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Alkylation of 2,6-di-*tert*-butylphenol with methyl acrylate catalyzed by potassium 2,6-di-*tert*-butylphenoxide

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The kinetics of catalytic alkylation of 2,6-di-*tert*-butylphenol (ArOH) with methyl acrylate (MA) in the presence of potassium 2,6-di-*tert*-butylphenoxide (ArOK) depends on the method for the preparation of ArOK. The reaction of ArOH with KOH at temperatures >180 °C affords monomeric ArOK, whose properties differ from those in the case of potassium 2,6-di-*tert*-butylphenoxide synthesized by the earlier methods. The regularities of ArOH alkylation depend on the ArOK concentration, the ArOH : MA ratio, and the effect of microadditives of polar solvents.

Key words: phenols, phenoxides, 2,6-di-*tert*-butylphenol, methyl acrylate, Michael reaction, potassium hydroxide, kinetics, catalysis.

Alkali derivatives of sterically hindered phenols are reactants and catalysts in the synthesis and technology of antioxidants. Most studies involve potassium 2,6-di-*tert*-butylphenoxide (ArOK) and potassium hydroxide (KOH), and the effect of the ratio of alkaline components on the kinetics of ArOH alkylation with methyl acrylate and the yield of the alkylation product, *viz*., methyl 3-(4-hydroxy-3,5-di-*tert*-butylphenyl)propionate (Ar´OH), was studied.[1—4] The mechanism of ArOH alkylation with methyl acrylate in the presence of ArOK and KOH is interpreted based on the structures of the intermediates and complexes as well as kinetic data. The effect of the *tert*-butyl groups in the *ortho*-position of a phenol molecule results in the appearance of specific properties related to the negative charge delocalization in the six-membered cycle (ambidentate ion) and a possibility of aromatic structure rearrangement to the cyclohexadienone structure. As a consequence, alkali 2,6-di-*tert*-butylphenoxide molecules can form supramolecular structures (dimers) and undergo *C*-alkylation reactions.[5] In continuation of these studies, it was of interest to study the catalytic properties of potassium 2,6-di-*tert*-butylphenoxide in the alkylation of phenol ArOH with methyl acrylate. In this work, we synthesized monomeric ArOK under the conditions of the high-temperature reaction of phenol ArOH with KOH and present the data concerning the properties of the monomer and earlier known ArOK dimers. Taking into account the studies of the kinetic regularities of ArOH alkylation with methyl acrylate, we propose a mechanism of catalytic alkylation involving monomeric ArOK.

Experimental

^{1}H NMR spectra were recorded on a Bruker WM-400 instrument (400 MHz) relative to the signal of residual protons of the deuterated solvent. IR spectra were measured on a Perkin—Elmer 1725-X spectrometer (KBr pellets, resolution 2 cm^{-1}). Molecular weights were determined by the thermoelectric method and calculated using the formula

$$M = kgM_s/[100(t_1 - t_2)],$$

where g is the weight of the sample in g (2—3% per 100 g of solvent), k is the coefficient of the instrument with thermistors, M_s is the molecular weight of the standard sample, and $t_1 - t_2$ is the magnitude equivalent to the temperature change in the cell with a solution of the sample on the potentiometer scale.

Kinetic data were obtained during the analysis of the reaction mixtures by liquid chromatography on a Bruker LC-31 chromatograph (IBM Cyano column, hexane—isopropyl alcohol—ethyl acetate (8 : 1 : 1, v/v/v) mixture as eluent, rate 0.4 mL min^{-1}).

Potassium 2,6-di-*tert*-butylphenoxide (ArOK). ***A.*** A flask was filled with ArOH (20.6 g, 0.1 mol), and the content was heated in an argon flow to 190 °C. Granulated 85% KOH (1.5 g) was added. After 10 min, crystals that formed were separated by high-temperature filtration under argon and washed with *n*-octane heated to 110—115 °C until the analysis to the presence of ArOH in the washings became negative. Solvent residues were removed by evacuation at 120—130 °C. Found: $M_{\min} = 260$. Calculated: $M_{\mathrm{ArOK}} = 244.28$. The IR spectrum of the synthesized sample coincides with that published earlier.[5]

B. The flask was filled with ArOH (20.6 g, 0.1 mol), and the content was heated in an argon flow to 190 °C. Granulated 85% KOH (1.5 g) was added. After 10 min, the reaction mixture

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as a suspension was cooled to ~20 °C, and heptane (50 mL) was added. The precipitate was filtered off and washed on the filter with heptane until the absence of ArOH in the washings was achieved. The yield of ArOK was 5.1 g (90%). Found: M_{min} = 480. Calculated: M_{ArOK} = 244.28. The ^{1}H NMR and IR spectra of the synthesized sample coincide with those described earlier.[5]

On cooling of the ArOK sample synthesized by method *A* to ~20 °C, the intensity of the IR bands at 1700—1300 cm^{-1} changes and the spectrum becomes identical to that of ArOK synthesized by method ***B***.

Alkylation of 2,6-di-*tert*-butylphenol with methyl acrylate in the presence of ArOK. ***A.*** Granulated 85% KOH (0.13 g, 0.002 mol) was added to ArOH (20.6 g, 0.1 mol) at 190 °C in an argon flow. After 10 min, the reaction mixture was cooled to 135 °C, and methyl acrylate (11.2 g, 0.13 mol) was added. After mixing of the reactants, the temperature of the reaction mixture was 116 °C, and this temperature was maintained during the experiment. After 40 min, the content of Ar´OH in the reaction mixture reached 98 mol.%.

B. Granulated 85% KOH (0.13 g, 0.002 mol) was added to ArOH (20.6 g, 0.1 mol) at 190 °C in an argon flow. After 10 min, the reaction mixture was cooled to 143 °C, and methyl acrylate (11.2 g, 0.13 mol) was added. After mixing of the reactants, the temperature of the reaction mixture was 125 °C, and this temperature was maintained during the experiment. After 40 min, the content of Ar´OH in the reaction mixture reached 97 mol.%.

C. Granulated 85% KOH (0.13 g, 0.002 mol) was added to ArOH (20.6 g, 0.1 mol) at 190 °C in an argon flow. After 10 min, the reaction mixture was cooled to 120 °C, and methyl acrylate (11.2 g, 0.13 mol) was added. After mixing of the reactants, the temperature of the reaction mixture was 105 °C, and this temperature was maintained during the experiment. After 40 min, the content of Ar´OH in the reaction mixture reached 96 mol.%.

D. Methyl acrylate (11 g, 0.13 mol) was added in an argon flow at 116 °C to a mixture of ArOH (20.6 g, 0.1 mol) and ArOK (0.488 g, 0.002 mol) synthesized according to method *B*. After 25 min, the content of Ar´OH in the reaction mixture was 15 mol.%. After 180 min of the reaction at 116 °C, the yield of Ar´OH reached 87%.

E. ArOH (20.6 g, 0.1 mol) was added to a solution of Bu^{t}OK (0.248 g, 0.002 mol) in Bu^{t}OH (20 mL). The solvent was distilled off *in vacuo* at 100 °C, and methyl acrylate (11.2 g, 0.13 mol) was added to the resulting suspension of ArOK in ArOH. The mixture was heated for 180 min at 116 °C with sampling and analysis of the samples to the content of ArOH and Ar´OH.

Influence of solvent additives on the catalytic alkylation of ArOH with methyl acrylate in the presence of ArOK. Granulated 85% KOH (0.13 g, 0.002 mol) was added to ArOH (20.6 g, 0.1 mol) at 190 °C in an argon flow. After 10 min, the reaction mixture was cooled to 135 °C, and methyl acrylate (11.2 g, 0.13 mol) and DMSO (0.2 mL) were added. The reactions with additives of HMPA, DMF, DME, and MeCN were carried out similarly.

Reaction of potassium 2,6-di-*tert*-butylphenoxide with methyl acrylate in the presence of methanol. Methanol (1 mL) was added at ~20 °C to a mixture of ArOK (0.25 g, 0.001 mol) in methyl acrylate (5 mL). The reaction resulted in the spontaneous heating of the reaction mixture and precipitation. According to the data of liquid chromatography, no products of Ar´OH alkylation and no methyl acrylate were found in the mother liquor. The precipitate is insoluble in acetone, toluene, and ether, which is characteristic of a methyl acrylate polymer.

Methyl acrylate oligomer. Potassium phenoxide ArOK (2.44 g, 0.01 mol) was added to methyl acrylate (33 g, 0.39 mol), and the mixture was kept for 8 days at ~20 °C. Then the mixture was neutralized with 10% HCl, extracted, and washed with heptane until the absence of ArOH in the washings was achieved. The heptane-insoluble mixture as a viscous liquid was dissolved in ether and dried over lithium hydride. After the solvent was distilled off, a thick viscous liquid soluble in acetone was formed. ^{1}H NMR (acetone-d$_6$), δ: 1.41 (s, 18 H, Bu^t); 1.82 (m, *n* (3 H), CH_2CH); 2.27 (m, *n* (4 H), CH_2CH_2); 3.62 (s, *n* (3 H), OMe); 3.64 (s, *n* (3 H), OMe); 6.32 (m, 3 H, $CH_2=CH$). M_{exp} = 12 000; M_{calc} = 12 500 (*n* = 143). The calculation was based on the ratio of integral intensities of the signals in the ^{1}H NMR spectrum from the protons of the MeO and Bu^t groups.

Results and Discussion

The quantitative data characterizing the dependence of the properties of potassium 2,6-di-*tert*-butylphenoxide (ArOK) on the method of its synthesis indicate the formation of two species: monomeric and dimeric. The interaction of 2,6-di-*tert*-butylphenol with KOH at temperatures >180 °C results in dimerization. The data of measurements of the molecular weight of ArOK in DMF indicate that the results depend on the method of synthesis of phenoxide samples. The minimum value of the molecular weight is close to that of the ArOK monomer, and the maximum value is close to the molecular weight of the dimer. The formation of dimeric associate has been found earlier[6] upon the reaction of sodium 2,6-di-*tert*-butylphenoxide with DMSO. The structure of this associate was confirmed by X-ray diffraction analysis. The IR spectrum of ArOK synthesized by the high-temperature treatment of the reaction mixture contains bands of the conjugated C=O group at 1653 and 1633 cm^{-1}. After the ArOK sample is cooled to ~20 °C, the intensity of these bands decreases with the simultaneous increase in the intensity of the band at 1601 cm^{-1}, which is characteristic of the dimeric molecular associates with the cyclohexadiene structure.[7]

The differences in the properties of two forms of ArOK are most pronounced when they are used as catalysts for the alkylation of phenol ArOH with methyl acrylate. The ArOK monomer was obtained by the reaction of KOH with ArOH at 180—190 °C and the molar ratio KOH : ArOH = 0.03—1. After the reaction mixture was cooled to 120—143 °C, methyl acrylate was added to the mixture. Under these conditions, alkylation ceases within 20—40 min to form Ar´OH in yields up to 98%. The data on the kinetics of this reaction in a temperature interval of 105—125 °C showed that the shape of the kinetic curves is temperature-independent (Fig. 1). The rate of the reaction of ArOH with methyl acrylate in the presence of the

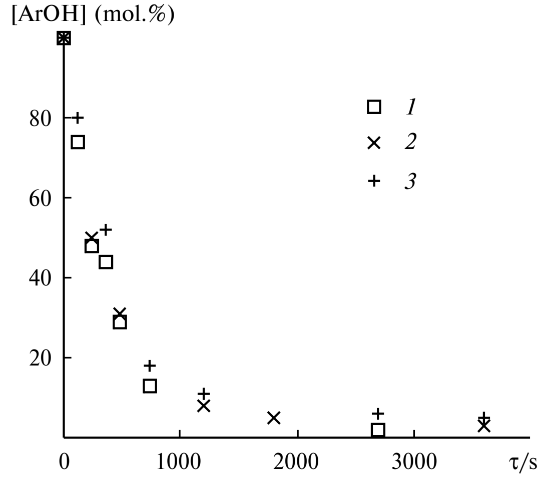


Fig. 1. Kinetic curves of the reaction of ArOH with methyl acrylate (MA) in the presence of the ArOK monomer at 125 (*1*), 116 (*2*), and 105 °C (*3*); $[ArOH]_0$ = 3.29 mol L^{-1}, $[MA]_0$ = 3.75 mol L^{-1}, and $[ArOK]_0$ = 0.08 mol L^{-1}.

ArOK dimer at 110 °C decreases, which is confirmed by the kinetics of ArOH consumption under the catalysis conditions in the presence of the ArOK monomer and dimer (Fig. 2). The shape of the kinetic curves for the alkylation of ArOH with methyl acrylate in the presence of the catalyst obtained by the reaction of 2,6-di-*tert*-butylphenol with potassium *tert*-butoxide was found to be identical to that detected for catalysis by the ArOK dimer. It is known that the polar solvents (DMSO, DMF) have earlier[8] been applied to the alkylation of phenol ArOH with methyl acrylate in the presence of the alkaline catalyst, and the yield of Ar´OH in this case was 80—85%. According to our data, the presence of polar solvents induces the inhibition of the process, and the negative influence of the solvents emerges when they are used in microamounts. Additives of the polar solvents were introduced into methyl acrylate, and these mixtures were used as reactants in the alkylation of ArOH in the presence of the ArOK monomer. We studied the kinetics of the reaction in the presence of DMSO, DMF, HMPA, DME, and MeCN. The rate of the reaction of ArOH with methyl acrylate under the catalytic alkylation conditions in the presence of these additives decreases, and the inhibition effect of the polar solvent additives increases in the following order: DMSO < HMPA < DMF < DME < MeCN. It can be assumed that these results are related to the interaction of ArOK with the polar solvent additives at a level of ion pairs or a complex, and this interaction competes with the step of formation of a transition state of molecules of phenoxide ArOK, ArOH, and methyl acrylate.

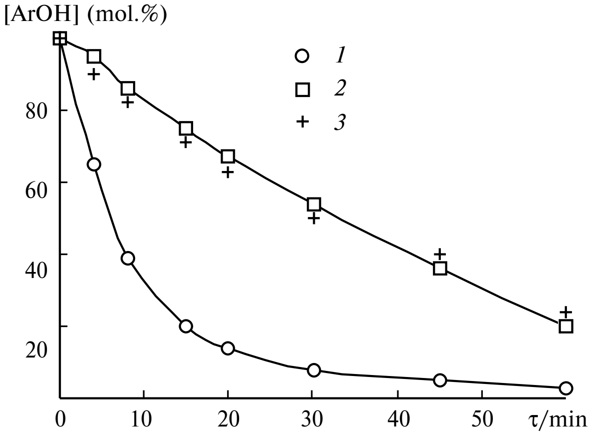


Fig. 2. Kinetic curves of the reaction of ArOH with methyl acrylate in the presence of the ArOK using methods *A* (*1*), *D* (*2*), and *E* (*3*); 116 °C, $[ArOH]_0$ = 3.29 mol L^{-1}, $[MA]_0$ = 3.75 mol L^{-1}, and $[ArOK]_0$ = 0.08 mol L^{-1}.

Taking into account the known data and present results, we can suggest the kinetic scheme for the inhibition of alkylation of phenol ArOH with methyl acrylate in the presence of the ArOK monomer and a polar solvent (Scheme 1).

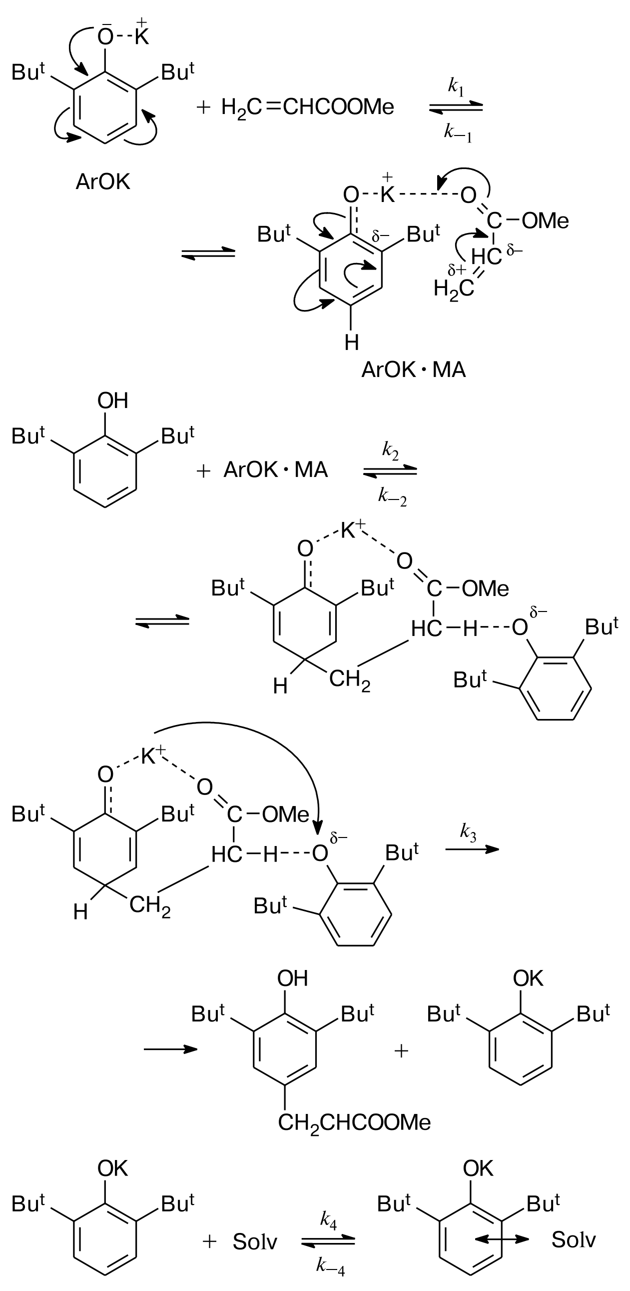
Under the assumption that $k_1 > k_{-1}$, $k_2 > k_{-2}$, $k_3 > k_1$, $k_3 > k_2$, and $[Solv]_0 = 0$, the results of calculation of the kinetic scheme coincide with the experimental data at $k_1 = 3.5 \cdot 10^{-2}$ and $k_2 = 1.5 \cdot 10^{-2}$ L mol^{-1} s^{-1}. The kinetics of inhibition of alkylation in the presence of solvent additives is shown in Fig. 3. The k_4 rate constants ($k_4 > k_{-4}$) are given below.

Reaction	$k_4 \cdot 10^{-2}$/L mol^{-1} s^{-1}
ArOK + DMSO	2.1
ArOK + HMPA	2.9
ArOK + DMF	3.5
ArOK + DME	4.2
ArOK + MeCN	9.5

Mathematical simulation was performed using the program for reaction kinetic calculation on the basis of the solution of a "rigid system" of differential equations. These regularities are characteristic of the reactions with solvent additives in the concentration comparable with that of ArOK phenoxide. According to this scheme, the formation of the Ar´OH reaction product is related to complex formation involving molecules of the ArOK monomer, phenol ArOH, and methyl acrylate and the migration of the metal cation. However, it cannot be excluded that the K^+ cation escapes to the bulk to form a kinetically independent species. In this case, the catalytic alkylation of 2,6-di-*tert*-butylphenol with methyl acrylate proceeds *via* the chain ion mechanism.

An increase in the ArOK concentration in the reaction mixture higher than the optimum value (5 mol.%) changes the character of the interaction between the reactants. The changes are associated with the activation of side reactions and the formation of methyl acrylate oligo-

Scheme 1



Solv is solvent.

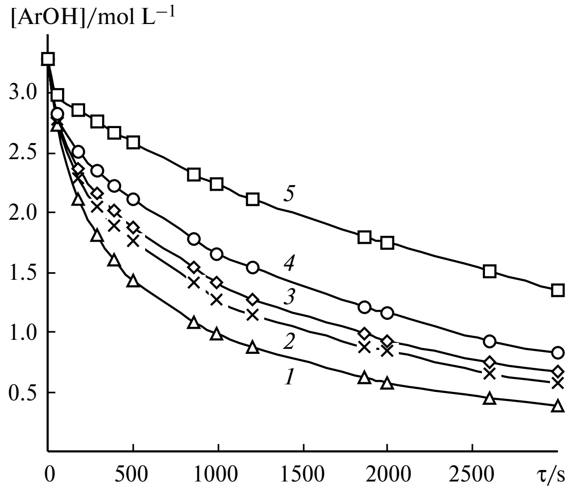


Fig. 3. Kinetic curves of ArOH consumption in the catalytic reaction with methyl acrylate in the presence of the ArOK monomer in DMSO (*1*), DMF (*2*), HMPA (*3*), DME (*4*), and MeCN (*5*) at 116 °C; $[\mathrm{ArOH}]_0$ = 3.29 mol L^{-1}, $[\mathrm{MA}]_0$ = 3.75 mol L^{-1}, $[\mathrm{ArOK}]_0$ = 0.08 mol L^{-1}, $[\mathrm{DMSO}]_0$ = 0.21 mol L^{-1}; $[\mathrm{DMF}]_0$ = 0.22 mol L^{-1}; $[\mathrm{HMPA}]_0$ = 0.19 mol L^{-1}; $[\mathrm{DME}]_0$ = 0.21 mol L^{-1}; $[\mathrm{MeCN}]_0$ = 0.24 mol L^{-1}.

mers. At the ratios ArOH : methyl acrylate > 3 and the ArOK content higher than 10 mol.%, the yield of the alkylation product (Ar´OH) is at most 25%, and the yield of methyl acrylate oligomers increases simultaneously.

Methyl acrylate oligomers were characterized by an average molecular weight of ~12 000. The ^{1}H NMR spectrum of the oligomer exhibits a narrow signal at δ 3.62 from the protons of the MeO group and a signal at δ 1.3 characteristic of the protons of the *tert*-butyl groups, which possibly indicate that an oligomer molecule contains the terminal phenol moiety. It is known**[9]** that the ^{1}H NMR spectrum of an analog of the oligomer, being the condensation product of 2,6-di-*tert*-butylphenol with three methyl acrylate molecules, contains signals of protons in the region characteristic of an oligomer with a higher content of the methyl acrylate fragments (n = 143).

The reaction of phenoxide ArOK with methyl acrylate in the presence of MeOH at room temperature affords a methyl acrylate polymer insoluble in organic solvents.

To summarize, depending on the reactant ratio and reaction conditions, potassium 2,6-di-*tert*-butylphenoxide can manifest the properties of the catalyst of both the alkylation of 2,6-di-*tert*-butylphenol (ArOH) with methyl acrylate and oligomerization. An alternative for the mechanism *via* this scheme is the chain ion mechanism involving the non-associated cation. The latter is favored by the temperature-dependent reaction kinetics and the inhibition of the alkylation by microadditives of polar solvents and the formation of methyl acrylate oligomers.

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