Effect of the nature of the cation in 2,6-di-*tert*-pentylphenolates on the kinetics and mechanism of the reaction of 2,6-di-*tert*-pentylphenol with methyl acrylate

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The nature of the cation (K or Na) in 2,6-di-*tert*-pentylphenolates (ArOK or ArONa) affects the kinetics of the reaction of 2,6-di-*tert*-pentylphenol (ArOH) with methyl acrylate. This is associated with the ability of ArONa to replace the cation with a proton during interaction with methyl 3-(4-hydroxy-3,5-di-*tert*-pentylphenyl)propionate (HOArAlkOMe) to form a more efficient catalyst, sodium 4-(2-methoxycarbonylethyl)-2,6-di-*tert*-pentylphenolate (NaOArAlkOMe). Two different kinetic schemes, which describe the kinetics of the consumption of ArOH in the presence of ArOK and ArONa, are proposed. The elemental-stage rate constants are calculated by mathematical simulation of the reaction kinetics with consideration of the features of catalysis in the presence of ArOK and ArONa.

Key words: 2,6-di-*tert*-pentylphenol, methyl acrylate, Na and K cations; kinetics.

In a continuation of investigations of the influence of steric factors on the kinetics of alkylation of 2,6-dialkylphenols in the presence of alkaline metal phenolates, alkylation of 2,6-di-*tert*-pentylphenol (2,6-di-*tert*-amylphenol, ArOH) with methyl acrylate (MA) catalyzed by potassium and sodium 2,6-di-*tert*-pentylphenolates (ArOK and ArONa, respectively) has been investigated in the present work. In the ArOH molecule, the hydroxyl group is surrounded by bulky *tert*-pentyl groups, which results in considerable steric hindrances for intermolecular interactions and favors the formation of compounds of the cyclohexadienone structure. These factors may substantially affect the mechanism of alkylation of 2,6-di-*tert*-pentylphenol with MA. Thus, it was interesting to investigate the influence of the nature of the metal cation (K and Na) in the corresponding phenolates on the reaction of ArOH with MA.

Earlier[1—3] it has been shown that the kinetics of the analogous reaction of 2,6-di-*tert*-butyl- or 6-*tert*-butyl-2-methylphenol with MA agrees with the specific properties of ion pairs that are formed as intermediates in the reaction of potassium and sodium 2,6-dialkylphenolates with MA in the absence of a solvent. However, the investigation of the reaction of ArOH with MA showed that the above kinetics is close to that observed only when MA reacts with ArOK, while in the presence of ArONa the reaction of ArOH with MA proceeds in a specific way, and its interpretation requires a principally different kinetic scheme taking into account the experimental data. The mathematical simulation of the kinetics of the reaction of ArOH with MA in the presence of ArOK is based on the previously described[3] Kinetic scheme I. This scheme implies that a series of consecutive reactions with participation of ArOK, MA, and ArOH occur (Scheme 1), leading to the formation of complexes F and GG, methyl 3-(4-hydroxy-3,5-di-*tert*-pentylphenyl)propionate (HOArAlkOMe), and potassium 3-(4-hydroxy-3,5-di-*tert*-pentylphenyl)propionate (HOArAlkOK).

This kinetic scheme also takes into account that the system contains $HOAr(AlkOMe)_2$ as a side product of the Michael reaction, poly(methyl acrylate), and various associates arising due to dimerization of ArOK, as well as the fact that these associates participate in the formation of HOArAlkOMe (Scheme 2).

Catalytic alkylation of ArOH with MA in the presence of ArONa is characterized by considerably higher initial rates and by the ability of HOArAlkOMe to participate in the exchange reaction with ArONa (Scheme 3).

It should be pointed out that HOArAlkOMe does not react with ArOK.

Subsequent investigations showed that 4-(2-methoxycarbonylethyl)-2,6-di-*tert*-pentylphenolate (NaOArAlkOMe) isolated as an individual species can also catalyze the alkylation, and the kinetics of the

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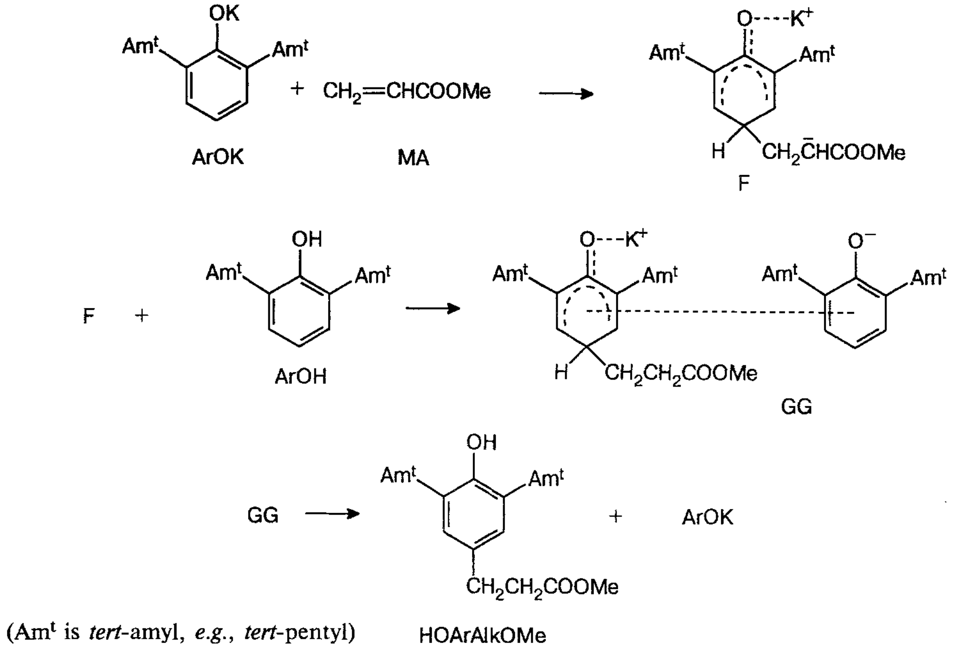
Scheme 1

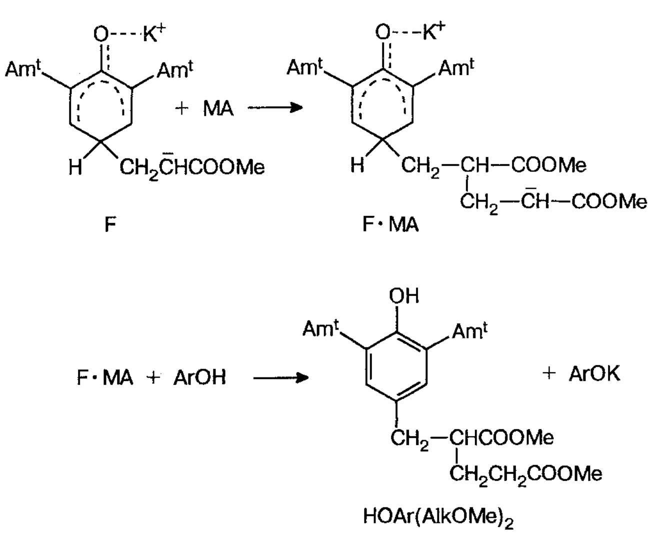


(Am^t is *tert*-amyl, *e.g.*, *tert*-pentyl)

reaction of ArOH with MA proved to be similar to the kinetics of the interaction of ArOH with MA in the presence of ArONa.

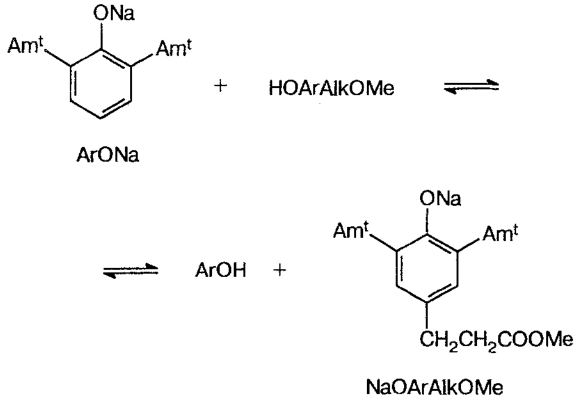
Thus, the alkylation of 2,6-di-*tert*-pentylphenol with MA revealed the fact that the metal cation in the corresponding phenolates influences to a great extent the kinetics of the process and its mechanism. Apparently, the formation of NaOArAlkOMe is associated with the stabilization of its molecule resulting from the intramolecular interaction between the Na cation and the oxygen atom of the carbonyl group, which agrees with the molecular model of the compound under consideration. Due to the larger effective radius of K and to steric hindrances, the analogous structure with the K cation becomes unstable, and potassium 4-(2-methoxycarbonylethyl)-2,6-di-*tert*-pentylphenolate can not be formed by the exchange reaction of HOArAlkOMe with ArOK. The above-mentioned considerations suggest that the corresponding sodium phenolates exhibit much more effective catalytic properties because NaOArAlkOMe can simultaneously accept a proton and retain the Na cation in a chelate complex according to Scheme 4.

Scheme 2

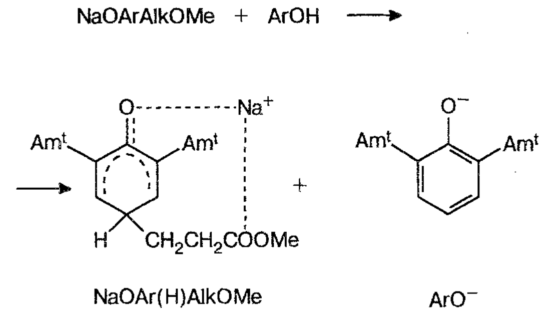


Accordingly it becomes possible for the non-associated 2,6-di-*tert*-pentylphenolate ion to react with MA to give an intermediate species L, which reacts with protonated phenolate NaOAr(H)AlkOMe. This results in the regeneration of the initial NaOArAlkOMe, which

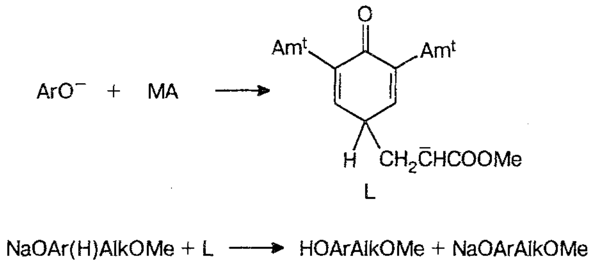
Scheme 3



Scheme 4



Scheme 5



can participate in the formation of HOArAlkOMe as the reaction product (Scheme 5).

The interpretation of the obtained results for the kinetics of the reaction of ArOH with MA in the presence of ArONa (or NaOArAlkOMe) agrees with Kinetic scheme II (see below), which brought the experimental data in correspondence with the calculated data.

Theoretical calculations. The calculations of the kinetic schemes were done on a PC 1640D20 computer using a program for calculation of the reaction kinetics based on the solution of a "rigid system" of differential equations.[4] The program, which included the data about the initial stages, the constants, the reaction components, and their initial concentrations, enabled us to efficiently vary the number of elemental stages and to change their constants. The calculated data were plotted as a graph reflecting the consumption of ArOH and MA and the accumulation of HOArAlkOMe. The mathematical simulation was performed using the principle of "block" optimization of all of the reactions that influence the kinetics of the process at fixed values of catalyst concentration, and with consideration of the data about the optimization of the elemental-stage constants.[3]

Kinetic scheme I (Table 1) involves 13 components and 23 elemental stages that describe the reaction mechanism in the presence of ArOK. This scheme has a solution that accounts for the interaction of associate (ArOK)·ArO⁻ with MA and the formation of HOArAlkOMe by the exchange reaction of ⁻OArAlkOMe with ArOH.

Table 1. The elemental-stage rate constants in the presence of ArOK at 116 °C

Kinetic scheme I	k /L mol^{-1} s^{-1}
ArOK + MA → F	4
F → ArOK + MA	1
F + ArOH → GG	$6\cdot10^{-1}$
F + MA → F·MA	$4\cdot10^{-1}$
F·MA → F + MA	10^{-2}
F·MA + ArOH → HOAr(AlkOMe)$_2$ + ArOK	$8\cdot10^{-4}$
GG → F + ArOH	10^{-3}
GG → HOArAlkOMe + ArOK	$2\cdot10^{-3}$
GG → HOArAlkOK + ArOMe	10^{-4}
ArOK + ArOK → (ArOK)$_2$	5
(ArOK)$_2$ → ArOK + ArOK	10^{-1}
(ArOK)$_2$ → ArOK·ArO$^-$ + K$^+$	$9\cdot10^{-1}$
ArOK·ArO$^-$ + K$^+$ → (ArOK)$_2$	10^{-1}
ArOK·ArO$^-$ + ArOK → (ArOK)$_2$ArO$^-$	10^{2}
K$^+$ + MA + MA → K$^+$·MA·MA	$5\cdot10^{-2}$
(ArOK)$_2$ + ArOK → (ArOK)$_3$	10^{2}
(ArOK)$_3$ → (ArOK)$_2$ + ArOK	10^{-1}
K$^+$·MA·MA + MA + MA → Polymer	10^{-2}
(ArOK)$_2$ArO$^-$ + MA → $^-$OArAlkOMe + (ArOK)$_2$	10^{-3}
$^-$OArAlkOMe + ArOH → HOArAlkOMe + ArO$^-$	$5\cdot10^{2}$
HOArAlkOMe + ArO$^-$ → $^-$OArAlkOMe + ArOH	10^{2}
ArO$^-$ + (ArOK)$_2$ → (ArOK)$_2$ArO$^-$	10
(ArOK)$_2$ArO$^-$ → ArO$^-$+ (ArOK)$_2$	10^{2}

Kinetic scheme II (Table 2) involves 17 components and 22 elemental stages that describe the reaction mechanism in the presence of ArONa. A specific feature of this scheme is that the dimeric associates have virtually no effect on the kinetics of consumption of ArOH.

The calculations of the kinetics of the accumulation of HOArAlkOMe agrees with the experimental data. Thus, Scheme II reflects the specific rates of the reaction of ArOH with MA, the possible interaction of ArONa with HOArAlkOMe, and the influence of the catalyst on the selectivity of the process and the routes of formation of side products.

Experimental

Kinetic and analytic measurements were done by known procedures.[1] ArOK and ArONa were prepared by the addition of calculated amounts of Bu^{t}OK or MeONa in the corresponding alcohols to ArOH and subsequent evaporation of the alcohol in a vacuum. HOArAlkOMe was isolated in the individual state as a viscous liquid by rectification of the reaction mixture in a vacuum. NaOArAlkOMe was obtained by the addition of MeONa to HOArAlkOMe.

^{1}H NMR for HOArAlkOMe (CDCl$_3$), δ: 0.67 (t, 6 H, CH$_2$C$\underline{H}_3$); 1.39 (s, 12 H, CCH$_3$); 1.83 (q, 4 H, C$\underline{H}_2$CH$_3$); 2.61 and 2.88 (both t, 4 H, CH$_2$CH$_2$CO); 3.68 (s, 3 H, COOCH$_3$); 5.03 (s, 1 H, OH); 6.92 (2 H, CH-arom.).

Table 2. The elemental-stage rate constants in the presence of ArONa at 116 °C

Kinetic scheme II	k /L mol^{-1} s^{-1}
ArOH + NaOArAlkOMe → HOArAlkOMe + + ArONa	$4 \cdot 10^{-1}$
HOArAlkOMe + ArONa → NaOArAlkOMe + + ArOH	10^{-1}
ArONa + MA → F	2
F → ArONa + MA	1
NaOArAlkOMe + ArOH → ArO$^-$ + + NaOAr(H)AlkOMe	10^{-2}
ArO$^-$ + NaOAr(H)AlkOMe → NaOArAlkOMe + + ArOH	10^{-2}
ArO$^-$ + MA → L	$3 \cdot 10^{-1}$
L → ArO$^-$ + MA	10^{-4}
L + NaOAr(H)AlkOMe → HOArAlkOMe + + NaOArAlkOMe	10^{-1}
HOArAlkOMe + NaOArAlkOMe → L + + NaOAr(H)AlkOMe	10^{-4}
ArOH + F → ArO$^-$ + NaOArAlkOMe	$2.5 \cdot 10^{-2}$
ArO$^-$ + NaOArAlkOMe → ArOH + F	$4 \cdot 10^{-4}$
NaOArAlkOMe → HOArAlkOONa	$5 \cdot 10^{-4}$
F + MA → F · MA	$4 \cdot 10^{-1}$
F · MA → F + MA	10^{-2}
F · MA + ArOH → HOAr(AlkOMe)$_2$ + ArONa	$8 \cdot 10^{-4}$
ArONa + ArONa → (ArONa)$_2$	10^2
(ArONa)$_2$ → ArONa + ArONa	10^{-1}
(ArONa)$_2$ → ArONa · ArO$^-$ + Na$^+$	1
Na$^+$ + MA + MA → Na$^+$ · MA · MA	$5 \cdot 10^{-2}$
Na$^+$ · MA · MA + MA + MA → Polymer	10^{-2}
ArONa · ArO$^-$ + Na$^+$ → (ArONa)$_2$	10^{-1}

Results and Discussion

The interpretation of the results of alkylation of ArOH with MA was based on the kinetic data for the dependence of the consumption of ArOH on the nature of the cation in ArOM (M = K or Na).

Figure 1 illustrates the dependence of the consumption of ArOH in the reaction with MA on the concentration of ArOK. It is noteworthy that the appearance of the kinetic curves is analogous to that of the curves previously obtained in the investigation of the reaction of 2,6-di-*tert*-butyl- or 6-*tert*-butyl-2-methylphenol with MA.[1—3] In addition, these curves indicate that in the presence of ArOK the reaction selectivity is rather low due to the formation of side products, *viz.*, HOAr(AlkOMe)$_2$, HOArAlkOK, and poly(methyl acrylate).

Figure 2 shows the dependence of the consumption of ArOH in the reaction with MA on the concentration of ArONa. In the case of catalysis with sodium phenolate, the initial rates increase by almost an order of magnitude, but it is not possible to obtain HOArAlkOMe in high yield due to the formation of the same side products. In addition, the activity of the catalyst dimin-

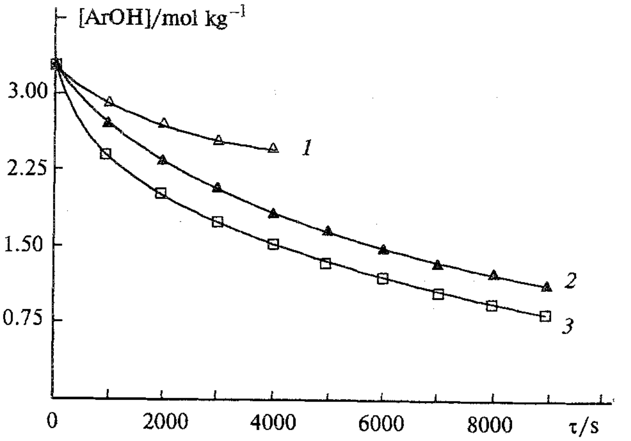


Fig. 1. Calculated (curves *1—3*) and experimental (points) data for the kinetics of the consumption of ArOH in the presence of ArOK at 116 °C, $[ArOH]_0$ = 3.29 mol kg^{-1}, $[MA]_0$ = 3.75 mol kg^{-1}; $[ArOK]_0$/mol kg^{-1}: 0.12 (*1*); 0.24 (*2*); 0.34 (*3*).

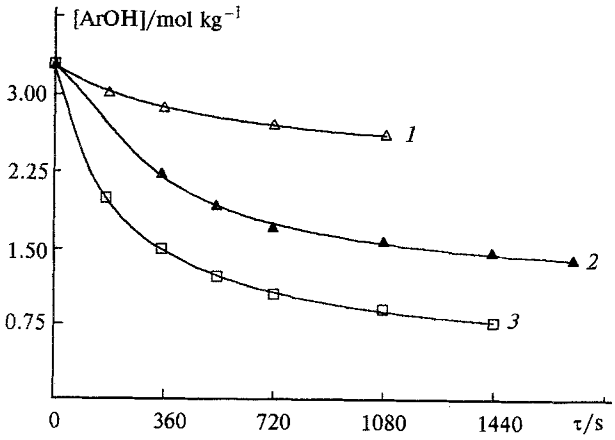


Fig. 2. Calculated (curves *1—3*) and experimental (points) data for the kinetics of the consumption of ArOH in the presence of ArONa at 116 °C, $[ArOH]_0$ = 3.29 mol kg^{-1}, $[MA]_0$ = 3.75 mol kg^{-1}; $[ArONa]_0$ /mol kg^{-1}: 0.12 (*1*); 0.24 (*2*); 0.48 (*3*).

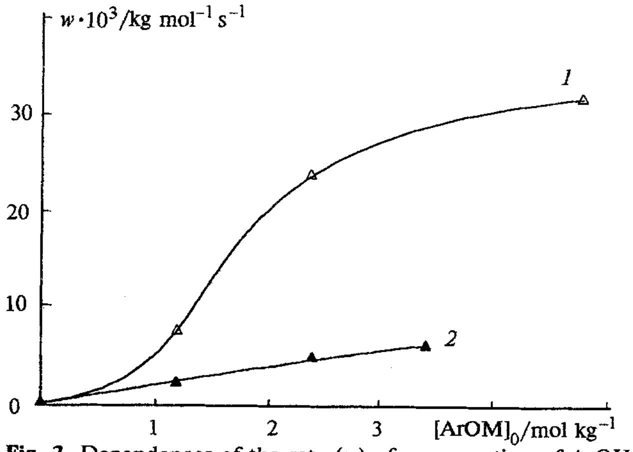


Fig. 3. Dependences of the rate (*w*) of consumption of ArOH (τ = 160 s) on the concentration of ArOM in the presence of ArOK (*1*) and ArONa (*2*); $[ArOH]_0$ = 3.29 mol kg^{-1}, $[MA]_0$ = 3.75 mol kg^{-1}.

ishes in the process of the interaction of the components.

Figure 3 shows the calculated dependences of the reaction rates *w* (τ = 160 s) on the concentrations of ArOK and ArONa, and their appearance also points to the difference between the catalytic mechanisms in the presence of the corresponding phenolates.

Thus, the obtained results altogether allow us to conclude that the nature of the cation (K or Na) in 2,6-di-*tert*-pentylphenolate substantially changes the catalytic properties of the alkaline reagent, when the reaction is carried out in the absence of a solvent.

References

1. A. A. Volod'kin, A. S. Zaitsev, V. L. Rubailo, V. A. Belyakov, and G. E. Zaikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 1829 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1989, **38**, 1677 (Engl. Transl.)].
2. A. A. Volod'kin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 989 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, **40**, 877 (Engl. Transl.)].
3. A. A. Volod'kin, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 504 [*Russ. Chem. Bull.*, 1993, **42**, 457 (Engl. Transl.)].
4. C. W. Gear, in *Numerical Initial Value Problems in Ordinary Differrential Equations*, Prentice, New Jersey, 1971, 158.

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