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# Potassium and sodium 2,6-di-*tert*-butylphenoxides and their properties

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The crucial factor of the reaction of 2,6-di-*tert*-butylphenol with alkali hydroxides is temperature, depending on which two types of potassium or sodium 2,6-di-*tert*-butylphenoxides are formed. These types exhibit different catalytic activity in the alkylation of 2,6-di-*tert*-butylphenol with methyl acrylate. More active forms of $2,6\text{-Bu}^t{}_2C_6H_3OK$ or $2,6\text{-Bu}^t{}_2C_6H_3ONa$ are synthesized at temperatures higher than 160 °C and are predominantly the monomers, which dimerize on cooling. The data of $^1H$ NMR, electronic, and IR spectra for the corresponding forms of $2,6\text{-Bu}^t{}_2C_6H_3OK$ and $2,6\text{-Bu}^t{}_2C_6H_3ONa$ isolated in the individual state are in agreement with cyclohexadienone structure. In DMSO or DMF, the dimeric forms of 2,6-di-*tert*-butylphenoxides react with methyl acrylate to form methyl 3-(4-hydroxy-3,5-di-*tert*-butylphenyl)propionate in 64—92% yield.

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

2,6-Di-*tert*-butylphenol-based compounds were often used as objects for development of theoretical concepts of the chemistry of sterically hindered phenols and for synthesis of 4-substituted phenols. Among the known reactions, those involving 2,6-di-*tert*-butylphenoxides, which are reactants or catalysts in syntheses of substances with useful properties, are poorly studied. Information on the chemistry and technology of alkylation of $2,6\text{-Bu}^t{}_2C_6H_3OH$ with methyl acrylate in the presence of potassium or sodium 2,6-di-*tert*-butylphenoxides is predominantly described in patents[1—5] indicating that $2,6\text{-Bu}^t{}_2C_6H_3OK$ and $2,6\text{-Bu}^t{}_2C_6H_3ONa$ are synthesized by the reactions of $2,6\text{-Bu}^t{}_2C_6H_3OH$ with alkali alkoxides or hydroxides at elevated temperature and reduced pressure. It is also known that at room temperature $2,6\text{-Bu}^t{}_2C_6H_3OH$ does not react with alkali hydroxides,[6] whereas at 100—140 °C the rate of this process is insufficient[7] for the preparation of 2,6-di-*tert*-butylphenoxides in the individual form due to reversibility of the process. The studied reactions of 2,6-dialkylphenoxides are described in the review[8] and publications[9—13] associated with the use of the corresponding phenoxides in the catalytic alkylation of 2,6-dialkylphenols. Despite interest in the alkylation of $2,6\text{-Bu}^t{}_2C_6H_3OH$, the data on the properties of individual phenoxides are insufficient, scanty, and contradictory. It remains unclear what compounds are formed in the reactions of $2,6\text{-Bu}^t{}_2C_6H_3OH$ with alkali alkoxides or hydroxides, and no data on the structure, properties, and reactivity of individual alkali 2,6-di-*tert*-butylphenoxides are available. In the patent[5] 2,6-di-*tert*-butylphenoxides are described as monomers, whereas other literature sources[14,15] show that some derivatives of 2,6-di-*tert*-butylphenoxides exist as dimers. Therefore, it seems of interest to reveal the true structure of $2,6\text{-Bu}^t{}_2C_6H_3OK$ and $2,6\text{-Bu}^t{}_2C_6H_3ONa$ and optimize the method of their synthesis. In the present work we continued previous studies[7] of the reactions of $2,6\text{-Bu}^t{}_2C_6H_3OH$ with potassium or sodium hydroxides at various temperatures and found that with the temperature increase from 160 to 200 °C the reaction rate becomes sufficient for the formation of water vapor as bubbles in the reaction mixture. As a result of water evaporation, the equilibrium shifts to the formation of alkali phenoxide. Under these conditions, $2,6\text{-Bu}^t{}_2C_6H_3OK$ and $2,6\text{-Bu}^t{}_2C_6H_3ONa$ are formed as crystals, which made it possible to isolate them in the individual state and study their properties. It turned out that the catalytic activities differ substantially for $2,6\text{-Bu}^t{}_2C_6H_3OK$ synthesized by the reaction of $2,6\text{-Bu}^t{}_2C_6H_3OH$ with KOH at 180—200 °C and the material obtained from $2,6\text{-Bu}^t{}_2C_6H_3OH$ and $\text{Bu}^tOK$ in $\text{Bu}^tOH$ when the solvent is removed *in vacuo* at ~100 °C.

The process at 100—140 °C produces a uniform gel-like mixture consisting of 2,6-di-*tert*-butylphenol, the corresponding phenoxide, and alkali hydroxide.

## Experimental

$^1H$ NMR spectra were recorded on a Bruker WM-400 instrument (400 MHz) in DMSO-$d_6$ (99.5%) using signals of the

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solvent as internal standard. The integral intensity from the water peak was less than 5% of the integral intensity of signals of residual protons of DMSO-$d_6$. IR spectra were obtained on a Perkin—Elmer 1725-X spectrometer in KBr pellets (resolution 2 $\mathrm{cm^{-1}}$). Electronic spectra were measured on a Shimadzu UV-3101 PC instrument. Molecular weights were determined by the thermoelectric method using a cell described previously[16] and calculated by the formula

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

where $g$ is a sample mass (g) per 100 g of solvent (2—3%), $k$ is the coefficient of the instrument and thermistors, $M_s$ is the molecular weight of a standard sample, and $t_1 - t_2$ is the value equivalent to the temperature change in the cell filled with a sample solution by the potentiometer scale. The temperature in the thermostat was 82 °C.

Kinetic data were obtained by liquid chromatography of reaction mixtures (Bruker LC-31 chromatograph, IBM Cyano column, hexane—propan-2-ol—ethyl acetate (8 : 1 : 1, v/v) mixture as the eluent, rate 0.4 mL $\mathrm{min^{-1}}$).

**Potassium 2,6-di-*tert*-butylphenoxide.** ***A.*** A flask was filled with $2,6\text{-Bu}^t{}_2C_6H_3OH$ (20.6 g, 0.1 mol) and heated under argon to 190 °C, and granulated (85%) KOH (1.5 g) was then added. After 10 min the crystals that formed were separated by high-temperature filtration under argon and washed with *n*-octane heated to 110—115 °C until no $2,6\text{-Bu}^t{}_2C_6H_3OH$ was found in the washings. Residues of the solvent were removed *in vacuo* at 120—130 °C to leave $2,6\text{-Bu}^t{}_2C_6H_3OK$ (5.3 g, 93.5%), which was placed under argon into a flask heated to 120—130 °C.

$^1$H NMR, δ: 1.30 (s, 18 H); 5.58 (t, 1 H, $J$ = 6 Hz); 6.58 (d, 2 H, $J$ = 6 Hz). $^1$H NMR spectrum of 2,6-di-*tert*-butylphenol (for comparison), δ: 1.37 (s, 18 H); 3.48 (s, 1 H); 6.74 (t, 1 H, $J$ = 8 Hz); 7.06 (d, 2 H, $J$ = 8 Hz). IR, $\nu/\mathrm{cm^{-1}}$: 1657, 1633 (—C=C—C=O, monomer); 1601 (—C=C—C=O, dimer); 1574 (—C=C—, aromatic structure) (Fig. 1, *a*). Found: $M_{\min}$ = 260. Calculated for $2,6\text{-Bu}^t{}_2C_6H_3OK$: $M$ = 244.28.

Upon heating the crystals above 220 °C they are partially decomposed with release of isobutylene. When this product is treated with 10% HCl, the LC analysis shows the presence of 2-*tert*-butylphenol.

***B.*** A flask was filled with $2,6\text{-Bu}^t{}_2C_6H_3OH$ (20.6 g, 0.1 mol) and heated under argon to 190 °C, and granulated (85%) KOH (1.5 g) was then added. After 10 min the reaction mixture as a suspension was cooled to ~20 °C, and heptane (50 mL) was added. The precipitate was filtered off and washed with heptane until no $2,6\text{-Bu}^t{}_2C_6H_3OH$ was found in the washings to leave 5.1 g (90%) of $2,6\text{-Bu}^t{}_2C_6H_3OK$. Its $^1$H NMR spectrum is identical to that recorded for the sample synthesized using method *A*. IR, $\nu/\mathrm{cm^{-1}}$: 1657, 1633 (—C=C—C=O, monomer); 1601 (—C=C—C=O, dimer); 1574 (—C=C—, aromatic structure) (Fig. 1, *b*). UV, $\lambda_{\max}$/nm (logε): 320 (3.48) (in DMSO); 317 (3.72) (in DMF). Found (%): C, 68.54; H, 8.40; K, 16.25. $C_{14}H_{21}KO$. Calculated (%): C, 68.79; H, 8.66; K, 16.00. Found: $M_{\max}$ = 480. Calculated for $2,6\text{-Bu}^t{}_2C_6H_3OK$: $M$ = 244.28.

On cooling the $2,6\text{-Bu}^t{}_2C_6H_3OK$ sample synthesized by method *A*, the intensity of the bands in the IR spectrum at 1700—1300 $\mathrm{cm^{-1}}$ changes below ~20 °C, and the spectrum becomes identical to that recorded for the sample obtained using method *B*.

**Sodium 2,6-di-*tert*-butylphenoxide** was synthesized similarly to method *B* in 86% yield. $^1$H NMR, δ: 1.30 (s, 18 H); 5.59 (t, 1 H, $J$ = 6 Hz); 6.57 (d, 2 H, $J$ = 6 Hz). IR, $\nu/\mathrm{cm^{-1}}$: 1656, 1633 (—C=C—C=O, monomer); 1601 (C=C—C=O, dimer); 1565 (—C=C—, aromatic structure). UV, $\lambda_{\max}$/nm (logε): 320 (3.55) (in DMSO); 322 (3.48) (in DMF). Found (%): C, 73.54; H, 9.40; Na, 10.25. $C_{14}H_{21}NaO$. Calculated (%): C, 73.65; H, 9.28; Na, 10.07. Found: $M_{\max}$ = 458. Calculated for $2,6\text{-Bu}^t{}_2C_6H_3ONa$: $M$ = 228.96.

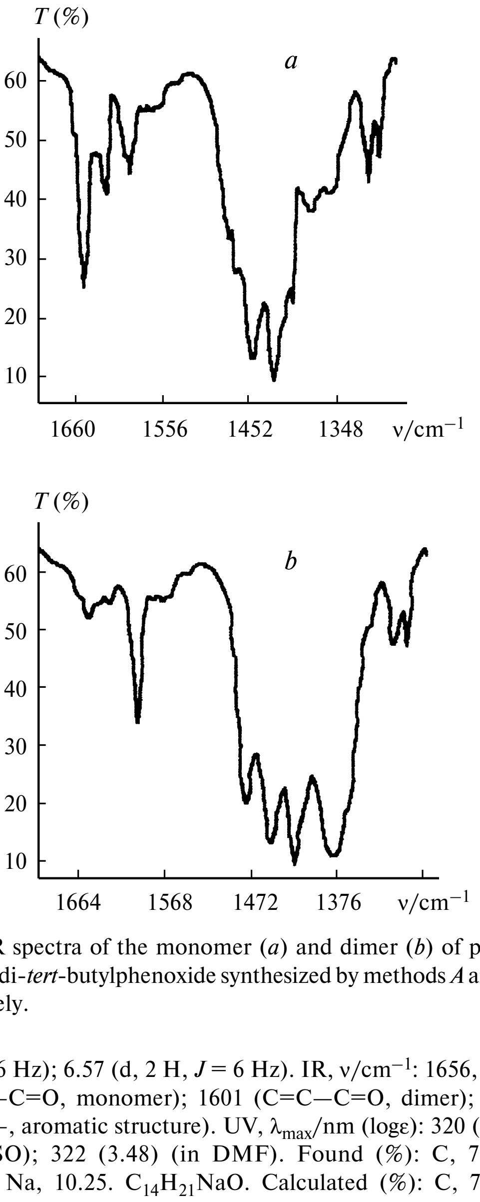

**Fig. 1.** IR spectra of the monomer (*a*) and dimer (*b*) of potassium 2,6-di-*tert*-butylphenoxide synthesized by methods *A* and *B*, respectively.

**Methyl 3-(4-hydroxy-3,5-di-*tert*-butylphenyl)propionate.** ***A.*** Methyl acrylate (2.5 mL, 0.03 mol) was added under argon to a solution of $2,6\text{-Bu}^t{}_2C_6H_3OK$ (4.88 g, 0.01 mol), which was synthesized by method *B*, in DMSO (9.4 mL) at 115 °C. After 3 h the reaction mixture was cooled to ~20 °C, 10% HCl was added to neutral pH, and the product was extracted with hexane. Methyl 3-(4-hydroxy-3,5-di-*tert*-butylphenyl)propionate was obtained in a yield of 5.16 g (88%), m.p. 66 °C (*cf.* Ref. 9: m.p. 66 °C). When DMSO was replaced with DMF, the yield of the product became 92%. When $2,6\text{-Bu}^t{}_2C_6H_3ONa$ in an equivalent amount (4.56 g) was used instead of $2,6\text{-Bu}^t{}_2C_6H_3OK$ in DMSO, the product yield was 64% (LC data).

***B.*** Granulated KOH (0.11 g, 0.002 mol) was added under argon to $2,6\text{-Bu}^t{}_2C_6H_3OH$ (20.6 g, 0.1 mol) at 190 °C. After 10 min the reaction mixture was cooled to 130 °C, and methyl acrylate (11 g, 0.13 mol) was added. After the reactants were mixed, the temperature of the reaction mixture decreased to 110 °C. After 25 min the content of the product in the reaction mixture was 98 mol.%.

***C.*** Methyl acrylate (11 g, 0.13 mol) was added under argon at 110 °C to a mixture of 2,6-$Bu^t_2C_6H_3OH$ (20.6 g, 0.1 mol) and 2,6-$Bu^t_2C_6H_3OK$ (0.488 g, 0.002 mol) synthesized by method *B*. After 25 min the content of the product in the reaction mixture became 15 mol.%, while after 3 h it reached 87%. Similarly, when 2,6-$Bu^t_2C_6H_3ONa$ (0.456 g, 0.002 mol) synthesized by method *B* was used, the product yield after 3 h was 72%.

## Results and Discussion

2,6-Di-*tert*-butylphenol does not react with alkali hydroxides at room temperature, whereas on heating to 140 °C the acid-base equilibrium is achieved with a low rate and is shifted to the starting components.[7] However, at a higher temperature (180—200 °C) the reaction rate is sufficient for the formation of water vapor as bubbles in a solution of 2,6-di-*tert*-butylphenol, which favors water removal from the reaction mixture and the shift of equilibrium. The reaction proceeds within a short time (5—10 min) and results in the formation of potassium or sodium 2,6-di-*tert*-butylphenoxide as crystals. The study of 2,6-$Bu^t_2C_6H_3OK$ and 2,6-$Bu^t_2C_6H_3ONa$ isolated in the individual state showed that they can exist as both monomers and dimers. At high temperature a monomer is formed and spontaneously transformed into a more stable dimeric form with the temperature decrease. The conclusion about the existence of two forms of the corresponding phenoxides is based on the results of measurements of the molecular weights, IR spectroscopic data, and observation of different catalytic activities in the reaction of 2,6-$Bu^t_2C_6H_3OH$ with methyl acrylate. To retain the primary properties of the monomeric forms of phenoxides (2,6-$Bu^t_2C_6H_3OK$ or 2,6-$Bu^t_2C_6H_3ONa$) from the moment of formation to the corresponding measurements, we proposed a method for conservation of a sample by storage in a vessel under argon at 120—130 °C. In the IR spectra of the samples obtained by methods *A* and *B* (monomer and dimer, respectively), the most informative is the region from 1700 to 1300 $cm^{-1}$. The IR spectra of these samples contain the characteristic bands at 1633 and 1656 $cm^{-1}$ (typical of the conjugated carbonyl group of quinolide compounds) and at 1601 $cm^{-1}$. It is known[17] that the band at 1601 $cm^{-1}$ is present in the IR spectrum of the dimer of 4-bromo-2,6-di-*tert*-butyl-4-methylcyclohexa-2,5-dienone, and it has earlier been assigned to the carbonyl group of the quinobromide compound in the dimer structure. In the IR spectra of the considered samples, the bands at 1633, 1656 $cm^{-1}$ and 1601 $cm^{-1}$ differ in intensity. For the 2,6-$Bu^t_2C_6H_3OK$ monomer the intensity of the bands at 1633, 1655 $cm^{-1}$ is much higher, whereas in the spectra of 2,6-$Bu^t_2C_6H_3OK$ the high-intensity band lies at 1601 $cm^{-1}$. The band at 1574 $cm^{-1}$, characteristic of the C=C bond of aromatic compounds,[18] has a low intensity in the spectra. The frequency region of 1475—1300 $cm^{-1}$ usually remains uninterpreted; however, it contains bands for the most part of quinolide compounds and methylene quinones. The $^1H$ NMR spectra of potassium and sodium 2,6-di-*tert*-butylphenoxides in DMSO-$d_6$ show that signals from the *meta*- and *para*-protons lie at δ 6.58 and 5.58, respectively, which corresponds to the region of olefinic protons. Compared to the spectrum of the initial 2,6-di-*tert*-butylphenol, these signals exhibit noticeable upfield shift. This result confirms that molecules of potassium and sodium 2,6-di-*tert*-butylphenoxides in solution exist in the quinolide form. The shape of the electronic spectra of dimers of potassium and sodium 2,6-di-*tert*-butylphenoxides in DMSO changes in time, which indicates, probably, the interaction of phenoxides with a polar aprotic solvent. The absorbance of the bands begins to change from the moment of preparation of the solution and continues during 4—6 h. This is accompanied by a decrease in the absorbance of the band with $\lambda_{max}$ = 320 nm and an increase in the absorbances of the bands with $\lambda_{max}$ = 260 and 481 nm, and these changes pass through the isosbestic points (Fig. 2).

It can be assumed that in a DMSO solution the 2,6-$Bu^t_2C_6H_3OK$ dimer (band with $\lambda_{max}$ = 320 nm) decomposes to form an ambidentate ion ($\lambda_{max}$ = 260 nm) and a complex with the solvent ($\lambda_{max}$ = 481 nm). The broad band with $\lambda_{max}$ = 767 nm is present in the initial spectrum of 2,6-$Bu^t_2C_6H_3OK$ and retained during transformation of the electronic spectrum with time. This fact can be related to vibrations of the metal cation in a molecule of the 2,6-$Bu^t_2C_6H_3OK$ dimer or 2,6-$Bu^t_2C_6H_3OK$ complex with the solvent. Their amplitude is sufficient for the formation of the electronic spectrum at λ = 767 nm. The time dependence of the absorbance of the band with $\lambda_{max}$ = 320—317 nm is linear and characterized by the $k_1$ constant depending on the solvent nature. Similar results were obtained for the electronic spectra of sodium 2,6-di-*tert*-butylphenoxide in DMSO and DMF solutions. The initial spectrum of the 2,6-$Bu^t_2C_6H_3ONa$ dimer contains bands with $\lambda_{max}$ = 320 nm (DMSO) and 322 nm (DMF), which undergo transformations at 478—481 nm.

Taking into account the obtained results, it seemed of interest to study regularities of the Michael reactions between the 2,6-$Bu^t_2C_6H_3OK$ and 2,6-$Bu^t_2C_6H_3ONa$ dimers and methyl acrylate in polar solvents, for instance, DMSO and DMF. It turned out that in these solvents the main direction is the addition of alkali 2,6-di-*tert*-butylphenoxides at the double bond of methyl acrylate affording methyl 3-(4-hydroxy-3,5-di-*tert*-butylphenyl)propionate. In the absence of solvent, the main direction is methyl acrylate polymerization.[11] The kinetics of the reaction of the 2,6-$Bu^t_2C_6H_3OK$ dimer with methyl acrylate was studied in DMSO and DMF solutions. Comparing the experimental and calculated data for the ki-

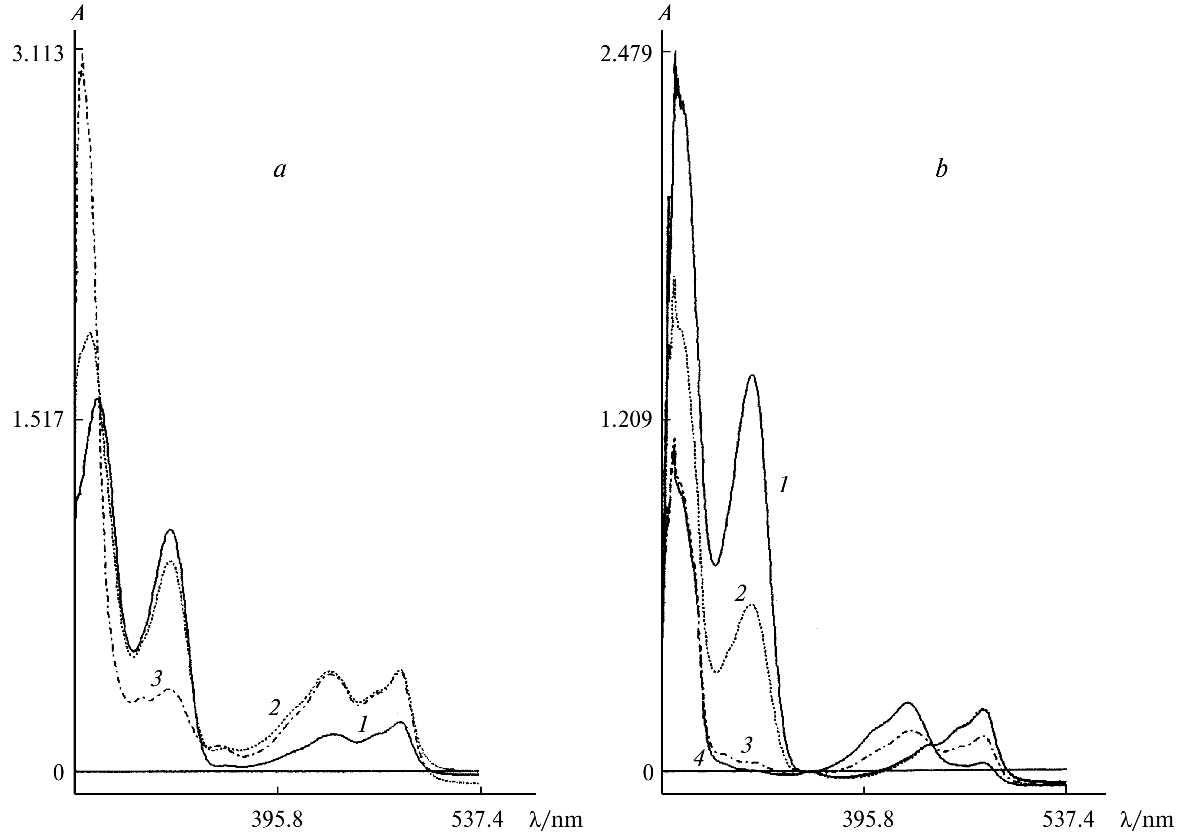

**Fig. 2.** Changes in the electronic spectra of potassium 2,6-di-*tert*-butylphenoxide in DMSO (*a*) and DMF (*b*); *a*: initial spectrum (*1*), spectrum in 48 (*2*) and 352 min (*3*) after dissolution; *b:* initial spectrum (*1*), spectrum in 37 (*2*), 118 (*3*), and 181 min (*4*) after dissolution.

netic scheme with account for the decomposition of the 2,6-$Bu^t_2C_6H_3OK$ dimer in polar solvents, we calculated the apparent rate constants ($k_2$) of the reaction of the ArOK—Solv complexes (Solv is solvent) with methyl acrylate (Scheme 1).

**Scheme 1**

$$(2,6\text{-}Bu^t_2C_6H_3OK)_2 + Solv \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$$

$$\rightleftharpoons 2\ (2,6\text{-}Bu^t_2C_6H_3OK)\text{—}Solv$$

$$2,6\text{-}Bu^t_2C_6H_3OK\text{—}Solv + MA \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}}$$

$$\rightleftharpoons 2,6\text{-}Bu^t_2C_6H_3OK\text{—}MA + Solv$$

$$2,6\text{-}Bu^t_2C_6H_3OK\text{—}MA \xrightarrow{k_3} ArOK$$

$$ArOK + H^+ \longrightarrow ArOH$$

MA is methyl acrylate, ArOH is methyl 3-(4-hydroxy-3,5-di-*tert*-butylphenyl)propionate

Using Scheme 1, we performed the mathematical simulation of the experimental kinetic data for ArOK accumulation taking into account $k_1 = 7.5 \cdot 10^{-5}\ s^{-1}$, which was determined from the plot of the decrease in the absorbance of the band with $\lambda_{max}$ = 320 nm of the 2,6-$Bu^t_2C_6H_3OK$ dimer in DMSO. The program for calculation of the reaction kinetics based on the solution of the "rigid system" of differential equations was used in mathematical simulation. The experimental data and calculated curve are shown in Fig. 3.

The results of calculation of the parameters ($k_1/s^{-1}$, $k_2$/L mol$^{-1}$ s$^{-1}$, $k_{-2}$/L mol$^{-1}$ s$^{-1}$, $k_3$) for [2,6-$Bu^t_2C_6H_3OK]_2$ (I), MA (II), and solvent (III) are given below.

| Solvent | $C_0$/mol L$^{-1}$ | | | $k_1 \cdot 10^{-4}$ | $k_2 \cdot 10^{-3}$ | $k_{-2} \cdot 10^{-5}$ | $k_3 \cdot 10^{-3}$ |
|---|---|---|---|---|---|---|---|
| | I | II | III | | | | |
| DMSO | 0.1 | 0.3 | 12 | 0.75 | 2.3 | 4 | 6 |
| DMF | 0.1 | 0.3 | 12 | 3.8 | 6.3 | 4 | 2 |

The calculation of the kinetic scheme of the reaction of methyl acrylate with 2,6-$Bu^t_2C_6H_3ONa$ and DMF gives the following reaction rate constants: $k_1 = 9.1 \cdot 10^{-4}\ s^{-1}$, $k_2 = 9.7 \cdot 10^{-4}$ L mol$^{-1}$ s$^{-1}$, $k_{-2} = 7.4 \cdot 10^{-4}$ L mol$^{-1}$ s$^{-1}$, and $k_3 = 8.2 \cdot 10^{-3}$.

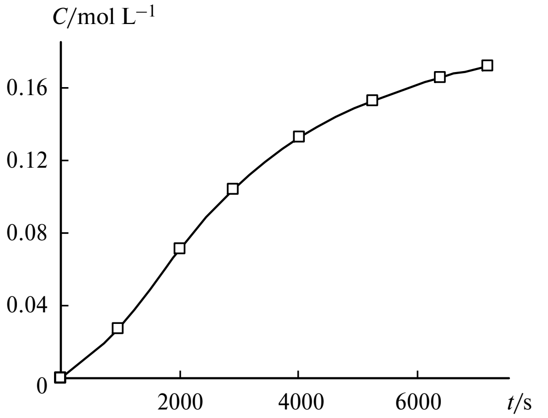

**Fig. 3.** Experimental data (points) and results of calculation (curve) of the kinetics of formation of potassium derivative of methyl 3-(4-hydroxy-3,5-di-*tert*-butylphenyl)propionate in the reaction of the potassium 2,6-di-*tert*-butylphenoxide dimer with methyl acrylate in DMSO; *C* is the concentration of potassium derivative of methyl 3-(4-hydroxy-3,5-di-*tert*-butylphenyl)propionate; $[(2,6\text{-Bu}^t{}_2C_6H_3OK)_2]_0$ = 0.01 mol L$^{-1}$, $[MA]_0$ = 0.3 mol L$^{-1}$, $[DMSO]_0$ = 12 mol L$^{-1}$, 115 °C.

Alkali 2,6-di-*tert*-butylphenoxides can add at methyl acrylate as stoichiometric reactants. It was of interest to study their ability to catalyze the addition of $2,6\text{-Bu}^t{}_2C_6H_3OH$ at methyl acrylate. It turned out that the catalytic properties of 2,6-di-*tert*-butylphenoxides in this reaction depend on the method of their preparation (method *A* or *B*). The $2,6\text{-Bu}^t{}_2C_6H_3OK$ dimer (method *B*) is similar in catalytic activity to the potassium *tert*-butoxide treated 2,6-di-*tert*-butylphenol, whereas the $2,6\text{-Bu}^t{}_2C_6H_3OK$ monomer (method *A*) is most efficient of the earlier known catalysts. When the content of the $2,6\text{-Bu}^t{}_2C_6H_3OK$ monomer is 1.5—3.0 mol.% of the content of $2,6\text{-Bu}^t{}_2C_6H_3OH$ at 110—115 °C, the reaction is completed within 15—20 min to form ArOH in up to 98% yield (Fig. 4, *a*). Under similar conditions, the use of potassium 2,6-di-*tert*-butylphenoxide synthesized *in situ* from $2,6\text{-Bu}^t{}_2C_6H_3OH$ and potassium *tert*-butoxide (>5 mol.%) makes the reaction to proceed within 2.5—3 h to form ArOH in a yield of at most 85% (Fig. 4, *b*). The catalytic properties of the monomeric forms of $2,6\text{-Bu}^t{}_2C_6H_3ONa$ and $2,6\text{-Bu}^t{}_2C_6H_3OK$ are similar, whereas the reaction of $2,6\text{-Bu}^t{}_2C_6H_3OH$ with methyl acrylate in the presence of the $2,6\text{-Bu}^t{}_2C_6H_3ONa$ dimers proceeds with a lower rate.

In summary, we found that the catalytic properties of potassium (sodium) 2,6-di-*tert*-butylphenoxides depend on the temperature of treatment of 2,6-di-*tert*-butylphenol with alkali hydroxides. Methyl 3-(4-hydroxy-3,5-di-*tert*-butylphenyl)propionate is formed predominantly in the reaction of the $2,6\text{-Bu}^t{}_2C_6H_3OK$ or $2,6\text{-Bu}^t{}_2C_6H_3ONa$ dimer with methyl acrylate in DMSO and DMF solutions. The results obtained indicate that charge separation with electron density distribution between the O atom and C atoms of the cyclohexadienone structure can occur in potassium (sodium) 2,6-di-*tert*-butylphenoxide molecules. A consequence of polarization of phenoxide molecules is their capability of dimerizing and interacting with metal cations through double bonding with the O and C atoms of the six-membered ring involving two phenoxide molecules. As follows from the atomic model of the dimer (Fig. 5), the oxygen and metal atoms are spatially shielded by the *tert*-butyl substituents, and their intramolecular arrangement favors the interaction of the metal cations with the O and C atoms of two six-membered rings. The monomeric form of $2,6\text{-Bu}^t{}_2C_6H_3OK$ or $2,6\text{-Bu}^t{}_2C_6H_3ONa$ phenoxides is presented by the nonassociated, more reactive metal cation, which predetermines their higher catalytic properties.

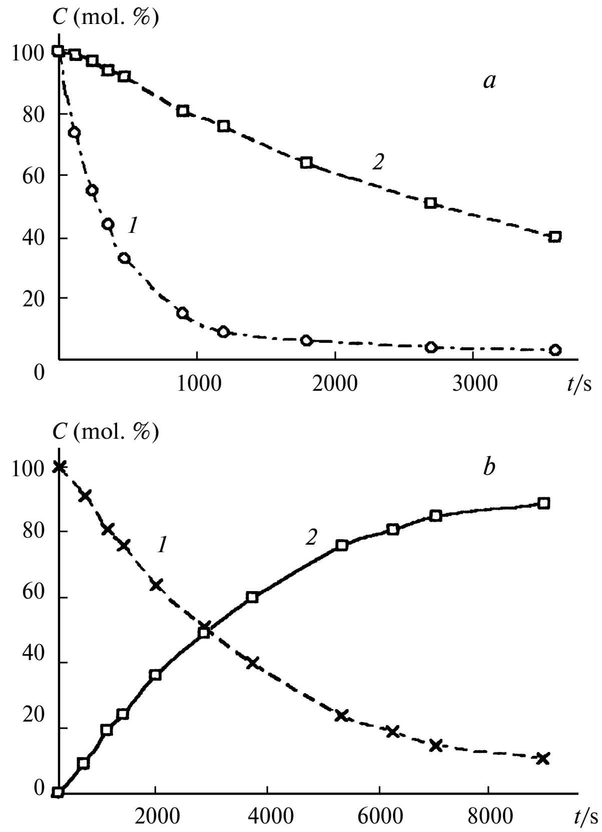

**Fig. 4.** Kinetics of consumption of $2,6\text{-Bu}^t{}_2C_6H_3OH$ in the catalytic reaction with methyl acrylate in the presence of the monomer and dimer of $2,6\text{-Bu}^t{}_2C_6H_3OK$ (*a*) and $2,6\text{-Bu}^t{}_2C_6H_3OK$ synthesized from $2,6\text{-Bu}^t{}_2C_6H_3OH$ and Bu$^t$OK (*b*); *a*: *1*, monomer; $[ArOH]_0$ = 3.29 mol L$^{-1}$, $[MA]_0$ = 3.75 mol L$^{-1}$, $[ArOK]_0$ = 0.066 mol L$^{-1}$, 115 °C; *2*, dimer; the $(2,6\text{-Bu}^t{}_2C_6H_3OK)_2$ dimer synthesized from $2,6\text{-Bu}^t{}_2C_6H_3OH$ and KOH at 190 °C and isolated at 20 °C, temperature of alkylation at 115 °C; $[ArOH]_0$ = 3.29 mol L$^{-1}$, $[MA]_0$ = 3.75 mol L$^{-1}$, $[(ArOK)_2]_0$ = 0.05 mol L$^{-1}$; *b*: *1*, kinetics of consumption of $2,6\text{-Bu}^t{}_2C_6H_3OH$; *2*, kinetics of formation of methyl 3-(4-hydroxy-3,5-di-*tert*-butylphenyl)propionate.

**Fig. 5.** Atomic model of the alkali 2,6-di-*tert*-butylphenoxide dimer.

*Note*. Fig. 5 is available in full color in the on-line version of the journal (http://www.springerlink.com/issn/1573-9171/current) and on the web-site of the journal (http://russchembull.ru).

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