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Formation and properties of a catalyst based on sodium and potassium hydroxides in the reaction of 2,6-di-*tert*-butylphenol with methyl acrylate

A. A. Volod´kin*★ and G. E. Zaikov

N. M. Emanuel´ Institute of Biochemical Physics, Russian Academy of Sciences,
4 ul. Kosygina, 119991 Moscow, Russian Federation.
Fax: +7 (095) 137 4101. E-mail: chembio@glasnet.ru

The nature of the cation (K^+ or Na^+) in hydroxides affects the temperature plot of the equilibrium constant of the reaction of KOH and NaOH with 2,6-di-*tert*-butylphenol (ArOH) and the conversion of KOH and (or) NaOH to potassium or sodium 2,6-di-*tert*-butyl phenoxides, which are catalysts for the alkylation of ArOH by methyl acrylate. The kinetic method for determination of the composition of the catalyst formed from NaOH and ArOH was proposed. The nature of the cation in phenoxides ArOK or ArONa is a factor determining the kinetics of the reaction of ArOH with methyl acrylate. Two different kinetic schemes were proposed to describe the transformation of ArOH in the presence of ArONa or ArOK.

Key words: 2,6-di-*tert*-butylphenol, potassium hydroxide, sodium hydroxide, potassium and sodium 2,6-di-*tert*-butyl phenoxides, kinetics, alkylation, methyl acrylate, methyl-3-(4-hydroxy-3,5-di-*tert*-butylphenyl) propionate.

The catalytic alkylation of 2,6-dialkylphenols in the liquid phase in the presence of 2,6-dialkyl phenoxides depends on the nature of the alkaline metal and the method of preparation of the catalyst by the interaction of 2,6-dialkylphenol with an alkaline agent.[1—6] The most promising alkaline agents are sodium and potassium hydroxides or their compositions, which found use in the synthesis of methyl-3-(4-hydroxy-3,5-di-*tert*-butylphenyl) propionate (R^1OH).[2] The reactions of 2,6-di-*tert*-butylphenol (ArOH) with KOH or NaOH are reversible and were studied only at the qualitative level.

In this work, we obtained quantitative data on the reactions of ArOH with KOH (NaOH) and of ArOK (ArONa) with H_2O in the temperature interval from 70 to 144 °C. When the process occurs in the gas—liquid system, water vapors diffuse from the liquid phase but, in authors´ opinion, diffusion has no substantial effect on the regularities of the reaction in the liquid phase.

The kinetics of the reaction of ArOH with methyl acrylate in the presence of the compositions containing ArONa and NaOH was studied. It was shown that only ArONa was the catalyst. The method for determination of the catalyst composition (contents of ArONa and NaOH) and the mechanism of the reaction of ArOH with methyl acrylate in the presence of ArONa or ArOK was proposed. In the presence of ArONa, sodium 4-(β-methoxycarboxyethyl)-2,6-di-*tert*-butyl phenoxide is formed, which makes it possible to interpret the reaction mechanism in the framework of the scheme different from that described previously.[7] The results of this work substantiate the use of the NaOH and KOH mixtures as initial alkaline agents for the preparation of the catalyst for ArOH alkylation by methyl acrylate.

Experimental

A Bruker LC-31 instrument with an IBM Cyano column was used for HPLC (hexane—isopropyl alcohol—ethyl acetate (8 : 1 : 1, v/v/v) as an eluent, working pressure 57 atm, rate 0.4 mL min^{-1}). IR spectra were recorded using a Beckman DU-8 spectrometer. ^1H NMR spectra were obtained with a Bruker WM-400 instrument (400 MHz, a solution in $CDCl_3$, Me_4Si as an internal standard).

Synthesis of sodium 4-(β-methoxycarboxyethyl)-2,6-di-*tert*-butyl phenoxide (R^1ONa). In an argon flow R^1OH (0.01 mol) was added to MeONa (0.01 mol) in MeOH (30 mL). The solution was refluxed for 30 min, then MeOH was distilled off *in vacuo*. The crystalline residue was twice washed with hexane and separated by filtration. The crystals decompose upon heating above 220 °C. Found (%): C, 68.55; H, 8.40; Na, 7.85. $C_{18}H_{27}O_3Na$. Calculated (%): C, 68.76; H, 8.66; Na, 7.32. IR (KBr), ν/cm^{-1}: 1568 (C—O); 1736 (C=O).

Kinetic and analytical measurements were carried out using a known procedure.[7] Individual ArOK and ArONa were obtained by the addition of calculated amounts of Bu^tOK in Bu^tOH (or MeONa in MeOH) to ArOH followed by the removal of aliphatic alcohol by evacuation.

The equilibrium $ArOH + MOH \rightleftharpoons ArOM + H_2O$ (M = K, Na) was studied as follows. A weighed sample of melted 2,6-di-*tert*-butylphenol was placed in a cylindrical vessel with a plunger and a pipe-bend in the bottom part for the connection of a needle. The plunger was removed, a weighed sample of

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ArOK (ArONa) and a measured volume of water were introduced into the cylinder, the plunger was connected, air was removed from the cylinder, and the needle was replaced by a plug. The reaction mixture thus prepared was stirred by shaking, placed in a thermostat, and stored at a specified temperature for a needed time. Then the plug was replaced by the needle, benzene (10—12 mL) was placed in the cylinder (reactor), and the precipitate formed was filtered off. The cylinder was filled with benzene (2—3 mL) three times more, and the precipitate on the filter was washed with benzene. The concentration of phenol in a benzene solution was determined by HPLC. Benzene with water was distilled off from phenol, and the content of water in a benzene solution was determined by the Fischer method. The filter with the alkali and phenoxide residue was placed in a flask, toluene (30 mL) was added, and residues of H_2O and ArOH with toluene were distilled off *in vacuo*. After cooling, a measured volume of H_2SO_4 with a known concentration was added to the residue, and the total concentration of alkali and phenoxide was determined by "inverse" titration using phenolphthalein as an indicator. Benzene (5 mL) was added to the same flask, phenol formed was extracted, and the amount of ArOH was determined by HPLC using solutions with the known concentration of ArOH. The concentration of ArOK or ArONa was calculated from the results of this analysis. The concentration of alkali in the reaction solution was determined from the difference between the total amount of bases found by titration and the amount of phenoxide calculated using the results of HPLC analysis. The results of studying the equilibrium are presented in Table 1.

The influence of the gaseous phase in the reactor was checked by a special experiment, during which nitrogen was introduced into the cylinder after removal of air (Table 2). The results are discussed further.

The reaction of ArONa with R^1OH was studied using a similar procedure.

A mixture of ArONa (0.024 mol) and R^1OH (0.065 mol) was boiled for 20—40 min at 116 °C. The yield of R^1ONa remained unchanged and was 0.014 mol (58% calculated on the basis of

Table 1. Initial (I) and equilibrium (II) concentrations (mol kg^{-1}) of the reactants and effective equilibrium constants (K_e^{eff}) of the reaction of ArOH with MOH (M = K, Na) in the condensed phase at different temperatures

T/°C	ArOH		MOH		ArOM		H_2O		K_e^{eff}
	I	II	I	II	I	II	I	II	
M = K									
144	4.718	4.495	0.467	0.0486	—	0.447	—	0.428	0.91
	4.667	4.111	0.657	0.0808	—	0.555	—	0.566	0.94
	4.349	4.374	—	0.0342	0.359	0.325	0.479	0.436	0.95
									0.93
116	4.312	4.398	—	0.0687	0.395	0.326	0.376	0.309	0.33
	4.748	4.448	0.358	0.0596	—	0.248	—	0.278	0.26
	4.654	4.119	0.703	0.208	—	0.511	—	0.519	0.31
									0.3
100	4.719	4.449	0.463	0.203	—	0.28	—	0.318	0.099
	4.261	4.492	—	0.2147	0.429	0.248	0.462	0,264	0.068
	2.167	3.624	—	1.457	1.745	0.249	5.36	2.704	0.13
									0.089
70	4.719	4.575	0.463	0.338	—	0.145	—	0.145	0.014
	4.329	4.649	—	0.302	0.373	0.071	0.497	0.195	0.009
									0.011
M = Na									
144	4.741	4.487	0.538	0.205	—	0.225	—	0.332	0.081
	4.316	4.451	—	0.222	0.206	0.278	0.222	0.293	0.082
	4.171	4.372	—	0.201	0.527	0.345	0.541	0.355	0.13
									0.1
116	4.634	4.178	1.089	0.574	—	0.416	—	0.475	0.082
	4.162	4.321	—	0.171	0.547	0.402	0.369	0.145	0.079
	4.089	4.406	—	0.243	0.597	0.355	0.523	0.299	0.099
									0.086
100	4.768	4.544	0.391	0.128	—	0.175	—	0.293	0.067
	4.447	4.593	—	0.118	0.289	0.165	0.369	0.243	0.073
	4.114	4.316	—	0.186	0.598	0.396	0.226	0.137	0.068
									0.069
70	4.725	4.519	0.619	0.356	—	0.216	—	0.253	0.034
	4.171	4.425	—	0.271	0.534	0.254	0.459	0.181	0.038
	4.651	4.721	—	0.077	0.145	0.068	0.239	0.181	0.034
									0.035

Table 2. Initial (I) and equilibrium (II) concentrations (mol kg^{-1}) of the reactants of the reaction of ArOH with MOH (M = K, Na) in the condensed phase (liquid—vapor) at 100 °C

τ/min	ArOH		MOH		ArOM, II	Yield of ArOM (%)	$\frac{[\mathrm{ArOM}]^2}{[\mathrm{ArOH}]\cdot[\mathrm{MOH}]}$
	I	II	I	II			
			M = K				
10	4.727	4.588	0.437	0.266	0.138	32	0.016
20	4.513	4.011	1.224	0.723	0.501	41	0.087
30	4.696	4.308	0.548	0.238	0.303	55	0.09
60	4.685	4.353	0.589	0.258	0.341	58	0.103
			M = Na				
10	4.758	4.669	0.448	0.348	0.109	24	0.007
20	5.012	4.694	0.499	0.219	0.098	31	0.009
30	4.725	4.509	0.619	0.356	0.216	35	0.029
40	4.762	4.379	0.429	0.138	0.155	36	0.039
60	4.731	4.372	0.584	0.277	0.287	49	0.068
90	6.781	4.565	0.334	0.129	0.205	61	0.071

ArONa consumed). According to the data of calculation, the equilibrium constant is $K_e = 0.41$.

The catalyst based on KOH and/or NaOH was synthesized by the addition of calculated amounts of KOH and/or NaOH to ArOH followed by the removal of H_2O by evacuation at 100—105 °C. The calculated amount of methyl acrylate was added to thus obtained catalytic mixture, the reaction was carried out at 116—118 °C in an argon atmosphere, and samples of the liquid phase for HPLC analysis were taken after 5, 10, 15, 20, and 30 min.

For example, NaOH (0.12 g, 0.003 mol) was added to ArOH (20.6 g, 0.1 mol) in an argon flow, and water was distilled off upon stirring for 60 min *in vacuo* (20 μbar). Methyl acrylate (9.8 g, 0.14 mol) was added to the reaction mixture, and the reaction was carried out at 116 °C. After 75 min, the yield of R^1OH was 92%.

The catalytic activity of R^1ONa in the reaction of ArOH with methyl acrylate was determined similarly. R^1ONa (0.006 mol) and methyl acrylate (0.14 mol) were added to ArOH (0.1 mol). The reaction was carried out at 116 °C with sampling for analysis. The yield of R^1OH after 75 min was 94%.

Results and Discussion

The quantitative data characterizing the change in the composition of a solution during the reaction of ArOH with alkaline metal hydroxides made it possible to examine in detail this reaction. The equilibrium concentrations of the components at 100 °C in the reaction of ArOH with KOH are established within 25—30 min after mixing the reactants at a constant temperature of the solution. The reaction of ArOH with NaOH occurs with a lower rate, and the equilibrium is established within 55—65 min. In a series of experiments (see Table 1), ArOK (ArONa) and H_2O with different initial concentrations were also used as the starting components. The processing of the results gave the equilibrium rate constants (K_e^{eff}) for the reactions of ArOH with KOH and NaOH and the plot in the coordinates of van´t Hoff equation (Fig. 1). A series of experiments in the condensed phase—gas (vapor) phase system was performed to elucidate the role of diffusion under static conditions. The results of determination of the concentrations of the initial and formed compounds at 100 °C and the $[\mathrm{ArOK}]^2/([\mathrm{ArOH}]\cdot[\mathrm{KOH}])$ ratios, which depend on the time of the reaction of ArOH with KOH, are presented in Table 2. After 30 min of the reaction of ArOH with KOH, this value becomes equal to K_e^{eff} determined for the reaction of ArOH with KOH in the liquid phase without a gaseous phase, and it remains virtually unchanged for 60 min in the condensed phase—vapor phase system. A similar result was obtained for the reaction of ArOH with NaOH. It follows from these data that diffusion has no substantial effect on the ratio of the concentrations of the formed and initial components.

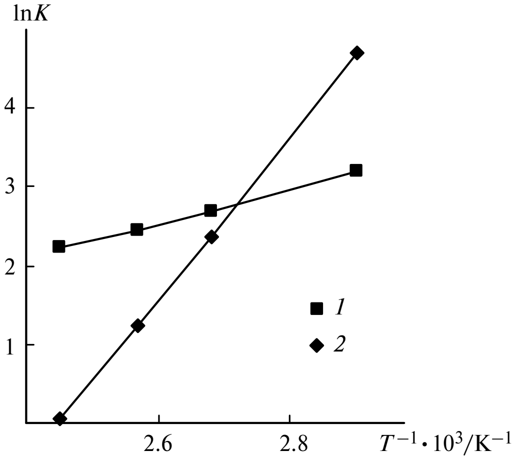
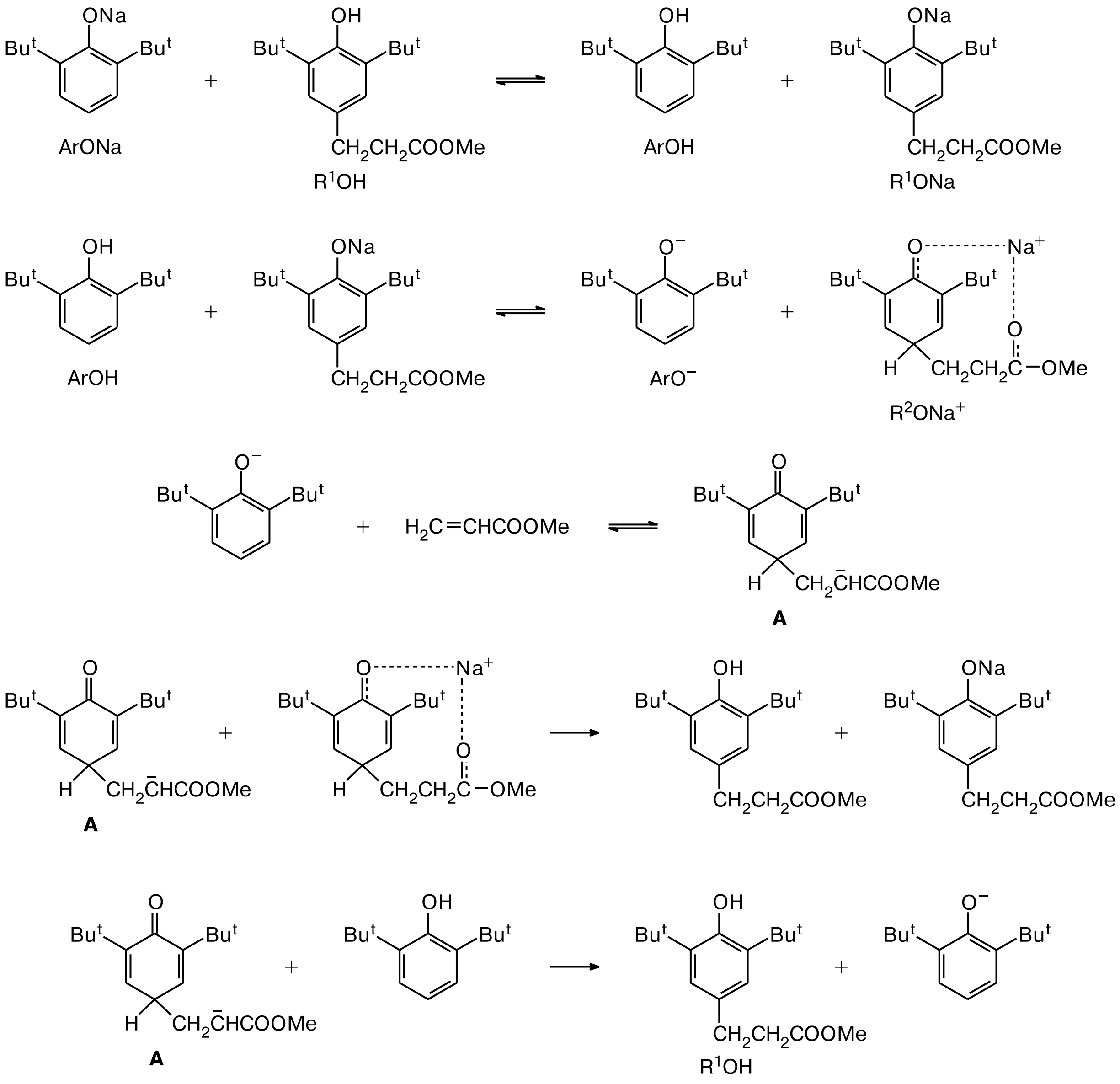


Fig. 1. Temperature plots of the equilibrium constant (K) of the reaction of ArOH with NaOH (*1*) and KOH (*2*).

Phenoxide ArONa is involved in the exchange reaction with R^1OH to form R^1ONa, whereas ArOK does not react with R^1OH.[7,8] The satisfactory coincidence of the experimental and calculated kinetic data for the reaction of ArOH with methyl acrylate in the presence of ArONa became possible if one takes into account the reaction of ArOH with R^1ONa, which affords the 2,6-di-*tert*-butyl phenoxide ion (ArO^-) and a compound with the cyclohexadienone structure (R^2ONa^+) in which the Na^+ cation is coordinated to three O atoms and is surrounded by two Bu^t groups (Scheme 1, Fig. 2). The effective radius of the Na^+ cation is optimal for the isomerization of the aromatic system of bonds to form the cyclohexadienone system. The effective radius of the K^+ cation is larger than that of the Na^+ cation. This is most likely related to the instability of a similar structure with the K^+ cation in the reaction of ArOK with R^1OH. According to Scheme 1, R^1ONa accepts a proton from ArOH and simultaneously retains the Na^+ cation in a chelate complex to produce the protonated form of a new R^2ONa^+ catalyst (autocatalysis). Therefore, now the nonassociated phenoxide ion (ArO^-) can interact with the methyl acrylate molecule to produce the **A** anion (see Scheme 1) followed by the protonation of this anion by the R^2ONa^+ cation or ArOH. The reaction of methyl acrylate with 2,6-di-*tert*-butylphenol deuterated at the phenolic OH group in the presence of ArONa or R^1ONa affords R^1OH and an analog of R^1OH with deuterium labels at the phenolic OH group

Scheme 1



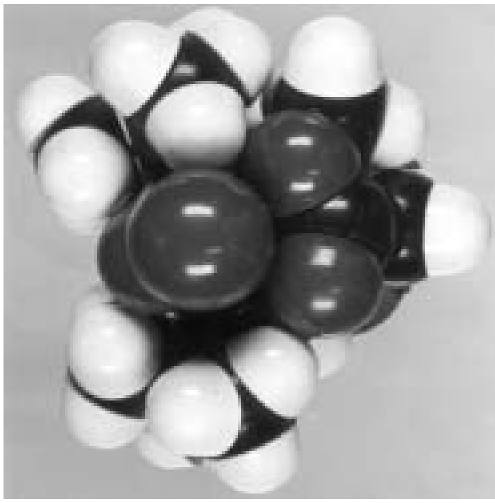


Fig. 2. Molecular model of R^1ONa.

and at the C_β atom in the lateral chain. The presence of the deuterium label at the phenolic OH group in the final product is attributed to the deuterium exchange between ArOD and R^1OH. The mechanism of the reaction of methyl acrylate with ArOD (40% enrichment) is interpreted on the basis of the data on the integral intensity of signals in the ^1H NMR spectrum of the partially deuterated analog of R^1OH. The signals are assigned to the H atom of the phenolic OH group (δ 5.10) and H atom at the C_β atom (δ 2.89).

It should also be noted that the IR spectrum repeatedly detected after the reaction of H_2O with R^1ONa in a pellet with KBr exhibited an increase in the intensity of the peak at $\nu = 1660$ cm^{-1}, which is characteristic of the conjugated carbonyl group of quinolide compounds.[9] This is most likely related to the formation of a compound with the cyclohexadienone structure.

The results of the kinetic studies of the reaction of ArOH with methyl acrylate in the presence of individual ArONa (or R^1ONa) show that the reaction between ArONa and R^1OH is fast because the kinetic curves obtained using ArONa and R^1ONa coincide completely (Fig. 3, curves *1* and *1′*).

Based on Scheme 1, we performed the mathematical simulation of the experimental kinetic data of the reaction at different initial concentrations of ArOH, methyl acrylate, ArONa, and NaOH taking into account the formation of R^1OH and by-products: the product of alkylation of 4-hydroxy-3,5-di-*tert*-butylphenol by two methyl acrylate molecules (Scheme 2), sodium salt of β-(4-hydroxy-3,5-di-*tert*-butylphenol)propionic acid (R^4ONa), and methyl acrylate polymers (oligomers).

Mathematical simulation was performed using the program of calculation of the reaction kinetics on the basis of the solution of the "rigid system" of ordinary differential equations.[10] The kinetic scheme consists of five sets of reactions (Table 3). The first set (Eqs. (1)—(8)) represent the reactions involving the R^1ONa catalyst (the numbers of constants correspond to the numbers of reactions in Table 3).

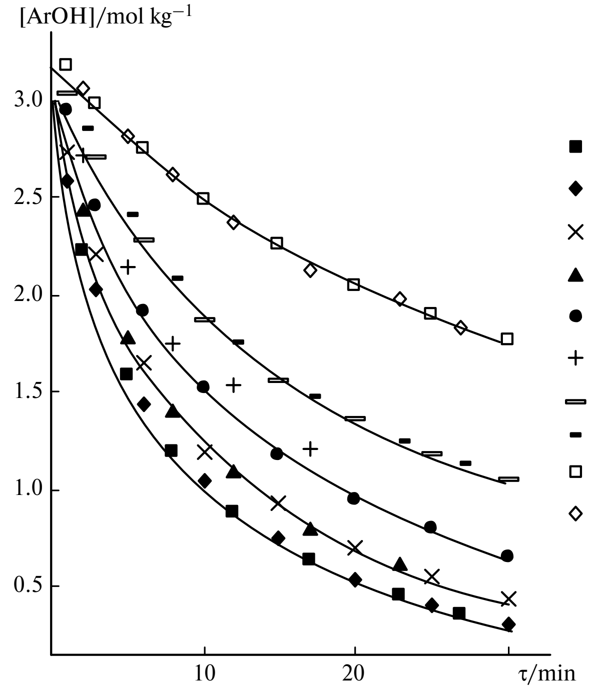
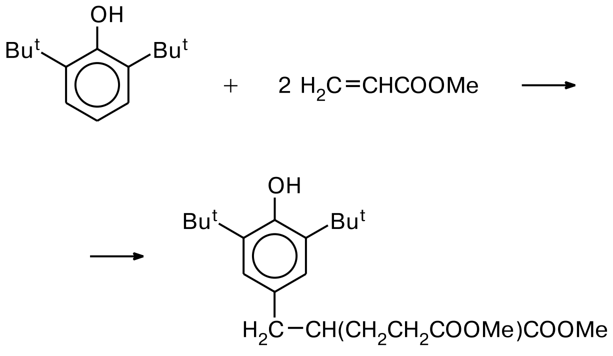


Fig. 3. Kinetics of the reaction of ArOH with methyl acrylate (MA) at $[ArONa]_0$ = 0.1 (*1*), 0.08 (*2*), 0.06 (*3*), 0.04 (*4*), and 0.02 (*5*). $[R^1ONa]_0$ = 0.1 (*1′*); $[ArONa]_0$ = 0.08, $[NaOH]_0$ = 0.02 (*2′*); $[ArONa]_0$ = 0.06, $[NaOH]_0$ = 0.04 (*3′*); $[ArONa]_0$ = 0.04, $[NaOH]_0$ = 0.06 (*4′*); $[ArONa]_0$ = 0.02, and $[NaOH]_0$ = 0.08 mol kg^{-1} (*5′*). Lines are calculation, points are experiment; 116 °C; $[ArOH]_0$ = 3.29, $[MA]_0$ = 3.75 mol kg^{-1}.

The second set contains three reactions involving the ArONa catalyst. The third set is composed of reactions (12)—(15) involving NaOH and yielding ArONa and by-products. The fourth and fifth sets consist of Eqs. (16)—(22) describing the irreversible con-

Scheme 2



R^3COOMe

Table 3. Kinetic scheme of the reaction of ArOH with methyl acrylate in the presence of ArONa, R^1ONa, and NaOH at 116 °C

Reaction	k [a]
$ArOH + R^1ONa \to R^1OH + ArONa$ (1)	$2.5 \cdot 10^{-2}$ [b]
$ArONa + R^1OH \to ArOH + R^1ONa$ (2)	$1 \cdot 10^{-2}$ [b]
$ArOH + R^1ONa \to R^2ONa^+ + ArO^-$ (3)	$6 \cdot 10^{-3}$ [b]
$ArO^- + R^2ONa^+ \to R^1ONa + ArOH$ (4)	$1 \cdot 10^{-3}$ [b]
$ArO^- + MA \to ArO^- \cdot MA$ (5)	$8 \cdot 10^{-2}$ [b]
$ArO^- \cdot MA \to ArO^- + MA$ (6)	$4 \cdot 10^{-3}$ [c]
$ArO^- \cdot MA + R^2ONa^+ \to R^1ONa + R^1OH$ (7)	$2 \cdot 10^{-2}$ [b]
$ArO^- \cdot MA + ArOH \to ArO^- + R^1OH$ (8)	$1.8 \cdot 10^{-2}$ [b]
$ArONa + MA \to ArONa \cdot MA$ (9)	$2 \cdot 10^{-2}$ [b]
$ArONa \cdot MA \to ArONa + MA$ (10)	$1 \cdot 10^{-3}$ [c]
$ArONa \cdot MA + ArOH \to ArONa + R^1OH$ (11)	$8 \cdot 10^{-2}$ [b]
$ArOH + NaOH \to ArONa + H_2O$ (12)	$1.7 \cdot 10^{-3}$ [b]
$ArONa + H_2O \to ArOH + NaOH$ (13)	$2 \cdot 10^{-2}$ [b]
$R^1OH + NaOH \to R^4ONa + MeOH$ (14)	$1 \cdot 10^{-1}$ [b]
$ArONa \cdot MA + H_2O \to R^1OH + NaOH$ (15)	$5 \cdot 10^{-3}$ [b]
$R^1ONa + MeOH \to R^1OH + MeONa$ (16)	$2 \cdot 10^{-3}$ [b]
$ArONa \cdot MA + MeOH \to R^1OH + MeONa$ (17)	$7 \cdot 10^{-3}$ [b]
$ArONa \cdot MA + MA \to ArONa \cdot 2MA$ (18)	$4 \cdot 10^{-5}$ [b]
$ArO^- \cdot MA + MA \to ArO^- \cdot 2MA$ (19)	$1 \cdot 10^{-4}$ [b]
$ArO^- \cdot 2MA + ArOH \to R^3COOMe + ArO^-$ (20)	$1 \cdot 10^{-4}$ [b]
$NaOH + MA + MA \to$ MA (oligomer) (21)	$8 \cdot 10^{-3}$ [d]
MA (oligomer) + MA + MA $\to$ MA (polymer) (22)	$5 \cdot 10$ [d]

[a] Calculated reaction rate constants, dimensionality

[b] $kg\ mol^{-1}\ s^{-1}$,

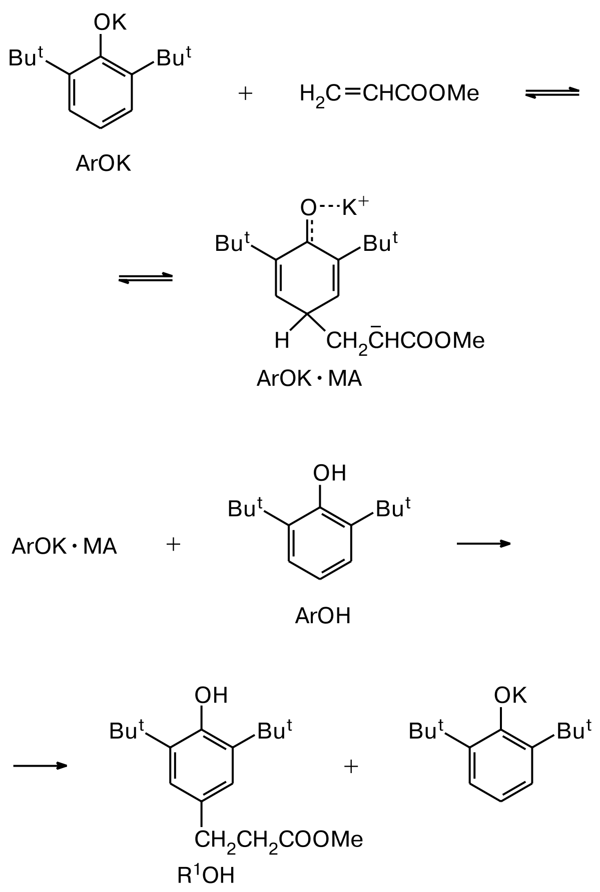
[c] s^{-1},

[d] $kg^2\ mol^2\ s^{-1}$.

sumption of the active forms of the catalyst and side processes. Reactions (14)—(22) are included to take into account the formation of by-products: R^4ONa, $R^3(CH_2CH_2COOMe)_2$, and methyl acrylate oligomers.

In the presence of ArOK, the mechanism of the reaction of ArOH with methyl acrylate differs from that considered above due to the formation of a contact pair of the ArO^- ion with the K^+ cation and the possibility of participation of the K^+ cation in the elementary act of interaction of the reacting species. It can be assumed that the methyl acrylate yields an intermediate product with the weakly bonded ion pair (ArOK • MA), which affords R^1OH due to the proton transfer from the ArOH (or methyl acrylate) molecule (Scheme 3).

Scheme 3



During phenoxide formation, the reaction of ArOH with KOH produces a gel-like mixture, whose properties affect the kinetics of the reaction of ArOH with methyl acrylate. Monomeric ArOK yields agglomerates in the form of dimeric associates, which decreases the efficiency of ArOK as a catalyst of the reaction.[10,11]

A comparison of the experimental results and calculation of the kinetics of the reaction of ArOH with methyl acrylate in the presence of the sodium compounds showed that the presence of NaOH in amounts comparable with concentrations of ArONa had no effect on the rate of the reaction of ArOH with methyl acrylate (see Fig. 3, curves *2*, *2´*, *3*, *3´*, *4*, *4´*, *5*, and *5´*). The above data also show that the yield of ArONa in the reversible reaction of ArOH with NaOH in the temperature interval from 80 to 140 °C does not exceed several percents. However, the yield of ArONa can be enhanced by the removal of water from the reaction mixture (for example, by evacuation[1—5]) but, in this case, a catalytic mixture is obtained. Therefore, the analytical determination of the composition of this catalytic mixture is an important problem.

The quantitative data considered above allow the use of mixtures of KOH and NaOH to obtain ArONa and ArOK simultaneously and to apply them as catalysts for the alkylation of ArOH by methyl acrylate. The present study made it possible to develop the kinetic method for analysis of the ArONa content in the reaction system under the conditions of partial distillation of water. The method is based on the determination of the rate of the reaction of ArOH with methyl acrylate and is especially suitable for systems with a low content of alkali (0.1—5 mol.% of the initial amount of ArOH).

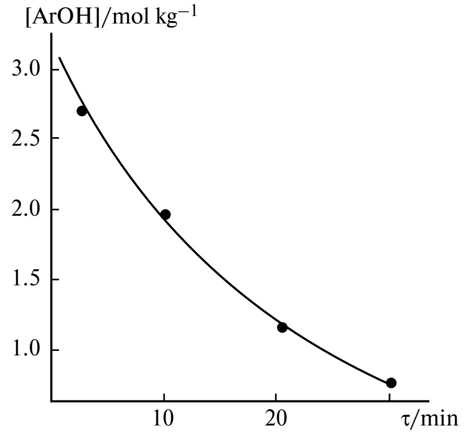


Fig. 4. Kinetics of the reaction of ArOH with methyl acrylate at 116 °C; $[ArOH]_0 = 3.29$, $[MA]_0 = 3.75$ mol kg^{-1}; line is calculation; points are the experiment with the unknown composition of the ArONa + NaOH catalyst, $[NaOH]_0 = 0.1$ mol kg^{-1}. The calculated data coincided with the points at $[ArONa]_0 = 0.048$ mol kg^{-1}.

The good coincidence of the results of calculation and experiment (Fig. 4) indicates the efficiency of the procedure.

It would be reasonable to elucidate the role of two different in nature components of the catalyst in their combined effect in the reaction of ArOH with methyl acrylate. The role of NaOH could be positive in the formation of a composition of ArONa, ArOK, and NaOH due to the separation of water during the interaction of NaOH and KOH with ArOH. This assumption is based on the known data that NaOH prevents the agglomeration of ArOK (by analogy to the effect of KOH).[7] In fact, as follows from Fig. 5 (curve *2*), the addition of 30% KOH to the starting NaOH is sufficient to obtain the catalyst, in the presence of which the initial rate of ArOH alkylation by methyl acrylate corresponds to the rate of the same reaction in the presence of individual ArONa (see Fig. 3, curve *1*). In this case, the final yield of R^1OH increases. The obtained result seems to be related to the stage-to-stage effect of ArONa and ArOK + NaOH, depending on the time of the interaction of ArOH with methyl acrylate.

Thus, the use of potassium and sodium hydroxides as initial alkaline components provides the catalyst for the alkylation of 2,6-di-*tert*-butylphenol by methyl acrylate, which is more efficient than individual ArOK or ArONa even in the case of the partial conversion of alkaline metals to the corresponding phenoxides. The analysis of the experimental and calculated data shows that the basic difference in the reactivity and catalysis by ArONa and ArOK is related to the form of participation of the metal ion in the reaction of ArOH with methyl acrylate.

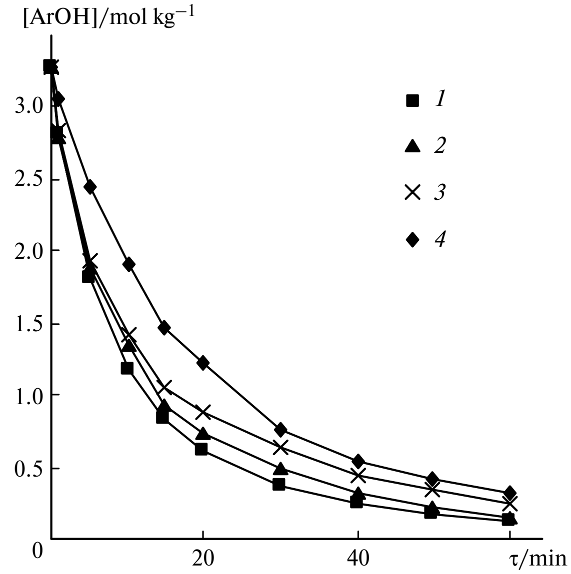


Fig. 5. Kinetics of the reaction of ArOH with methyl acrylate in the presence of ArONa, ArOK, and NaOH at 116 °C, $[ArOH]_0 = 3.29$, and $[MA]_0 = 3.75$ mol kg^{-1}: $[ArONa]_0 = 0.06$, $[ArOK]_0 = 0.06$, $[NaOH]_0 = 0.04$ mol kg^{-1} (*1*); $[ArONa]_0 = 0.06$, $[ArOK]_0 = 0.02$, $[NaOH]_0 = 0.04$ mol kg^{-1} (*2*); $[ArONa]_0 = 0.06$, $[ArOK]_0 = 0$, $[NaOH]_0 = 0.04$ mol kg^{-1} (*3*); and $[ArONa]_0 = 0.02$, $[ArOK]_0 = 0.12$ mol kg^{-1} (*4*). Lines are calculation; points are experiment.

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