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POTASSIUM AND SODIUM 2,6-DI-*TERT*-BUTYL PHENOXIDES AND THEIR PROPERTIES

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Absract. The determining factor of the reaction of 2,6-di-*tert*-butylphenol with alkaline metal hydroxides is temperature, depending on which two types of potassium or sodium 2,6-di-*tert*-butyl phenoxides are formed with different catalytic activity in alkylation of 2,6-di-*tert*-butylphenol with methyl acrylate. More active forms of 2,6-$Bu^t_2C_6H_3OK$ or 2,6-$Bu^t_2C_6H_3ONa$ are synthesized at temperatures higher than 433 K representing predominantly monomers of 2,6-di-tert-butylphenoxides which produce dimers when cooling. The data of NMR ^{1}H, electronic, and IR spectra for the corresponding forms of 2,6-$Bu^t_2C_6H_3OK$ and 2,6-$Bu^t_2C_6H_3ONa$ isolated in the individual state showed a cyclohexadienone structure. In DMSO or DMF media 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 with 64–92 % yield.

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

1. Introduction

Compounds based on 2,6-di-*tert*-butylphenol were often used as objects of studies for development of theoretical concepts of sterically hindered phenols chemistry and for synthesis of 4-substituted phenols. Among the known reactions, those involving 2,6-di-*tert*-butyl phenoxides, which are reactants and catalysts in syntheses of substances with useful properties, have been poorly studied. Information on chemistry and technology of alkylation of 2,6-$Bu^t_2C_6H_3OH$ with methyl acrylate in the presence of potassium or sodium 2,6-di-*tert*-butyl phenoxides is predominantly concentrated in patents [1-5] from which it follows that 2,6-$Bu^t_2C_6H_3OK$ and 2,6-$Bu^t_2C_6H_3ONa$ are synthesized by the reactions of 2,6-$Bu^t_2C_6H_3OH$ with alkaline metal alkoxides or hydroxides at elevated temperature in vacuum. It is also known that at room temperature 2,6-$Bu^t_2C_6H_3OH$ does not react with alkaline metalhydroxides [6], whereas at 273–413 K the rate of this process is insufficient [7] for the preparation of 2,6-di-*tert*-butyl phenoxides in the individual form due to reversibility of the process. The studied reactions of 2,6-dialkyl phenoxides 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 the interest in alkylation of 2,6-$Bu^t_2C_6H_3OH$, 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-$Bu^t_2C_6H_3OH$ with alkaline metal alkoxides or hydroxides, and no data on the structure, properties, and reactivity of individual alkaline metal 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-$Bu^t_2C_6H_3OK$ and 2,6-$Bu^t_2C_6H_3ONa$ and optimize the method of their synthesis. In the present work we proceed with previous studies [7] of the reactions of 2,6-$Bu^t_2C_6H_3OH$ with potassium or sodium hydroxides at different temperatures and found that with the temperature increase from 433 to 473 K the reaction rate becomes sufficient for the formation of steam as bubbles in the reaction mixture. As a result of water evaporation, the equilibrium shifts to the formation of alkaline metal phenoxide. Under these conditions, 2,6-$Bu^t_2C_6H_3OK$ and 2,6-$Bu^t_2C_6H_3ONa$ are formed as crystals, which make it possible to isolate them in the individual state and study their properties. It turns out that the catalytic activities differ substantially for 2,6-$Bu^t_2C_6H_3OK$ synthesized by the reaction of 2,6-$Bu^t_2C_6H_3OH$ with KOH at 453–473 K and the material obtained from 2,6-$Bu^t_2C_6H_3OH$ and

Bu^{t}OK in Bu^{t}OH when the solvent is removed in vacuum at ~373 K. The process at 373–413 K produces a uniform gel-like mixture consisting of 2,6-di-*tert*-butylphenol, the corresponding phenoxide, and alkaline metal hydroxide.

2. Experimental

NMR ^{1}H spectra were recorded on a Bruker WM-400 instrument (400 MHz) in DMSO-d$_6$ (99.5 %) signals of the solvent as internal standard. The integral intensity from the water peak was less than 5 % of the integral intensity of residual protons of DMSO-d$_6$ signals. IR spectra were obtained on a Perkin-Elmer 1725-X spectrometer in KBr pellets (resolution 2 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:

$$M = \frac{k \cdot g \cdot M_s}{100(t_1 - t_2)}$$

where g is a weighed sample 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 355 K. Kinetic data were obtained by liquid chromatography of reaction mixtures (Bruker LC-31 chromatograph, IBM Cyano column, hexane-isopropyl alcohol ethyl acetate (8 : 1 : 1, v/v) mixture as eluent, rate 0.4 ml·min^{-1}).

2.1. Potassium 2,6-Di-*tert*-Butyl Phenoxide

A. A flask was filled with 2,6-Bu$^t_2$C$_6$H$_3$OH (20.6 g, 0.1 mol) and heated in an argon flow to 463 K, and granulated (85 %) KOH (1.5 g) was added. After 10 min the crystals that formed were separated by high-temperature filtration under argon and washed with *n*-octane heated to 383–388 K until no 2,6-Bu$^t_2$C$_6$H$_3$OH was found in the mother liquor. Residues of the solvent were separated in vacuum at 393–403 K to obtain 2,6-Bu$^t_2$C$_6$H$_3$OK (5.3 g, 93.5 %), which was placed under argon into a flask heated to 393–403 K. NMR ^{1}H, *d*: 1.30 (s, 18 H); 5.58 (t, 1 H, J = 6 Hz); 6.58 (d, 2 H, J = 6 Hz). NMR ^{1}H spectrum of 2,6-di-*tert*-butylphenol (for comparison), *d*: 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, v/cm^{-1}: 1657, 1633 (—C=C—C=O, monomer); 1601 (—C=C—C=O, dimer); 1574 (—C=C—, aromatic structure) (Fig. 1a). Found: M_{min} = 260. Calculated for 2,6-Bu$^t_2$C$_6$H$_3$OK: M = =244.28.Upon heating the crystals above 493 K they are

partially decomposed with the 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-Bu$^t_2$C$_6$H$_3$OH (20.6 g, 0.1 mol) and heated in an argon flow to 463 K, and granulated (85 %) KOH (1.5 g) was added. After 10 min the reaction mixture as a suspension was cooled to ~293 K, and heptane (50 ml) was added. The precipitate was filtered off and washed with heptane until no 2,6-Bu$^t_2$C$_6$H$_3$OH was found in the washing solutions to obtain 5.1 g (90 %) of 2,6-Bu$^t_2$C$_6$H$_3$OK. Its NMR ^{1}H spectrum is identical to that recorded for the sample synthesized using method A. IR, v/cm^{-1}: 1657, 1633 (—C=C—C=O, monomer); 1601 (—C=C—C=O, dimer); 1574 (—C=C—, aromatic structure) (Fig. 1b). UV, l_{max}/nm (logε): 320 (3.48) (DMSO solvent); 317 (3.72) (DMF solvent). 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-Bu$^t_2$C$_6$H$_3$OK: M = 244.28. When cooling the 2,6-Bu$^t_2$C$_6$H$_3$OK sample synthesized by method A, the intensity of the bands in the IR spectrum at 1700–1300 cm^{-1} changes below ~293 K, and the spectrum becomes identical to that recorded for the sample obtained using method B.

2.2. Sodium 2,6-Di-*tert*-Butylphenoxide

Sodium 2,6-di-tert-butylphenoxide was synthesized similarly to method B with 86 % yield. NMR ^{1}H, *d*: 1.30 (s, 18 H); 5.59 (t, 1 H, J = 6 Hz); 6.57 (d, 2 H, J = 6 Hz). IR, v/cm^{-1}: 1656, 1633 (—C=C—C=O, monomer); 1601 (C=C—C=O, dimer); 1565 (—C=C—, aromatic structure). UV, l_{max}/nm (logε): 320 (3.55) (solvent DMSO); 322 (3.48) (solvent 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-Bu$^t_2$C$_6$H$_3$ONa: M = 228.96.

2.3. Methyl 3-(4-Hydroxy-3,5-Di-*tert*-Butylphenyl) Propionate

A. Methyl acrylate (2.5 ml, 0.03 mol) was added in an argon flow to a solution of 2,6-Bu$^t_2$C$_6$H$_3$OK (4.88 g, 0.01 mol), which was synthesized by method B, in DMSO (9.4 ml) at 388 K. After 3 h the reaction mixture was cooled to ~293 K, 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 with the yield of 5.16 g (88 %), m.p. 339 K (cf. [9]: m.p. 388 K). When DMSO was replaced with DMF, the yield of the product became 92 %. When 2,6-Bu$^t_2$C$_6$H$_3$ONa in an equivalent amount (4.56 g) was used instead of 2,6-Bu$^t_2$C$_6$H$_3$OK in DMSO, the product yield was 64 % (LC data).
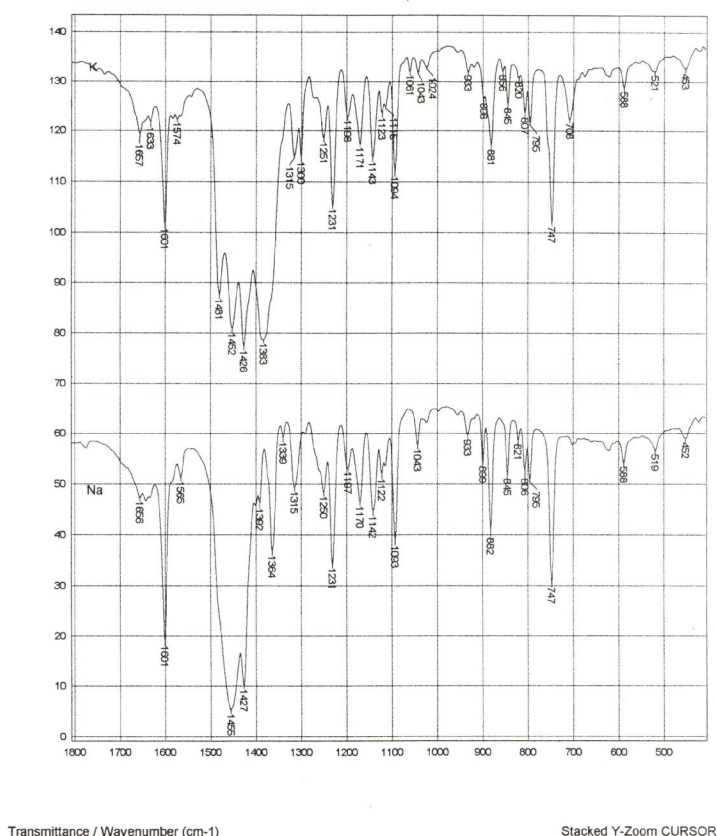
Fig. 1. IR spectra of the monomer and dimer of potassium 2,6-di-*tert*-butyl phenoxide synthesized by methods A and B, respectively

B. Granulated KOH (0.11 g, 0.002 mol) was added in an argon flow to 2,6-Bu$^t_2$C$_6$H$_3$OH (20.6 g, 0.1 mol) heated to 463 K. After 10 min the reaction mixture was cooled to 403 K, and methyl acrylate (11 g, 0.13 mol) was added. After the reactants were mixed, the temperature of the reaction mixture decreased to 383 K. 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 in an argon flow at 383 K to a mixture of 2,6-Bu$^t_2$C$_6$H$_3$ OH (20.6 g, 0.1 mol) and 2,6-Bu$^t_2$C$_6$H$_3$OK (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$^t_2$C$_6$H$_3$ONa (0.456 g, 0.002 mol) synthesized by method B was used, the product yield after 3 h became 72 %.

3. Results and Discussion

2,6-Di-*tert*-butylphenol does not react with alkaline metal hydroxides at room temperature, whereas on heating to 413 K the acid-base equilibrium is achieved with a low rate and shifts to the initial components [7]. However, at higher temperatures (453–473 K) the reaction rate is sufficient for steam bubbles to form in a solution of 2,6-di-*tert*-butylphenol, which favors their removal from the reaction mixture and the shift of equilibrium. The reaction proceeds within a short time (5–10 min) and is accompanied by the formation of potassium or sodium 2,6-di-*tert*-butyl phenoxide as crystals. The study of 2,6-Bu$^t_2$C$_6$H$_3$OK and 2,6-Bu$^t_2$C$_6$H$_3$ONa isolated in the individual state found 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$^t_2$C$_6$H$_3$OH with methyl acrylate. To retain the primary properties of the monomeric forms of 2,6-Bu$^t_2$C$_6$H$_3$OK or 2,6-Bu$^t_2$C$_6$H$_3$ONa phenoxides from the moment of formation to the corresponding measurements, we proposed a method for conservation of a sample by storage in a flask under argon at 393–403 K. 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} containing 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.
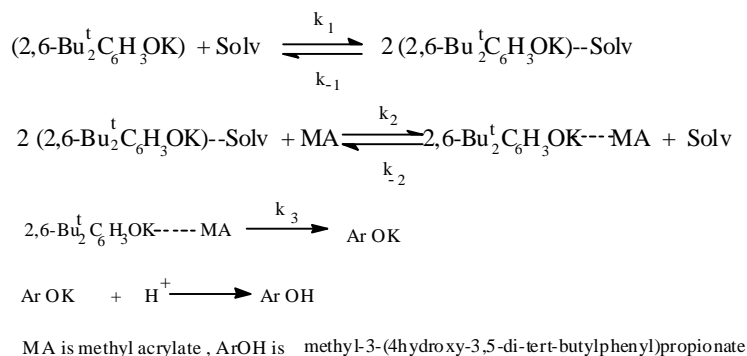
In the IR spectra of the considered samples, the bands at 1633, 1656 and 1601 cm^{-1} differ in intensity. For 2,6-Bu$^t_2$C$_6$H$_3$OK monomer the intensity of the bands at 1633, 1655 cm^{-1} is much higher, whereas in the spectra of 2,6-Bu$^t_2$C$_6$H$_3$OK the high-intensity band lies at 1601 cm^{-1}. The band at 1574 cm^{-1}, which belongs to 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 NMR ^{1}H spectra of potassium and sodium 2,6-di-*tert*-butyl phenoxides in DMSO-d$_6$ show that signals from the *meta*- and *para*-protons lie at $d = 6.58$ 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*-butyl phenoxides in solution exist in the quinolide form. The shape of the electronic spectra of dimers of potassium and sodium 2,6-di-*tert*-butyl phenoxides 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 the solution preparation and continues during 4–6 h. This is accompanied by a decrease in the absorbance of the band with $l_{max} = 320$ nm and an increase in the absorbances of the bands with $l_{max} = 260$ and 481 nm, and these changes pass through the isosbestic points (Fig. 2). It can be assumed that in DMSO solution 2,6-Bu$^t_2$C$_6$H$_3$OK dimer (band with $l_{max} = 320$ nm) decomposes to form an ambidentate ion ($l_{max} = 260$ nm) and a complex with the solvent ($l_{max} = 481$ nm). The broad band with $l_{max} = 767$ nm is present in the initial spectrum of 2,6-Bu$^t_2$C$_6$H$_3$OK and retains during transformation of the electronic spectrum with time. This fact can be related to vibrations of the metal cation in a molecule of 2,6-Bu$^t_2$C$_6$H$_3$OK dimer or 2,6-Bu$^t_2$C$_6$H$_3$OK complex with the solvent. Their amplitude is sufficient for the formation of the electronic spectrum at $l = 767$ nm. The time dependence of the absorbance of the band with $l_{max} = 320$–317 nm is linear and characterized by the k_l constant depending on the solvent nature.
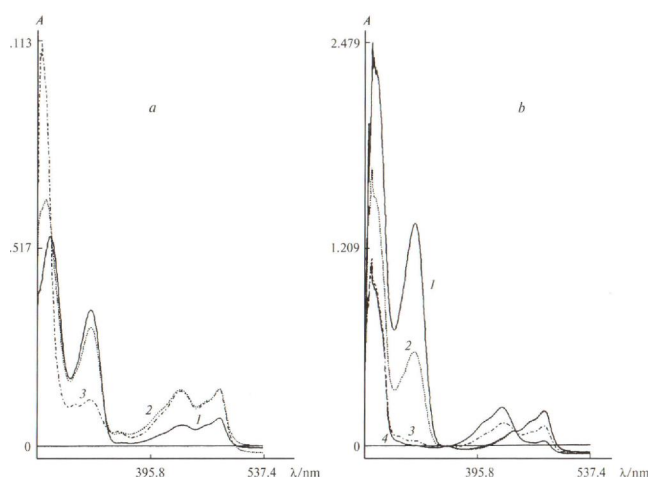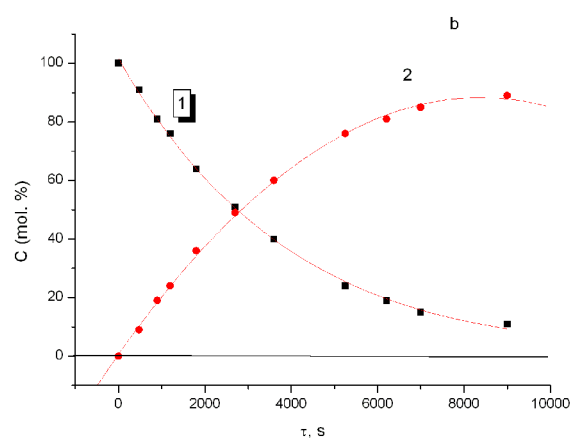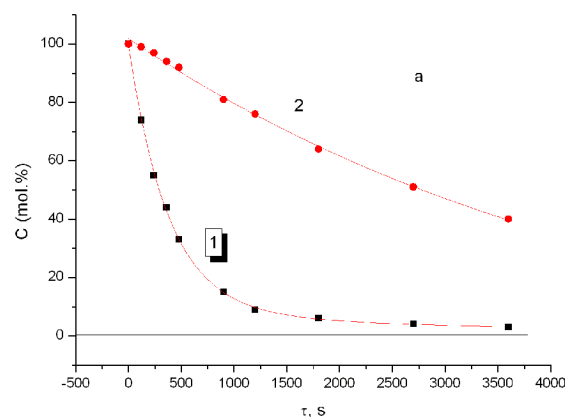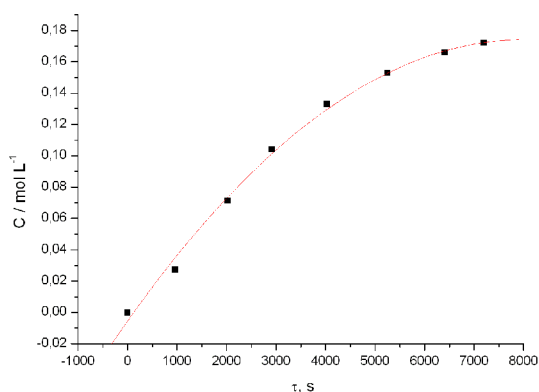

Fig. 2. Changes in the electronic spectra of potassium 2,6-di-*tert*-butyl phenoxide in solutions of DMSO (a) and DMF (b); a: initial spectrum (1), spectrum in 48 (2) and 352 min (3) after dissolution; b: initial spectrum (1), spectrum in 37 (2), 118 (3), and 181 min (4) after dissolution

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$^t_2$C$_6$H$_3$ONa dimer contains bands with $l_{max} = 320$ 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 2,6-Bu$^t_2$C$_6$H$_3$OK and 2,6-Bu$^t_2$C$_6$H$_3$ONa dimers and methyl acrylate in polar solvents, for instance, DMSO and DMF. It turned out that in these solvents the main direction is the reaction of alkaline metal 2,6-di-tert-butyl phenoxides with 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 2,6-Bu$^t_2$C$_6$H$_3$OK dimer with methyl acrylate was studied in DMSO and DMF solutions. Comparing the experimental and calculated data for the kinetic scheme with account for the decomposition of 2,6-Bu$^t_2$C$_6$H$_3$OK dimer in polar solvents, we calculated the apparent rate constants (k_2) of the reaction of ArOK–Solv complexes (Solv is solvent) with methyl acrylate (Scheme 1).

Using Scheme 1, we performed the mathematical simulation of the experimental kinetic data for ArOK accumulation taking into account $k_l = 7.5 \cdot 10^{-5}$ s^{-1}, which was determined from the plot of the decrease in the absorbance of the band with $l_{max} = 320$ nm of 2,6-Bu$^t_2$C$_6$H$_3$OK 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.

$$(2,6\text{-Bu}^t_2\text{C}_6\text{H}_3\text{OK}) + \text{Solv} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\,(2,6\text{-Bu}^t_2\text{C}_6\text{H}_3\text{OK})\text{--Solv}$$

$$2\,(2,6\text{-Bu}^t_2\text{C}_6\text{H}_3\text{OK})\text{--Solv} + \text{MA} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 2,6\text{-Bu}^t_2\text{C}_6\text{H}_3\text{OK}\text{---MA} + \text{Solv}$$

$$2,6\text{-Bu}^t_2\text{C}_6\text{H}_3\text{OK}\text{----MA} \overset{k_3}{\longrightarrow} \text{Ar OK}$$

$$\text{Ar OK} + \text{H}^+ \longrightarrow \text{Ar OH}$$

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

Scheme 1

Fig. 3. Experimental data (points) and results of calculation (curve) of the kinetics of formation of potassium methyl 3-(4-hydroxy-3,5-di-*tert*-butylphenyl) propionate in the reaction of the potassium 2,6-di-*tert*-butyl phenoxide dimer with methyl acrylate in DMSO solution; *C* is the concentration of potassium methyl 3-(4-hydroxy-3,5-di-*tert*-butylphenyl) propionate;
$[(2,6\text{-Bu}^t_2\text{C}_6\text{H}_3\text{OK})_2]_0 = 0.01$ mol·l⁻¹,
$[\text{MA}]_0 = 0.3$ mol·l⁻¹, $[\text{DMSO}]_0 = 12$ mol·l⁻¹, 388 K

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 and k_3) for [2,6-Bu$^t_2$C$_6$H$_3$OK]$_2$ (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$^t_2$C$_6$H$_3$ONa and DMF gives the following reaction rate constants: $k_1 = 9.1 \cdot 10^{-4}$·s⁻¹, $k_2 = 9.7 \cdot 10^{-4}$, $k_{-2} = 7.4 \cdot 10^{-4}$ l·mol⁻¹·s⁻¹, and $k_3 = 8.2 \cdot 10^{-3}$. Alkaline metal 2,6-di-tert-butyl phenoxides can be added to methyl acrylate as stoichiometric reactants. It was of interest to use them as catalysts of the reactions of 2,6-Bu$^t_2$C$_6$H$_3$OH with methyl acrylate. It turned out that the catalytic properties of 2,6-di-*tert*-butyl phenoxides in this
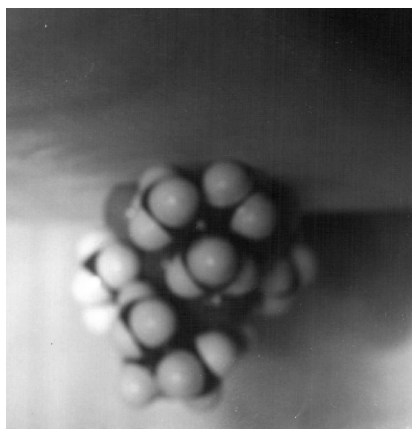

Fig. 4. Kinetics of consumption of 2,6-Bu$^t_2$C$_6$H$_3$OH in the catalytic reaction with methyl acrylate in the presence of the monomer and dimer of 2,6-Bu$^t_2$C$_6$H$_3$OK (a) and 2,6-Bu$^t_2$C$_6$H$_3$OK synthesized from 2,6-Bu$^t_2$C$_6$H$_3$OH and Bu^{t}OK (b)
a: 1 – monomer; $[\text{ArOH}]_0 = 3.29$ mol·l⁻¹,
$[\text{MA}]_0 = 3.75$ mol·l⁻¹, $[\text{ArOK}]_0 = 0.066$ mol·l⁻¹, 388 K;
2 – dimer; (2,6-Bu$^t_2$C$_6$H$_3$OK)$_2$ dimer synthesized from 2,6-Bu$^t_2$C$_6$H$_3$OH and KOH at 463 K and isolated at 293 K, temperature of alkylation 388 K; $[\text{ArOH}]_0 = 3.29$ mol·l⁻¹,
$[\text{MA}]_0 = 3.75$ mol·l⁻¹, $[(\text{ArOK})_2]_0 = 0.05$ mol·l⁻¹;
b: 1 – kinetics of consumption of 2,6-Bu$^t_2$C$_6$H$_3$OH;
2 – kinetics of formation of methyl 3-(4-hydroxy-3,5-di-*tert*-butylphenyl) propionate

reaction depend on the method of their preparation (method A or B). 2,6-Bu$^t_2$C$_6$H$_3$OK dimer (method B) is similar in catalytic activity to the product of the reaction of 2,6-di-*tert*-butylphenol with potassium *tert*-butoxide, whereas 2,6-Bu$^t_2$C$_6$H$_3$OK monomer (method A) is the most efficient between known catalysts. When the content of 2,6-Bu$^t_2$C$_6$H$_3$OK monomer is 1.5–3.0 mol % of the content of 2,6-Bu$^t_2$C$_6$H$_3$OH at 383–388 K, the reaction ceases within 15–20 min to form ArOH with up to 98 % yield (Fig. 4a). Under similar conditions, the reaction of potassium 2,6-di-tert-butyl phenoxide synthesized *in situ* from 2,6-Bu$^t_2$C$_6$H$_3$OH and potassium tert-butoxide (> 5 mol %) proceeds within 2.5–3 h to form ArOH with the yield of at most 85 % (Fig. 4b). The catalytic properties of the monomeric forms of 2,6-Bu$^t_2$C$_6$H$_3$ONa and 2,6-Bu$^t_2$C$_6$H$_3$OK are similar, whereas the reaction of 2,6-Bu$^t_2$C$_6$H$_3$OH with methyl acrylate in the presence of 2,6-Bu$^t_2$C$_6$H$_3$ONa dimers proceeds with a lower rate.

Conclusions

Thus, we found that the catalytic properties of potassium (sodium) 2,6-di-*tert*-butyl phenoxides depend on the temperature of their synthesis by the reaction of 2,6-di-*tert*-butylphenol with alkaline metal hydroxides. Methyl 3-(4-hydroxy-3,5-di-*tert*-butylphenyl) propionate is formed predominantly in the reaction of 2,6-Bu$^t_2$C$_6$H$_3$OK or 2,6-Bu$^t_2$C$_6$H$_3$ONa dimer with methyl acrylate in DMSO and DMF solutions. The data obtained indicate, possibly, that charge separation with electron density distribution between the O atom and C atoms of the cyclohexadienone structure occurs in a molecule of potassium and sodium 2,6-di-*tert*-butyl phenoxides. A consequence of polarization of phenoxide molecules is their capability of dimerizing and interacting with metal cations through double bonding with 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 O and C atoms of two six-membered rings. The monomeric form of 2,6-Bu$^t_2$C$_6$H$_3$OK or 2,6-Bu$^t_2$C$_6$H$_3$ONa phenoxides is presented by the nonassociated, more reactive metal cation, which just predetermines their higher catalytic properties.

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Fig. 5. Atomic model of the alkaline metal 2,6-di-*tert*-butyl phenoxide dimer

2,6-ДИ-ТРЕТ-БУТИЛФЕНОЛЯТИ КАЛІЮ І НАТРІЮ ТА ЇХ ВЛАСТИВОСТІ

Анотація. *Показано, що вирішальним чинником реакції 2,6-ди-трет-бутилфенолу з лужними металами є температура, в залежності від якої утворюються два типи 2,6-ди-трет-бутилфенолятів калію або натрію з різною каталітичною активністю в реакціях алкілування 2,6-ди-трет-бутил фенолу з метилакрилатом. При температурах вищих за 433 К синтезовано більш активні форми 2,6-Bu$^t_2$C$_6$H$_3$OK або 2,6-Bu$^t_2$C$_6$H$_3$ONa. Циклогексадієнову структуру 2,6-Bu$^t_2$C$_6$H$_3$OK і 2,6-Bu$^t_2$C$_6$H$_3$ONa підтверджено методами ЯМР ^{1}H електронної та IЧ-спектроскопії. Визначено, що у середовищі диметилформаміду або диметилсульфоксиду димерні форми 2,6-ди-трет-бутилфенолу реагують з метилакрилатом з утворенням метил 3-(4-гідрокси-3,5-ди-трет-бутилфенил)пропіонату, вихід якого становить 64–92 %.*

Ключові слова*: феноли, феноляти, 2,6-ди-трет-бутилфенол, метилакрилат, кінетика, димери, гідроксид калію, гідроксид натрію.*