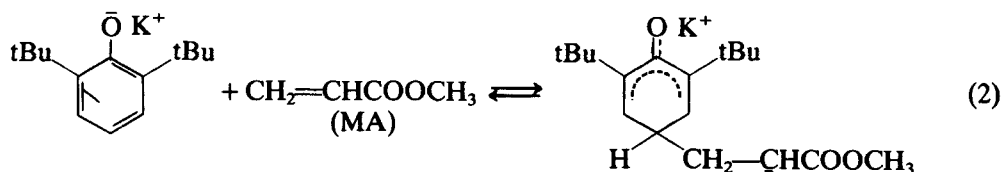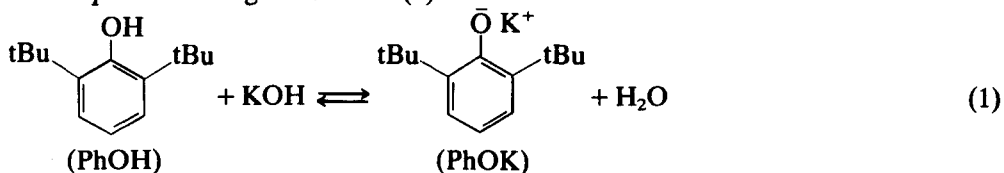
had a certain effect on the development of the theory and practice of 2,6-di-tert. butyl phenol alkylation in the conditions of alkali catalyst. In theoretical studies the primary attention was given to the regularities of the reaction with the participation of 2,6-di-tert. butylate ion, whereas the solution of practical tasks was connected with the development of the methods for obtaining 2,6-di-tert. butyl phenolates. In the alkaline medium, when the solvent (superconcentrated solutions) is absent, the reaction of 2,6-di-tert. butyl phenol with the reagent (substrate) can proceed specifically since it is necessary to take into account the role of ion pairs in the elementary act of interaction: 2,6-di-tert. butyl phenolate ion-metal cation. It is known that the solvent affects the solvation of cations and the reaction mechanism as a whole. The absence of the solvent can considerably change the character of the reagents interaction.

The catalytic system consisting in 2,6-di-tert. butyl phenolate of alkali metal or alkali metal hydroxide, is most efficient in the alkylation reaction of 2,6-di-tert. butyl phenol by methyl acrylate.[4,5] However, the perception of the reaction mechanism described earlier[6] from classical approach cannot be used to explain all the experimental data and the peculiarities of this reaction.

Theoretical calculations

For the investigation of the reaction mechanism of 2,6-di-tert. butyl phenol (PhOH) alkylation by methyl acrylate (MA) in the presence of 2,6-di-tert. butyl phenolate of potassium (PhOK) and alkali (KOH) on the basis of the consumption kinetics of PhOH, the computer calculation procedure was used for the kinetic system containing 14 components with lifetimes differing by a few magnitudes of order, the algorithm and subprogram for the solution of "rigid systems" of ordinary differential equations according to.[7] The program was adapted for the operation in the operational system PT-60 of MINICOMPUTER (Model MERA-660). The calling subprogram made up in FORTRAN-4 algorithmic language permitted operational changes in the values of the reaction rate constants and the initial concentrations. In calculating, the relative accuracy of 10% was given, the initial step of integration was 10–12 s, the calculation time was equal to 10 minutes. The kinetic scheme consists of 28 elementary stages which describe (in the first approximation) the formation mechanism of methyl ether of β-(4-hydroxy-3,5-di-tert. butyl phenyl)-propionic acid (F–I), (4-hydroxy,3,5-di-tert. butyl phenyl) potassium propinate (F–K) as well as water, methyl alcohol, alkali monohydrate and ion pairs, the formation of the latter being logical in the conditions of the reaction proceeding in the absence of the solvent. The proposed kinetic scheme is based on the reversible reaction of PhOH with KOH (studied in the model conditions). In the course of this reaction H_2O is formed according to reaction (1) and H_2O participates in stabilization of the intermediately formed ion pair (F) according to the reaction of PhOK with MA (reaction 2). The formation of F as the stage reaction of PhOK with MA is obvious. However, in the absence of the solvent the spontaneous intramolecular transfer of hydrogen from the carbon atom of the six-membered cycle towards the side chain of the ion pair F appears to be unlikely, whereas the interaction of H_2O with carbionic center of F is logical resulting in the formation of the G-type

ion pair according to reaction (3)

$$\text{(PhOH)} + KOH \rightleftharpoons \text{(PhOK)} + H_2O \qquad (1)$$

$$\text{(PhOK)} + CH_2{=}CHCOOCH_3 \text{ (MA)} \rightleftharpoons \qquad (2)$$

$$+ H_2O \longrightarrow \qquad (3)$$

Three directions with the participation of G were considered: monomolecular degradation yielding F-1 and KOH (reaction 4), bimolecular reaction of G with H_2O (reaction 5) and bimolecular reaction of G with KOH (reaction 6). The probability of reactions (4–6) can be evaluated by comparing the calculated and experimental data on the PhOH consumption kinetics (see Table I).
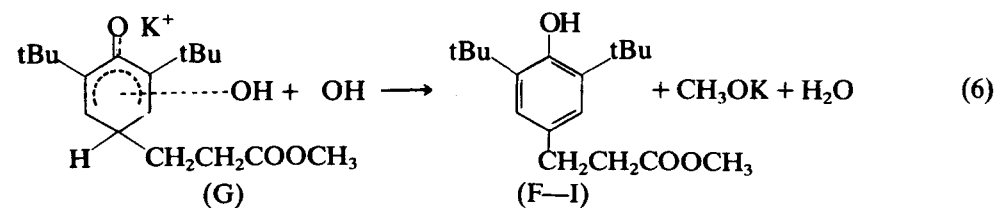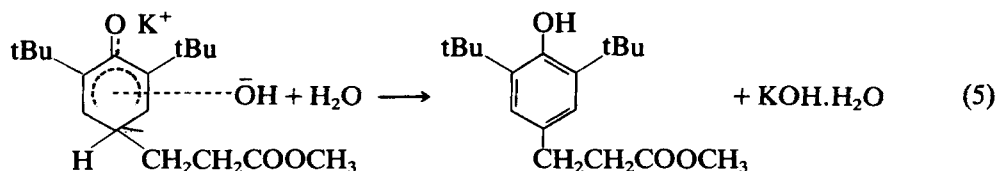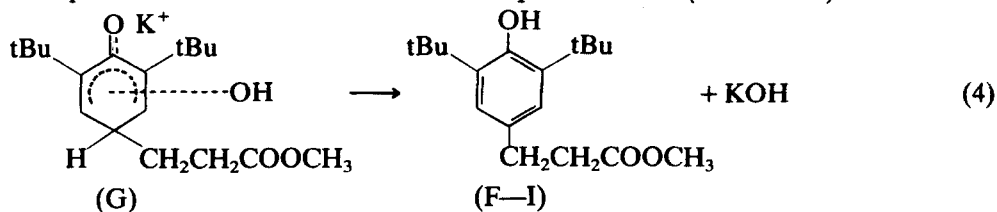
$$(G) \longrightarrow (F{-}I) + KOH \qquad (4)$$

$$(G) \cdots \bar{O}H + H_2O \longrightarrow (F{-}I) + KOH.H_2O \qquad (5)$$

$$(G) \cdots OH + \ ^-OH \longrightarrow (F{-}I) + CH_3OK + H_2O \qquad (6)$$

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TABLE I

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

Nos.	Reaction	k
1	$PhOH + KOH \rightarrow PhOK + H_2O$	$3 \cdot 10^2$
2	$PhOK + H_2O \rightarrow PhOH + KOH$	10^3
3	$PhOK + MA \rightarrow F$	4
4	$F \rightarrow PhOK + MA$	1
5	$F + H_2O \rightarrow G$	10
6	$G \rightarrow F\text{-}I + KOH$	10^{-1}
7	$G + H_2O \rightarrow F\text{-}I + KOH.H_2O$	1
8	$G + KOH \rightarrow F\text{-}K + CH_3OK + H_2O$	10^{-3}
9	$KOH.H_2O \rightarrow KOH + H_2O$	10^7
10	$KOH + H_2O \rightarrow KOH.H_2O$	$6 \cdot 10^6$
11	$CH_3OK + H_2O \rightarrow CH_3OH + KOH$	10^8
12	$CH_3OH + KOH \rightarrow CH_3OK + H_2O$	10^7
13	$PhOH + CH_3OK \rightarrow PhOK + CH_3OH$	$5 \cdot 10^3$
14	$PhOK + CH_3OH \rightarrow PhOH + CH_3OK$	10^4
15	$F + CH_3OH \rightarrow D$	10
16	$D + H_2O \rightarrow F\text{-}I + KOH + CH_3OH$	1
17	$D + CH_3OH \rightarrow F\text{-}I + CH_3OH.CH_3OK$	10^{-1}
18	$D \rightarrow F\text{-}I + CH_3OK$	10^{-3}
19	$KOH.H_2O + H_2O \rightarrow KOH.2H_2O$	$5 \cdot 10^6$
20	$KOH.2H_2O \rightarrow KOH.H_2O + H_2O$	10^6
21	$KOH.2H_2O + H_2O \rightarrow KOH.3H_2O$	$5 \cdot 10^6$
22	$KOH.3H_2O \rightarrow KOH.2H_2O + H_2O$	10^6
23	$KOH.H_2O + MA \rightarrow MAK + CH_3OH + H_2O$	10^{-3}
24	$KOH.2H_2O + MA \rightarrow MAK + CH_3OH + 2H_2O$	2
25	$KOH.3H_2O + MA \rightarrow MAK + CH_3OH + 3H_2O$	20
26	$KOH.2H_2O + F\text{—}I \rightarrow F\text{-}K + CH_3OH + 2H_2O$	1
27	$KOH.3H_2O + F\text{—}I \rightarrow F\text{-}K + CH_3OH + 3H_2O$	5
28	$F + MA \rightarrow$	$6 \cdot 10^{-3}$

It was established experimentally that in the process of 2,6-di-tert. butyl phenol alkylation by methyl acrylate the initial concentration of alkali catalyst decreases and F–K is formed. In addition to reaction (6), the formation of F–K is also possible in the reaction of F-1 hydrolysis. However, in the system under consideration one should distinguish between the hydrolysis (according to the reaction constants) with the participation of monohydrate ($KOH.H_2O$) and with the participation of solvated hydrate of potassium oxide (loose ion pairs: $KOH.2H_2O$; $KOH.3H_2O$). The consumption of KOH according to the reaction of methyl acrylate hydrolysis is also taken into account in the kinetic scheme. It is obvious that CH_3OH resulting from the hydrolysis will compete with H_2O towards the reaction of the ion pair F yielding complex D similar in its structure. The ratios of KOH, H_2O, $KOH.H_2O$, CH_3OH and CH_3OK in the reaction mixture are interrelated by reversible reactions (7) and (8)

$$KOH.H_2O \rightleftarrows KOH + H_2O \qquad (7)$$

$$CH_3OK + H_2O \rightleftarrows CH_3OH + KOH \qquad (8)$$

Since reactions (7) and (8) are connected with the proton transfer, their rates should be sufficiently high.[8] Finally, the reactions of PhOH with CH_3OK and the

reactions of the ion pair D analogous to the reactions of the ion pair F were also considered in the kinetic scheme. H_2O in this kinetic scheme performs a double function. On the one hand, it is the reagent which participates in the formation of the target product, (F-1), on the other, the same reagent causes the formation of by-products and the consumption of alkali catalyst. It is also possible that in the case of critical concentration H_2O can exhibit the inhibiting properties toward the alkylation of 2,6-di-tert. butyl phenol by methyl acrylate.

DISCUSSION OF RESULTS

The alkylation reactions of 2,6-di-tert. butyl phenol by methacrylate in the presence of PhOK and KOH proceed in catalytic conditions with the selectivity to 98%.[4] The shape of the kinetic curves in the experiment depends on the total concentration of PhOK and KOH, the ratio of these components, that is, characteristic dependences of PhOH consumption on the concentration of the catalyst and its components. Therefore, following the experimental kinetic dependences of the reaction under consideration and the calculation data for the proposed kinetic scheme it seems possible to suggest the alkylation mechanism of 2,6-di-tert. butyl phenol by methyl acrylate in superconcentrated solution. In calculating the kinetic scheme, the results of the determination of the reversible reaction (1) equilibrium constants and the tabulated data on the system equilibrium were taken into account: $KOH—H_2O$.[9]

The data in Figure 1 show that the PhOH consumption kinetics found experimentally and calculated on the computer with the constants of the elementary stages of the studies reaction tabulated in Table I is in good agreement. This kinetics shows the dependence of PhOH consumption in the
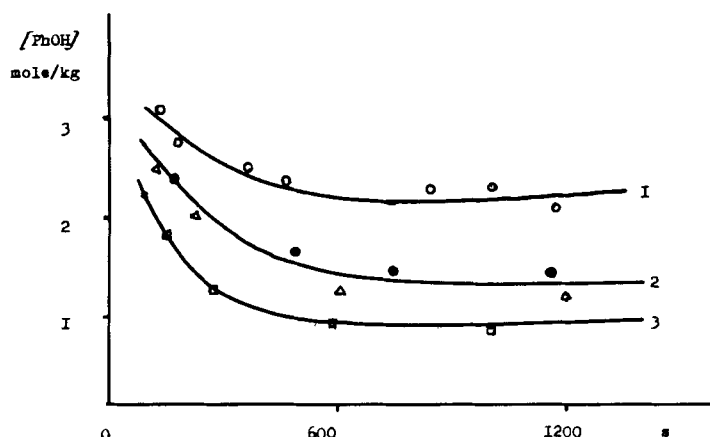

FIGURE 1 Calculated and experimental data on the kinetics of PhOH consumption; 116°C. $[PhOH]_0 = 3.29$ mole/kg; $[MA]_0 = 3.75$ mole/kg; $[PhOK]_0 + [KOH]_0 = 0.118$ mole/kg 1–KOH–37% mole; 2–60% mole; 3–84% mole. Experiment: ●●●—KOH 37% mole; OOO—KOH 60% mole; ▲▲▲—KOH 70% mole; □□□—80% mole.
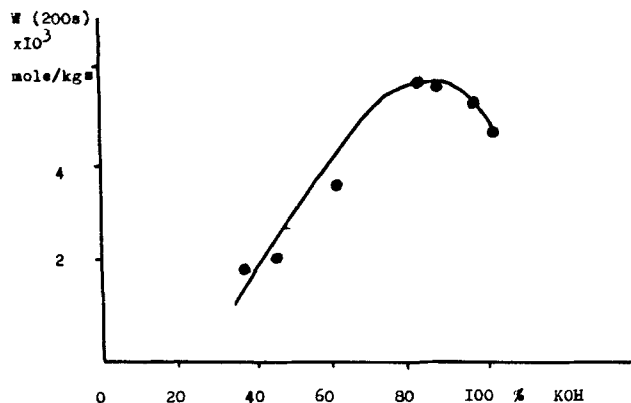
FIGURE 2   Calculated and experimental data on the dependences of the PhOH consumption rate (200 s) on the catalyst composition; 116°C. $[PhOH]_0 = 3.29$ mole/kg; $[MA]_0 = 3.75$ mole/kg; $[PhOK]_0 + [KOH]_0 = 0.118$ mole/kg. 1-calculated. ●●●—experimental.

presence of PhOK and KOH (PhOK and KOH = 0.118 mole/kg) upon different KOH content. The higher the content of KOH in the PhOK–KOH mixture, the higher the PhOH consumption rate at the initial part of the kinetic curve. The growth of the initial PhOH conversion depth and an increase of F-1 yield proceed in the same sequence. Figure 2 gives the dependence of the change in the PhOH consumption rate (at 200 s) on the KOH content in the catalytic system. The characteristic form of this dependence with the maximum PhOH consumption rate (the KOH content in the catalytic system being 80%) seems to be a serious argument in favour of the proposed reaction mechanism. Figure 3 shows

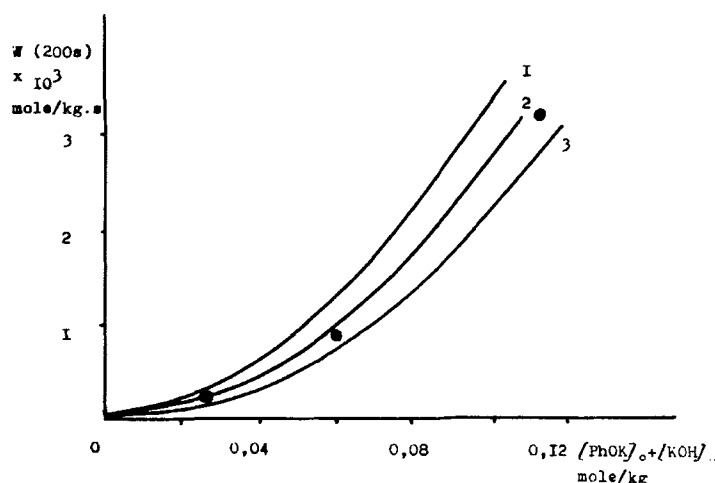FIGURE 3   Calculated and experimental data on the dependences of the PhOH consumption rate (200 s) on the catalyst concentration; 116°C. $[PhOH]_0 = 3.29$ mole/kg; $[MA]_0 = 3.75$ mole/kg; Calculated: 1—KOH 70% mole; 2—KOH 60% mole; 3—KOH 50% mole. Experimental: KOH 170% mole.

experimental and calculated data concerning the character of the dependence of the reaction rate (at 200 s) on the concentration of the alkali catalyst at the constant ratio of PhOK and KOH. This dependence is non-linear specific, approaches the quadratic function. Thus, the series of experimental and calculated data on the kinetics of PhOH consumption, the character of the dependences of the reaction rate on the KOH concentration, the total concentration of PhOK and KOH lead to a conclusion that the proposed kinetic scheme seems to be sufficiently objective for the description of the reaction mechanism of 2,6-di-tert. butyl phenol with methyl acrylate in the presence of PhOK and KOH as catalysts. This mechanism is based on the perception about the high reactivity of ion pairs in superconcentrated solutions and specific action of KOH and H_2O which participate and at the same time are formed in the reactions interrelated by the cycles, i.e., the mechanism by its nature appears to be the chain one (catalytically chain mechanism). In this particular case, the mechanism is the inhibitor mechanism and is related with the KOH consumption in side reactions.

To prove the inhibiting action of H_2O upon the alkylation reaction of 2,6-di-tert. butyl phenol by methyl acrylate the kinetics of this reaction has been studied, water being added to the reaction mixture in the course of the reaction. Figure 4 shows the kinetics of PhOH consumption in the presence of 0.118 mole/kg of the catalysts: PhOK and KOH (the ratio is 30% mole PhOK and 70% mole KOH) and the kinetics of the same reaction when 0.12 mole/kg of H_2O was introduced after 4 minutes. These data show that approximately equimolar amounts of H_2O with respect to the alkali catalyst practically stop the process of alkylation completely.

In terms of structure, the G- and D-type ion pairs are close to the complex with the charge transfer and therefore one can expect that these ion pairs would exhibit the properties characteristic for such complexes which are known[9] to be
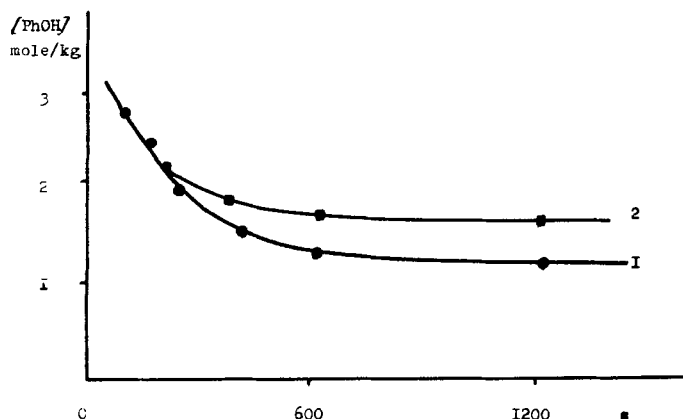
FIGURE 4 The kinetics of the reaction of PhOH with MA and the inhibiting effect of H_2O. 1—$[PhOH]_0 = 3.29$ mole/kg; $[MA]_0 = 3.75$ mole/kg; $[PhOK]_0 = 0.045$ mole/kg; $[KOH]_0 = 0.083$ mole/kg;   116°C.   2—$[PhOH]_0 = 3.29$ mole/kg; $[MA]_0 = 3.75$ mole/kg; $[PhOK]_0 = 0.045$ mole/kg; $[KOH]_0 = 0.083$ mole/kg; $[H_2O] = 0.12$ mole/kg (H_2O was incorporated into the reaction 4 minutes after it started).
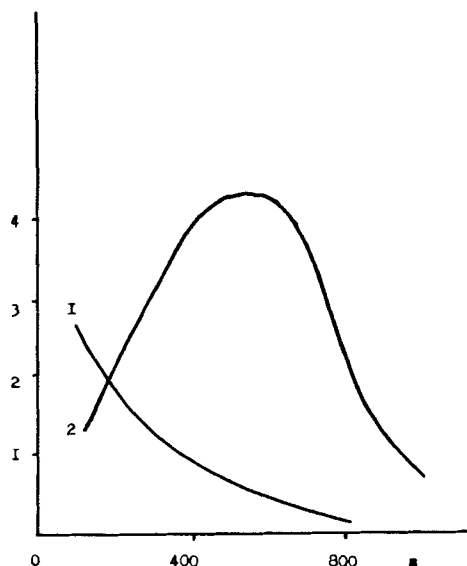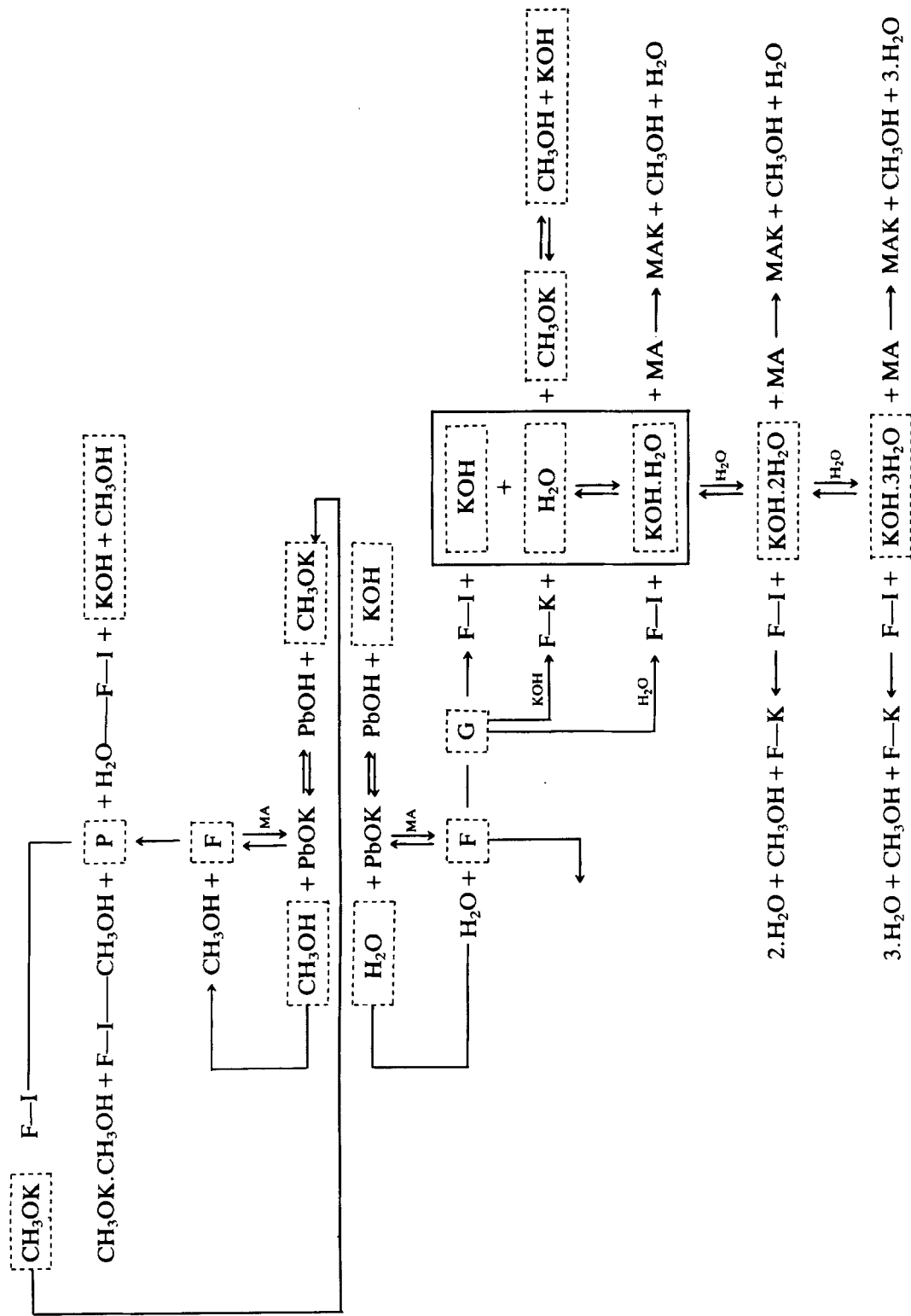
FIGURE 5 Calculaed concentrations of ion pairs as a function of time, 116°C. $[PhOH]_0 =$ 3.29 mole/kg; $[MA]_0 = 3.75$ mole/kg; $[PhOK]_0 = 0.047$ mole/kg; $[KOH]_0 = 0.071$ mole/kg. 1—G; 2—D.

peculiar by absorption in the longwave range. In fact, the reaction mixtures are coloured at the reaction temperature, the intensity and the shade of the colour changing in the course of the reaction. It should be also noted that according to the calculation of the kinetic scheme on the computer, the concentration of the G-type ion pair (in relative units) decreases with time, whereas the concentration of the D-type ion pair passes the maximum (Figure 5). In the experiment, according to the spectroscopy data, the reaction mass (5 minutes after the reaction starts, at 116°C) has the absorption at the 550–800 nm with the maximum at 664 nm.

It should be noted that in the model conditions which are close to the modelling of reaction (2) of the kinetic scheme, the character of the reagents interaction in the PhOK-MA system changes drastically. For example, individual PhOK does not react with methyl acrylate at room temperature, however, when the reaction mixture is heated to 78°C the components react to yield a complex reaction mixture in which are present (according to LC, 17%), a mixture of condensation products of PhOK with MA and polymeric methyl acrylate. Thus, these results agree with an assumption that the intramolecular transfer of hydrogen from the six-membered cycle towards the side chain upon the stabilization of the F-type ion pair in the conditions of the reaction under investigation is improbable.

Experimental

Industrial 2,6-di-tert. butyl phenol was distilled in vacuo and crystallized from n-hexane, m.p. 36–37°C. Methyl acrylate was stored over LiH for 72 hours and

$$CH_3OK \quad | \quad F{-}I$$

$$CH_3OK.CH_3OH + F{-}I \longrightarrow CH_3OH + F{-}I + KOH + CH_3OH$$

$$CH_3OH + \boxed{F} \xrightarrow{MA} \boxed{P} + H_2O \longrightarrow F{-}I + KOH + CH_3OH$$

$$CH_3OH + PbOK \rightleftharpoons PbOH + CH_3OK$$

$$H_2O + PbOK \rightleftharpoons PbOH + KOH$$

$$H_2O + \boxed{F} \xrightarrow{MA} \boxed{G} \longrightarrow F{-}I +$$

$$\xrightarrow{KOH} F{-}K +$$

$$\xrightarrow{H_2O} F{-}I +$$

$$\boxed{\boxed{KOH} + \boxed{H_2O} \rightleftharpoons \boxed{KOH.H_2O}} + MA \longrightarrow MAK + CH_3OH + H_2O$$

$$\boxed{CH_3OK} \rightleftharpoons \boxed{CH_3OH + KOH}$$

$$2.H_2O + CH_3OH + F{-}K \longleftarrow F{-}I + \boxed{KOH.2H_2O} + MA \longrightarrow MAK + CH_3OH + H_2O$$

$$3.H_2O + CH_3OH + F{-}K \longleftarrow F{-}I + \boxed{KOH.3H_2O} + MA \longrightarrow MAK + CH_3OH + 3.H_2O$$

then distilled, b.p. 85°C. PhOK was obtained by adding a calculated amount of potassium tert. butylate in tert. butyl alcohol to 2,6-di-tert. butyl phenol. Tert. butyl alcohol was distilled in vacuo. KOH was obtained by adding the calculated amount of H_2O to potassium tert. butylate.

Procedure

The calculated amount of potassium tert, butylate solution in tert. butyl alcohol (1 ml of the solution contained $8 \cdot 10^{-4}$ g-equiv. to potassium tert. butylate) was added to 10 g (0.048 mole) in the flow of argon in the flask. Tert. butyl alcohol was distilled in vacuo at 80–90°C, H_2O (0.002–0.03 ml) and 5 ml (0.055 mole) of MA were added to the reaction mixture. The latter was poured into ampoules and sealed. The ampoules containing the reaction mixture were placed into the thermostat simultaneously, then the ampoules were taken out at definite intervals of time, cooled. The reaction mixtures were analyzed by LC. There were used: a Bruker LC-31 liquid chromatograph, IBM Cyano column, eluent: hexane-isopropyl alcohol-ethylacetate (8:1:1, vol.), the working pressure 57 atm, rate 0.4 ml/min. Analytical measurements were taken in iso conditions. 40 minutes after the reaction starts, hexane was added to the reaction mass, the precipitate was filtered off. 2,6-di-tert. butyl phenolate of potassium (PhOK), 4-hydroxy-3,5-di-tert. butyl phenylpropionate of potassium (F–K) and potassium acrylate (MAK) were identified in the precipitate. Spectroscopic measurements of the reaction masses were performed on a Beckman DU-8 Model spectrophotometer, the recording rate was 0.2 cm/min. The reaction mass obtained after the reaction completed was used as a reference for comparison (2 hours, 116°C).

CONCLUSIONS

1. The reaction mechanism of 2,6-di-tert. butyl phenol with methyl acrylate in the presence of 2,6-di-tert. butyl phenolate of potassium and potassium oxide hydrate was proposed. The constants of the elementary reaction stages sufficient for the interpretation of the experimental data were found on the basis of the kinetic scheme calculations performed on the computer.

2. The interpretation of the results of 2,6-di-tert. butyl phenol alkylation by methyl acrylate are based on the assumption about the participation of ion pairs in the reaction and about the catalytically inhibited chain mechanism.

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