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MECHANISM OF THE ALKYLATION OF 2,6-DI-tert-BUTYLPHENOL BY METHYL
ACRYLATE IN THE PRESENCE OF POTASSIUM 2,6-DI-tert-BUTYLPHENOXIDE
AND ALKALI

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A mechanism is proposed for the reaction of 2,6-di-tert-butylphenol with methyl
acrylate in the presence of potassium 2,6-di-tert-butylphenoxide and KOH and,
based on a computer calculation of the kinetic scheme, the constants have been
found for the elementary stages of the reaction, sufficient to interpret the ex-
perimental data. The alkylation of 2,6-di-tert-butylphenol by methyl acrylate
takes place by an inhibited catalytic chain mechanism involving the participation
of ion pairs in the reaction.

Much attention is being paid to problems of the retardation of radical-chain oxidation
processes of organic compounds [1]. This is important both from the point of view of devel-
oping the theory of inhibited oxidation and for practical problems. Sterically hindered
phenols are frequently used as inhibitors of free-radical oxidation processes [2].

The alkylation of 2,6-di-tert-butylphenol ArOH under alkaline catalysis conditions is
used in the synthesis of antioxidants, radical reaction inhibitors, and in the technology
for obtaining polymer stabilizers. The acidic properties of ArOH (pK_a 11.5) are less than
for unsubstituted phenol, and, consequently, phenoxides are not formed in the action of
alkalis on a sterically hindered phenol in aqueous or aqueous alcohol solution [3]. These
results have affected the development of the theory and practice of ArOH alkylation under
alkaline catalysis conditions. In theoretical studies principal attention has been paid to
the features of reactions involving the participation of the ArO^- ion, whereas the solution
to the practical problems have been associated with the development of methods for obtaining
2,6-di-tert-butylphenoxides. In alkaline medium in the absence of a solvent (superconcen-
trated solutions) the reaction of ArOH with a reactant (the substrate) may take place
specifically, since account should be taken of the role of ion pairs in the elementary act
of the reaction: ion-ArO^-—metal cation. As is well known, a solvent affects the solvation
of cations and the reaction mechanism as a whole. However, the absence of a solvent may
alter the nature of the interaction of the reactants substantially.

A catalytic system consisting of a 2,6-di-tert-butylphenoxide of an alkali metal and an
alkali hydroxide is most effective in the alkylation of ArOH by methyl acrylate [4, 5].
However, ideas put forward previously [6] on the mechanism of this reaction from classical
points of view may not explain all the experimental data and the particular features of this
reaction.

Theoretical Calculations. To study the mechanism of the alkylation of 2,6-di-tert-
butylphenol (ArOH) by methyl acrylate (MA) in the presence of potassium 2,6-di-tert-butyl-
phenoxide (ArOK) and alkali (KOH) based on the kinetics of ArOH consumption we used a method
of calculating on a computer a kinetic scheme containing 14 components having lifetimes
differing by several orders of magnitude, an algorithm, and a subprogram for solving a
"stiff system" of ordinary differential equations according to [7]. The subprogram was
adapted for work in the RT-60 operation system of a "Mera-660" minicomputer. The program
produced, formulated in the algorithm language FORTRAN 4, enabled the values of the rate
constants of the reaction and the initial concentrations to be altered interactively. A
relative accuracy of 10% was set in the calculation, the initial integration interval was
10-12 sec, and the calculation period ∿10 min. The kinetic scheme contains 28 elementary

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TABLE 1. Rate Constants for the Elementary Stages of the Reaction of 2,6-Di-tert-butylphenol with Methyl Acrylate at 116°C (calculated)

Reaction	k
$ArOH + KOH \rightarrow ArOK + H_2O$	$3 \cdot 10^2$
$ArOK + H_2O \rightarrow ArOH + KOH$	10^3
$ArOK + MA \rightarrow$ (I)	4
(I) $\rightarrow ArOK + MA$	1
(I) $+ H_2O \rightarrow$ (II)	10
(II) $\rightarrow AralkOMe + KOH$	10^{-1}
(II) $+ H_2O \rightarrow AralkOMe + KOH \cdot H_2O$	1
(II) $+ KOH \rightarrow AralkOK + CH_3OK + H_2O$	10^{-3}
$KOH \cdot H_2O \rightarrow KOH + H_2O$	10^7
$KOH + H_2O \rightarrow KOH \cdot H_2O$	$6 \cdot 10^6$
$CH_3OK + H_2O \rightarrow CH_3OH + KOH$	10^8
$CH_3OH + KOH \rightarrow CH_3OK + H_2O$	10^7
$ArOH + CH_3OK \rightarrow ArOK + CH_3OH$	$5 \cdot 10^3$
$ArOK + CH_3OH \rightarrow ArOH + CH_3OK$	10^4
(I) $+ CH_3OH \rightarrow$ (III)	10
(III) $+ H_2O \rightarrow AralkOMe + KOH + CH_3OH$	1
(III) $+ CH_3OH \rightarrow AralkOMe + CH_3OH \cdot CH_3OK$	10^{-1}
(III) $\rightarrow AralkOMe + CH_3OK$	10^{-3}
$KOH \cdot H_2O + H_2O \rightarrow KOH \cdot 2H_2O$	$5 \cdot 10^6$
$KOH \cdot 2H_2O \rightarrow KOH \cdot H_2O + H_2O$	10^6
$KOH \cdot 2H_2O + H_2O \rightarrow KOH \cdot 3H_2O$	$5 \cdot 10^6$
$KOH \cdot 3H_2O \rightarrow KOH \cdot 2H_2O + H_2O$	10^6
$KOH \cdot H_2O + MA \rightarrow CH_2 = CHCOOK (MAK) + CH_3OH + H_2O$	10^{-3}
$KOH \cdot 2H_2O + MA \rightarrow MAK + CH_3OH + 2H_2O$	2
$KOH \cdot 3H_2O + MA \rightarrow MAK + CH_3OH + 3H_2O$	20
$KOH \cdot 2H_2O + AralkOMe \rightarrow AralkOK + CH_3OH + 2H_2O$	1
$KOH \cdot 3H_2O + AralkOMe \rightarrow AralkOK + CH_3OH + 3H_2O$	5
(I) $+ MA \rightarrow$ Products	$6 \cdot 10^{-3}$

stages representing to a first approximation the mechanism of the formation of the methyl ether of β-(4-hydroxy-3,5-di-tert-butylphenyl)propionic acid (AralkOMe), AralkOK, as well as water, MeOH, alkali monohydrate, and ion pairs, the formation of which it is logical to allow under the conditions of carrying out the reaction in the absence of a solvent.

The proposed kinetic scheme is based on the reversible reaction of ArOH and KOH studied under model conditions, during which water is formed by reaction (1), and the water participates in the stabilization of the intermediately formed ion pair (I) by the reactic of ArOK with MA (reaction (2)). The formation of (I) in the reaction of ArOH with MA is obvious. However, in the absence of a solvent the spontaneous intramolecular transfer of an H atom from a C atom in the six-membered ring to the side-chain of the ion pair (I) seems unlikely, whereas the reaction of water with a carbanion center (I), which leads to the formation of an ion pair of type (II) by reaction (3)

$$(1)$$
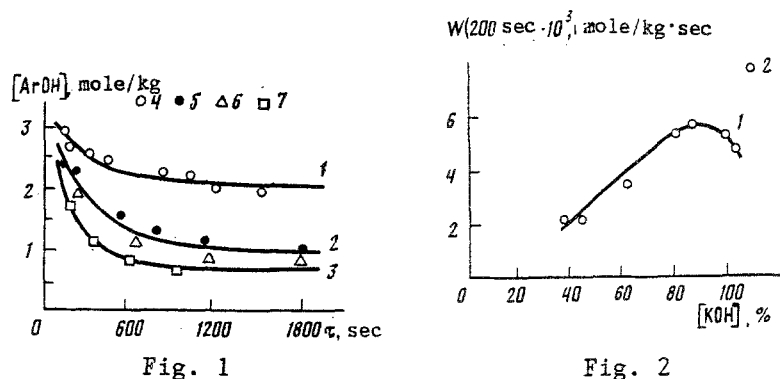

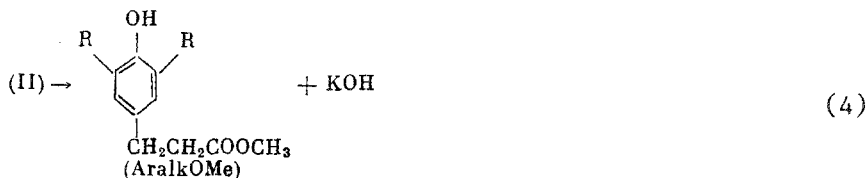$$(2)$$

$$(3)$$
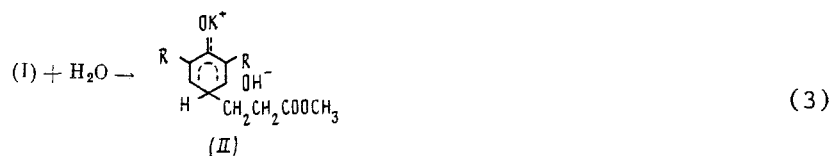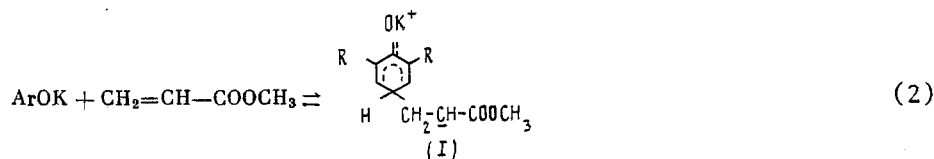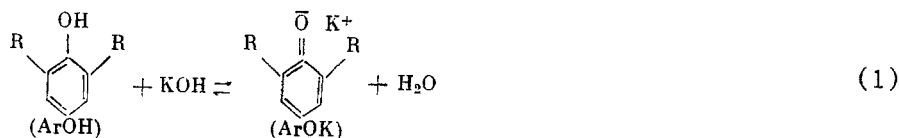
$R = t\text{-Bu}$,

Fig. 1. Calculated (1-3) and experimental (4-7) data on the kinetics of ArOH consumption (116°C, $[ArOH]_0 = 3.29$, $[MA]_0 = 3.75$, $[ArOK]_0 + [KOH]_0 = 0.118$ mole/kg). KOH, mole %: 1) 37; 2) 60; 3) 84; 4) 37; 5) 60; 6) 70; 7) 80.

Fig. 2. Calculated and experimental data for the dependence of the rate of ArOH consumption (200 sec) on the composition of the catalyst (116°C, $[ArOH]_0 = 3.29$, $[MA]_0 = 3.75$, $[ArOK]_0 + [KOH]_0 = 0.118$ mole/kg): 1) calculation; 2) experiment.

is more logical.

Three directions in which (II) participates are considered: monomolecular decomposition involving the formation of AralkOMe and KOH (reaction (4)), a bimolecular reaction of (II) with water (reaction (5)) and a bimolecular reaction of (II) with KOH (reaction (6)). The probability of reactions (4)-(6) can be estimated from a comparison of the calculated and experimental data on the kinetics of ArOH consumption (see the table)

$$(II) \rightarrow \quad \underset{CH_2CH_2COOCH_3}{\underset{(AralkOMe)}{\overset{OH}{\underset{R}{\overset{|}{\bigcirc}}R}}} \quad + KOH \tag{4}$$

$$(II) + H_2O \rightarrow AralkOMe + KOH \cdot H_2O \tag{5}$$

$$(II) + KOH \rightarrow AralkOK + CH_3OK + H_2O \tag{6}$$

It has been established experimentally that during alkylation of ArOH by methyl acrylate a decrease is observed in the initial concentration of the alkali catalyst and the formation of AralkOK. Apart from reaction (6) the formation of the latter is possible by the hydrolysis of AralkOK. However, in the system being considered we should distinguish between hydrolysis involving KOH monohydrate ($KOH \cdot H_2O$) and solvated KOH (loose ion pairs $KOH \cdot 2H_2O, KOH \cdot 3H_2O$). In the kinetic scheme account is also taken of the consumption of KOH by the hydrolysis of MA. Evidently, the CH_3OH formed in the hydrolysis will compete with the reactions of the ion pair (I) with H_2O to form the complex (III) of similar structure. The ratios of KOH, H_2O, $KOH \cdot H_2O$, CH_3OH and CH_3OK in the reaction mixture are connected with each other by the reversible reactions (7) and (8)

$$KOH \cdot H_2O \rightleftarrows KOH + H_2O \tag{7}$$

$$CH_3OK + H_2O \rightleftarrows CH_3OH + KOH \tag{8}$$

Since reactions (7) and (8) are connected with the transfer of a proton, then their rates should be fairly high [8]. In the kinetic scheme the reaction of ArOH with CH_3OK and the reaction of the ion pair (III), similar to the reactions of the ion pair (II), are considered. In this kinetic scheme water performs a double function. On the one hand, this is the reactant which participates in the formation of the product AralkOMe, and, on the other, this same reactant leads to the formation of by-products and the consumption of the alkali catalyst, and it can be expected that from a certain critical concentration water will exhibit the properties of an inhibitor for the alkylation of ArOH by methyl acrylate.

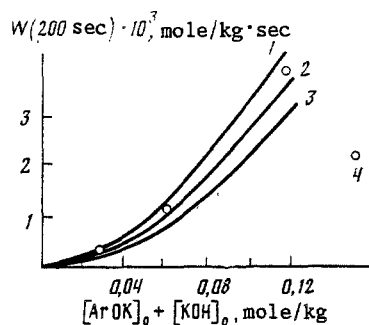$W(200\ sec)\cdot 10^7,\ mole/kg\cdot sec$

$[Ar\,OK]_0 + [KOH]_0,\ mole/kg$

Fig. 3. Calculated (1-3) and experimental (4) data for
the dependence of the rate of ArOH consumption (200 sec)
on the catalyst concentration (116°C, $[ArOH]_0 = 3.29$,
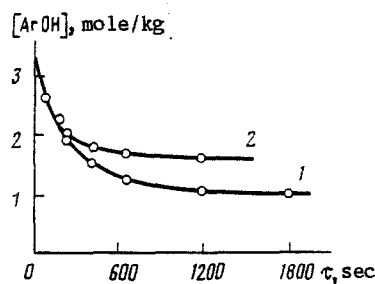$[MA]_0 = 3.75$ moles/kg). KOH, mole %: 1) 70; 2) 60; 3) 50;
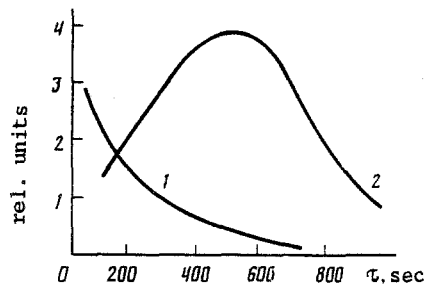4) 70.

$[ArOH]$, mole/kg

Fig. 4

rel. units

Fig. 5

Fig. 4. Kinetics of the reaction of ArOH with MA (1) and the inhibiting effect
of water (2) (116°C, $[ArOH]_0 = 3.29$, $[MA]_0 = 3.75$, $[ArOK]_0 = 0.045$, $[KOH]_0 =$
0.083 mole/kg); 2) $[H_2O] = 0.12$ mole/kg (introduced into the reaction after 4
min into the course of the reaction).

Fig. 5. Calculated concentrations of (II) and (III) as a function of time (116°C,
$[ArOH]_0 = 3.29$, $[MA]_0 = 3.74$, $[ArOK]_0 = 0.047$, $[KOH]_0 = 0.071$ mole/kg): 1)
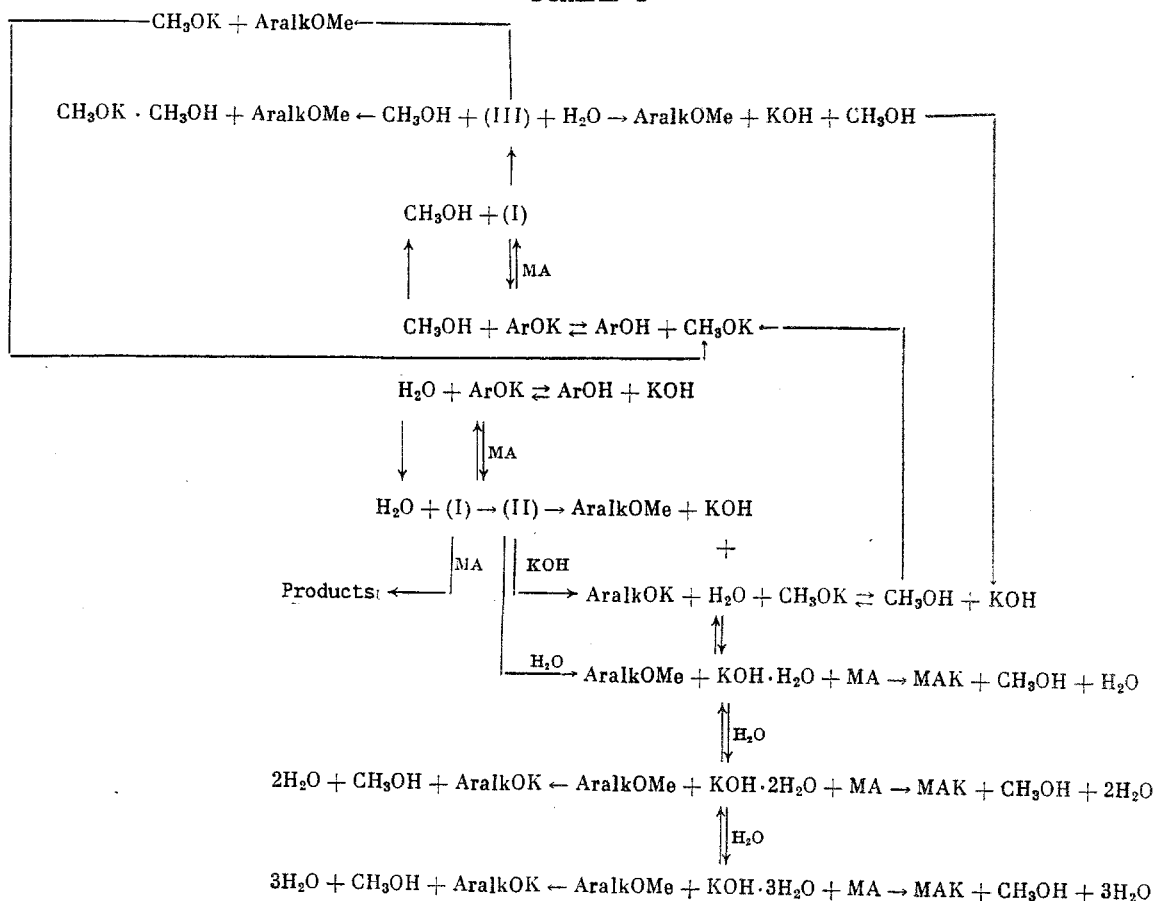(II); 2) (III).

RESULTS AND DISCUSSION

The alkylation of ArOH by MA in the presence of ArOK and KOH takes place under catalytic
conditions with a selectivity of up to 96% [4]. Experimentally the form of the kinetic
curves depends on the overall concentration of ArOK and KOH and the ratio of these compo-
nents, i.e., characteristic relationships are observed between ArOH consumption and the con-
centration of the catalyst and its components. Based on the experimental kinetic relation-
ships for the reaction being studied and the data from calculating the kinetic scheme, a
mechanism can be proposed for the alkylation of ArOH by MA in a superconcentrated solution.
When calculating the kinetic scheme the results of determining the equilibrium constant of
the reversible reaction (1) and the tabulated data on the equilibrium in the $KOH-H_2O$ system
were taken into account [9].

As follows from the data in Fig. 1, there is satisfactory agreement between the kinetics
of the ArOH consumption found experimentally and calculated by a computer program using the
constants listed in the table for the elementary stages of the reaction studied. In these
kinetics the relationship is represented for ArOH consumption in the presence of ArOK and
KOH ($[ArOK]_0 + [KOH]_0 = 0.118$ mole/kg) for a different KOH content. The rate of ArOH con-
sumption over the initial section of the kinetic curve is higher the higher the KOH content
in the ArOK-KOH mixture. The increase in the conversion of the initial ArOH and the in-
crease in the yield of AralkOMe occur in the same sequence. Figure 2 shows the relationship
for the variation in the rate of PhOH consumption (for 200 sec) as a function of the KOH
concentration in the catalytic system. The characteristic form of this relationship having
a maximum rate of ArOH consumption for a KOH content of ∿80% in the catalytic system is a

fairly strong argument in favor of the mechanism proposed for the reaction. Figure 3 presents the experimental and calculated data concerning the nature of the dependence of the rate of reaction (for 200 sec) on the concentration of the alkaline catalyst for a constant ratio of ArOK and KOH contents. This relationship is nonlinear, specific, and approaches a quadratic function. Thus, the combination of experimental and calculated data on the kinetics of ArOH consumption, the nature of the relationships between the rate of the reaction and KOH concentration and the total ArOK and KOH concentration give reason to suppose that the proposed kinetic scheme represents the true mechanism of the reaction of ArOH with MA in the presence of ArOK and KOH catalyst sufficiently objectively. This mechanism rests on concepts concerning the high reactivity of ion pairs in superconcentrated solutions and the specific action of KOH and water, which participate and are formed simultaneously in reactions connected with each other by cycles, i.e., the mechanism is essentially a chain one (a catalytic chain mechanism). In this case the mechanism is inhibited and associated with the consumption of KOH in the side reactions (see scheme 1).

SCHEME 1

$$CH_3OK + AralkOMe$$

$$CH_3OK \cdot CH_3OH + AralkOMe \leftarrow CH_3OH + (III) + H_2O \rightarrow AralkOMe + KOH + CH_3OH$$

$$CH_3OH + (I)$$

$$MA$$

$$CH_3OH + ArOK \rightleftarrows ArOH + CH_3OK$$

$$H_2O + ArOK \rightleftarrows ArOH + KOH$$

$$MA$$

$$H_2O + (I) \rightarrow (II) \rightarrow AralkOMe + KOH$$

$$+$$

Products $\xleftarrow{MA}$ $\xrightarrow{KOH}$ $AralkOK + H_2O + CH_3OK \rightleftarrows CH_3OH + KOH$

$$\xrightarrow{H_2O} AralkOMe + KOH \cdot H_2O + MA \rightarrow MAK + CH_3OH + H_2O$$

$$H_2O$$

$$2H_2O + CH_3OH + AralkOK \leftarrow AralkOMe + KOH \cdot 2H_2O + MA \rightarrow MAK + CH_3OH + 2H_2O$$

$$H_2O$$

$$3H_2O + CH_3OH + AralkOK \leftarrow AralkOMe + KOH \cdot 3H_2O + MA \rightarrow MAK + CH_3OH + 3H_2O$$

To confirm the inhibiting action of water on the alkylation of ArOH by MA we studied the kinetics of this reaction, over the course of which water was introduced into the reaction mixture. Figure 4 shows the kinetics of ArOH consumption in the presence of 0.118 mole/kg of catalyst (30 mole % ArOK and 70 mole % KOH) and the kinetics of the same reaction over the course of which 0.12 mole/kg of water was introduced at the fourth minute. It follows from these data that an approximately equivalent amount of water relative to the alkali catalyst stops the alkylation process almost completely.

Ion pairs of the type (II) or (III) approximate a charge-transfer complex in structure, and it could have been expected that these ion pairs would exhibit characteristic properties, e.g., [8] associated with absorption in the longwave region. In fact, the reaction mixtures are colored at the reaction temperature, the intensity and the shade of color varying over the course of the reaction. Here it should be noted that according to the data from the computer calculation of the kinetic scheme the concentration of the ion pair (II) (in rel. units) decreases in time, while the concentration of the ion pair (III) passes through a

maximum (Fig. 5). According to the spectroscopic data for the experiment the reaction mass (five minutes after commencement of the reaction, 116°C) has absorption over the range 550-800 nm with a maximum at 664 nm.

It should also be noted that under model conditions approximating the modeling of reaction (2) of the kinetic scheme the nature of the reaction of the reactants in the ArOK—MA system alters greatly. For example, at room temperature ArOK does not react on its own with MA, but on heating the reaction mass to 78°C the components react to form a complex reaction mixture in which AralkOMe is present (17% according to liquid chromatography results), a mixture of the products from the condensation of ArOK with MA, and polymeric methyl acrylate. Thus, these results agree with the suggestion that the intramolecular transfer of an H atom from the six-membered ring to the side chain on stabilization of the ion pair (I) is improbable under the conditions of the reaction studied.

EXPERIMENTAL

Technical ArOH was redistilled under vacuum and crystallized from n-hexane, mp 36-37°C. MA was allowed to stand for 3 days over LiH and redistilled, bp 85°C. ArOK was obtained by adding to 2,6-di-tert-butylphenol the calculated amount of t-BuOK in t-BuOH, the latter being distilled off under vacuum. KOH was obtained by adding the calculated amount of water to t-BuOK.

Procedure for Kinetic Experiments. Into a flask in a flow of Ar to 10 g (0.048 mole) ArOH was added the calculated amount of the solution of t-BuOK in t-BuOH (1 ml of solution contained $8 \cdot 10^{-4}$ g-eq t-BuOK). t-BuOH was distilled off under vacuum at 80-90°C, and 0.002-0.03 ml of water and 5 ml (0.055 mole) of MA were added to the reaction mixture. This was poured into (6-8) ampuls and sealed. The ampuls containing the reaction mixture were placed simultaneously in a thermostat, removed after definite intervals of time, cooled, and the reaction mixtures analyzed by liquid chromatography. We used a "Bruker LC-31" liquid chromatograph with an IBM Cyano column, the eluent being hexane—isopropanol-ethyl acetate (8:1:1 by vol.); the working pressure was 57 atm and the flowrate 0.4 ml/min. The analytical measurements were conducted under isocratic conditions. Forty minutes after the commencement of the reaction hexane was added to the reaction mass and the residue filtered off. In the precipitate we identified potassium 2,6-di-tert-butylphenoxide ArOK, AralkOK and potassium acrylate (MAK). The spectroscopic measurements of the reaction masses were conducted with a "Beckman DU-8" spectrophotometer, the rate of recording being 0.2 cm/min. The reaction mass obtained after cessation of the reaction (2 h, 116°C) was used as the reference standard.

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