# KINETICS OF THE REACTION OF 2,6-DI-t-BUTYLPHENOL WITH METHYL ACRYLATE IN THE PRESENCE OF POTASSIUM 2,6-DI-t-BUTYLPHENOLATE AND THE EFFECT OF PROTON-DONOR COMPONENTS ON THE MECHANISM OF THIS REACTION

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A kinetic scheme is proposed for the reaction of 2,6-di-t-butylphenol with methyl acrylate in the presence of potassium 2,6-di-t-butylphenolate. Rate constants have been calculated for the elementary stages which describe the mechanism of catalysis and the effect on the kinetic laws of the proton-donor components 2,6-di-t-butylphenol, water, and methanol. The kinetic scheme contains 30 components and includes 62 rate constants for the elementary stages, which were calculated by mathematical modeling of the kinetics of the process. The calculated results are compared with experimental data for the dependence of the rate of consumption of 2,6-di-t-butylphenol on the concentration of potassium 2,6-di-t-butylphenolate and on the concentrations of the proton-donor components.

It was shown previously [1] that the kinetic scheme for the reaction of 2,6-di-t-butyl-phenol (ArOH) with methyl acrylate (MA) in the presence of potassium 2,6-di-t-butylphenolate (ArOK) and alkali (KOH) is described satisfactorily by a reaction mechanism containing 14 components and 28 elementary stages. This mechanism applies in the absence of a solvent (highly concentrated solutions); it involves ion pairs and assumes a stage in which potassium 2,6-di-t-butylphenolate reacts with methyl acrylate with the participation of water or methanol to stabilize the ion pair formed as an intermediate
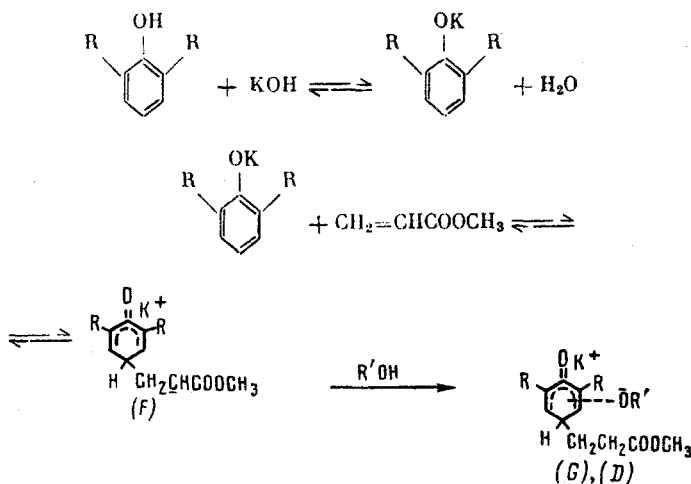
$R = C(CH_3)_3$; $R' = H$ (G), CH_3 (D).

The mathematical modeling of the kinetic process (the direct problem) gave a set of constants for the elementary stages which provided adequate correlation between the calculated and the experimental data over a wide range of concentrations of ArOK and KOH (50% and more) in a catalyst consisting of ArOK and KOH. However, for high contents of ArOK in the catalyst
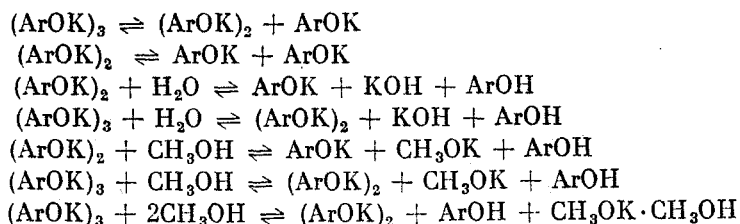
qualitative changes were observed in the properties of the system, as a consequence of which the kinetic scheme had to be modified subsequently to allow for special features of the reaction of ArOH with MA in the presence of pure ArOK.

Theoretical Calculations. The calculations of the kinetic scheme were carried out on a PC 1640HD20 computer, using a program for reaction kinetics based on the solution of a "rigid system" of ordinary differential equations [2]. The program included a description of the elementary stages, their rate constants, the reaction components, and their initial concentrations. During the operation of the program changes could be made in the number of elementary stages, their rate constants, and the initial concentrations of the components. This was effected by editing the text according to the Norton Commander program. The results of the calculations were recorded as graphs showing the kinetics of the consumption of ArOH and MA and of the accumulation of the methyl ester of β-(4-hydroxy-3,5-di-t-butylphenyl)propionic acid (ArAlkOMe). The mathematical modeling employed the principle of "block" optimization of the set of reactions, i.e., the effect on the kinetics for a catalyst of fixed composition and concentration, taking into account the results given previously [1] for the optimization of the rate constants of the elementary stages.

The improved kinetic scheme contained 30 components and 62 elementary stages for describing the reaction mechanism and the formation by interactions between the reagents of both the desired and secondary reaction products: ArOMe, condensation products from the Michaelis reaction, $ArAlk(OMe)_2$, potassium β-(4-hydroxy-3,5-di-t-butylphenyl)propionate (ArAlkOK), methyl acrylate polymer (polymer), potassium acrylate (MAK), 4-methyl-2,6-di-t-butylphenol (ArOMe), and also intermediate complexes formed by the interaction of ArOK with MA (F), of the complex (F) with water (G), of the complex (F) with methanol (D), of the complex (F) with ArOH (GG), and of the complex (F) with MA (F·MA). As compared with the scheme described previously [1] the proposed kinetic scheme contains an additional stage for the formation of ArAlkOMe by the reaction of the complex (F) with ArOH, which becomes important when the reaction of ArOH with MA is catalyzed by the species ArOK. However, it is then necessary to allow for the fact that the species potassium 2,6-di-t-butylphenolate is only partially (incompletely) dissolved in the mixture of reagents and may exist in the form $(ArOK)_2$. It should also be noted that the dimerization of sterically hindered phenols has been reported in the literature [3].

There are also reports of the nonequivalence of the cations in the corresponding dimers [4], which may be the reason for the initiation of the polymerization of methyl acrylate, for example, on account of the formation of loose cationic pairs of the dimer of potassium 2,6-di-t-butylphenolate (ArOK, ArO + K) and the interaction of the potassium cation with methyl acrylate. The limited solubility of potassium 2,6-di-t-butylphenolate can be expressed to a first approximation by the formation of its trimer $(ArOK)_3$. The dimers and trimers of ArOK can react with water or MeOH to form the monomer ArOK and KOH or potassium methoxide, as is also reflected in the kinetic scheme:

$$(ArOK)_3 \rightleftharpoons (ArOK)_2 + ArOK$$
$$(ArOK)_2 \rightleftharpoons ArOK + ArOK$$
$$(ArOK)_2 + H_2O \rightleftharpoons ArOK + KOH + ArOH$$
$$(ArOK)_3 + H_2O \rightleftharpoons (ArOK)_2 + KOH + ArOH$$
$$(ArOK)_2 + CH_3OH \rightleftharpoons ArOK + CH_3OK + ArOH$$
$$(ArOK)_3 + CH_3OH \rightleftharpoons (ArOK)_2 + CH_3OK + ArOH$$
$$(ArOK)_3 + 2CH_3OH \rightleftharpoons (ArOK)_2 + ArOH + CH_3OK \cdot CH_3OH$$

Finally, the kinetic scheme allows for the effect of the association of MeOH and MeOK in the formation of ArAlkOMe, which is also apparent in the alkylation of 2,6-di-t-butyl phenol in the presence of ArOK and MeOH. The inhibiting effect of the association of the alcoholates of alkali metals in reactions involving alcoholates is well known [5].

Thus, according to the proposed kinetic scheme the formation of ArAlkOMe can be the result of cationic exchange of the complex (GG), containing two phenolic fragments, thus generating ArOK.

The decomposition of the complex (GG) into ArAlkOK and ArOMe proceeds in parallel, but the rate of this reaction should be lower by three orders of magnitude than the rate of its decomposition to form ArAlkOMe.
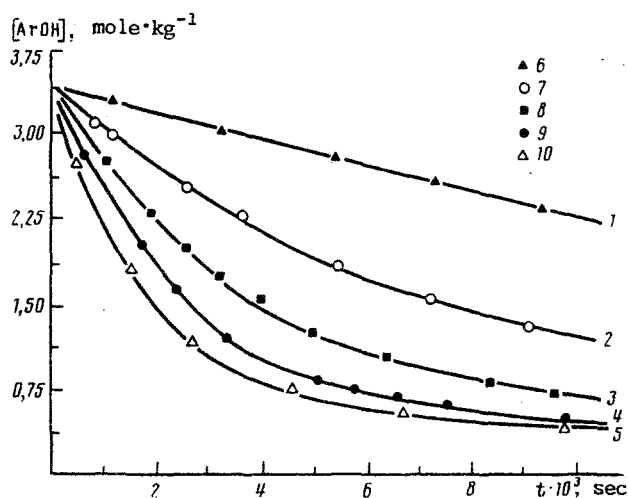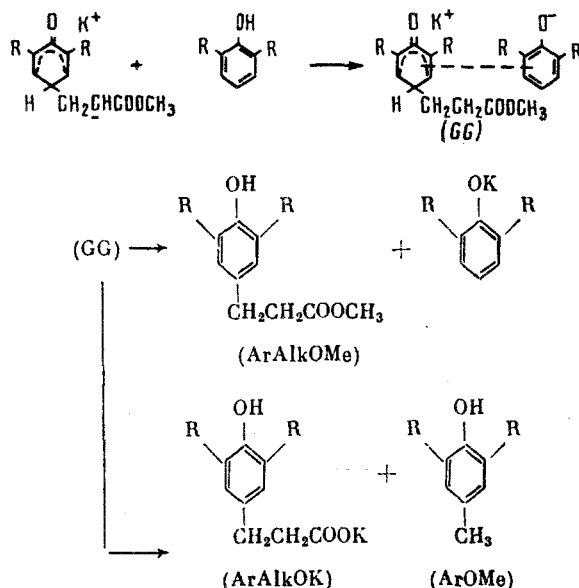
Fig. 1. Calculated (1-5) and experimental values (6-10) for
the kinetics of the consumption of ArOH (116°C, $[ArOH]_0 = 3.29$,
$[MA]_0 = 3.75$ mole·kg^{-1}). $[ArOK]_0$, mole·kg^{-1}: 1) 0.01; 2) 0.03;
3) 0.06; 4) 0.118; 5) 0.2.

(ArAlkOMe)

(ArAlkOK)   (ArOMe)

ArOMe was detected by gas—liquid chromatography.

EXPERIMENTAL

The kinetic and analytical measurements were carried out as in [1]. ArOK was prepared
by adding equivalent amounts of t-BuOK and t-BuOH to ArOH; after filtration the crystalline
product was washed with hexane.

RESULTS AND DISCUSSION

The alkylation of ArOH with methyl acrylate (MA) in the presence of ArOK differs from the reac-
tion catalyzed by ArOK and H_2O. The differences are particularly apparent in the presence of a
catalyst with a high water content, and are reflected in the reaction rate, the selectivity of the
process, and the extent of conversion of ArOH. However, in the presence of a catalyst with a low
water content the kinetics of the consumption of ArOH follow different laws, which can be
derived from the proposed kinetic scheme. By choosing the rate constants of the elementary
stages satisfactory agreement between the calculated and the experimental data can be ob-
tained over a wide range of concentrations of ArOK and H_2O and of the ratio of ArOK to H_2O.

TABLE 1. Calculated Rate Constants for the Elementary Stages of the Reaction of 2,6-Di-t-butylphenol with Methyl Acrylate at 116°C

Reaction	k
$ArOH+KOH \rightarrow ArOK+H_2O$	$3 \cdot 10^2$
$ArOK+H_2O \rightarrow ArOH+KOH$	10^3
$ArOK+MA \rightarrow F$	$2,5$
$F \rightarrow ArOK+MA$	1
$F+H_2O \rightarrow G$	40
$G \rightarrow ArAlkOMe+KOH$	$5 \cdot 10^{-2}$
$G+H_2O \rightarrow ArAlkOMe+KOH \cdot H_2O$	6
$G+KOH \rightarrow ArAlkOMe+CH_3OK+H_2O$	$3 \cdot 10^{-3}$
$KOH \cdot H_2O \rightarrow KOH+H_2O$	10^6
$KOH+H_2O \rightarrow KOH \cdot H_2O$	$6 \cdot 10^5$
$CH_3OK+H_2O \rightarrow CH_3OH+KOH$	10^6
$CH_3OH+KOH \rightarrow CH_3OK+H_2O$	10^5
$ArOH+CH_3OK \rightarrow ArOK+CH_3OH$	$5 \cdot 10^3$
$ArOK+CH_3OH \rightarrow ArOH+CH_3OK$	10^4
$F+CH_3OH \rightarrow D$	70
$D+H_2O \rightarrow ArAlkOMe+KOH+CH_3OH$	$6 \cdot 10^{-1}$
$D+CH_3OH \rightarrow ArAlkOMe+CH_3OH \cdot CH_3OK$	$6 \cdot 10^{-1}$
$D+CH_3OH+CH_3OH \rightarrow ArAlkOMe+CH_3OH \cdot CH_3OH \cdot CH_3OK$	10^5
$D+CH_3OH \cdot CH_3OH \cdot CH_3OK \rightarrow ArAlkOMe+2CH_3OH \cdot CH_3OK$	$2 \cdot 10^{-2}$
$CH_3OH \cdot CH_3OH \cdot CH_3OK \rightarrow CH_3OH \cdot CH_3OK+CH_3OH$	$7 \cdot 10^{-2}$
$CH_3OH \cdot CH_3OK \rightarrow CH_3OK+CH_3OH$	10^{-3}
$CH_3OK+CH_3OH \rightarrow CH_3OH \cdot CH_3OK$	50
$D \rightarrow ArAlkOMe+CH_3OK$	10^{-1}
$F+CH_3OH \cdot CH_3OH \cdot CH_3OK \rightarrow ArAlkOMe+CH_3OK+CH_3OH \cdot CH_3OK$	10^{-4}
$KOH \cdot H_2O+H_2O \rightarrow KOH \cdot 2H_2O$	$5 \cdot 10^4$
$KOH \cdot 2H_2O \rightarrow KOH \cdot H_2O+H_2O$	10^4
$KOH \cdot 2H_2O+H_2O \rightarrow KOH \cdot 3H_2O$	$7 \cdot 10^4$
$KOH \cdot 3H_2O \rightarrow KOH \cdot 2H_2O+H_2O$	10^4
$MA+KOH \rightarrow CH_2=CHCOOK(MAK)+CH_3OH$	10^{-1}
$MA+KOH \cdot H_2O \rightarrow MAK+CH_3OH+H_2O$	10^{-1}
$MA+KOH \cdot 2H_2O \rightarrow MAK+CH_3OH+2H_2O$	$1,5$
$MA+KOH \cdot 3H_2O \rightarrow MAK+CH_3OH+3H_2O$	50
$2H_2O \rightarrow H_2O+H_2O$	10^7
$H_2O+H_2O \rightarrow 2H_2O$	10^7
$3H_2O \rightarrow 2H_2O+H_2O$	10^7
$2H_2O+H_2O \rightarrow 3H_2O$	10^7
$ArAlkOMe+KOH \rightarrow ArAlkOK+CH_3OH$	10^{-1}
$ArAlkOMe+KOH \cdot H_2O \rightarrow ArAlkOK+CH_3OH+H_2O$	1
$ArAlkOMe+KOH \cdot 2H_2O \rightarrow ArAlkOK+CH_3OH+2H_2O$	2
$ArAlkOMe+KOH \cdot 3H_2O \rightarrow ArAlkOK+CH_3OH+3H_2O$	10^2
$F+MA \rightarrow F \cdot MA$	$2 \cdot 10^{-1}$
$F \cdot MA \rightarrow F+MA$	$4 \cdot 10^{-2}$
$F \cdot MA+ArOH \rightarrow ArAlk(OMe)_2+ArOK$	$3 \cdot 10^{-4}$
$F+ArOH \rightarrow GG$	$8 \cdot 10^{-2}$
$GG \rightarrow F+ArOH$	10^{-3}
$GG \rightarrow ArAlkOMe+ArOK$	$4 \cdot 10^{-2}$
$GG \rightarrow ArOCH_3+ArAlkOK$	$5 \cdot 10^{-5}$
$ArOK+ArOK \rightarrow (ArOK)_2$	10^2
$(ArOK)_2 \rightarrow ArOK+ArOK$	10^2
$(ArOK)_2 \rightarrow ArOK \cdot ArO-K$	15
$ArOK \cdot ArO-K \rightarrow (ArOK)_2$	5
$ArOK \cdot ArO+K \rightarrow ArOK \cdot ArO^-+K^+$	$5 \cdot 10^{-2}$
$MA+MA+K^+ \rightarrow MA \cdot MA \cdot K^+$	$2 \cdot 10^3$
$(ArOK)_2+ArOK \rightarrow (ArOK)_3$	10^3
$(ArOK)_3 \rightarrow (ArOK)_2+ArOK$	10^{-5}
$MA \cdot MA \cdot K^++MA+H_2O \rightarrow$ **polymer**	10^5
$(ArOK)_2+H_2O \rightarrow ArOK+KOH+ArOH$	10^{-1}
$(ArOK)_3+H_2O \rightarrow (ArOK)_2+KOH+ArOH$	10^{-1}
$(ArOK)_2+CH_3OH \rightarrow ArOK+CH_3OK+ArOH$	10^{-1}
$(ArOK)_3+CH_3OH \rightarrow (ArOK)_2+CH_3OK+ArOH$	10
$(ArOK)_3+CH_3OH+CH_3OH \rightarrow (ArOK)_2+ArOH+CH_3OH \cdot CH_3OK$	10^4
$CH_3OH \cdot CH_3OK+CH_3OH \rightarrow CH_3OH \cdot CH_3OH \cdot CH_3OK$	10^3

Figure 1 shows the dependence of the kinetics of consumption of ArOH in its reaction with MA on the concentration of ArOK in the presence of pure ArOK. These results show that there is almost complete agreement between the experimental results and those calculated from the kinetic scheme with the constants given in Table 1 for the elementary stages. There is also agreement between calculation and experiment for the accumulation of a similar product, ArAlk(OMe)$_2$, in the alkylation of ArOH with methyl acrylate.

There is good agreement between experiment and calculation for the kinetics of the reaction of ArOH with MA in the presence of ArOK and H$_2$O. Figure 2 shows the kinetic curves for
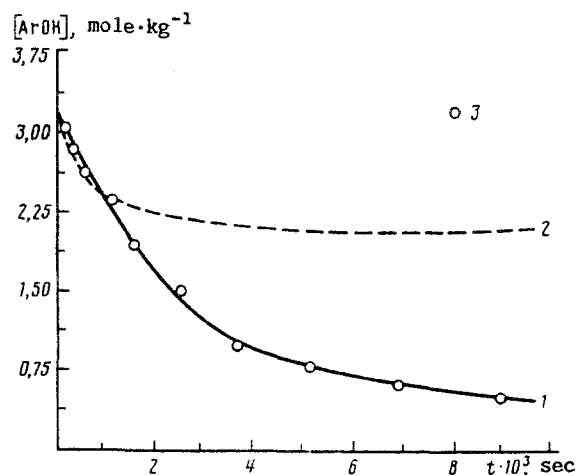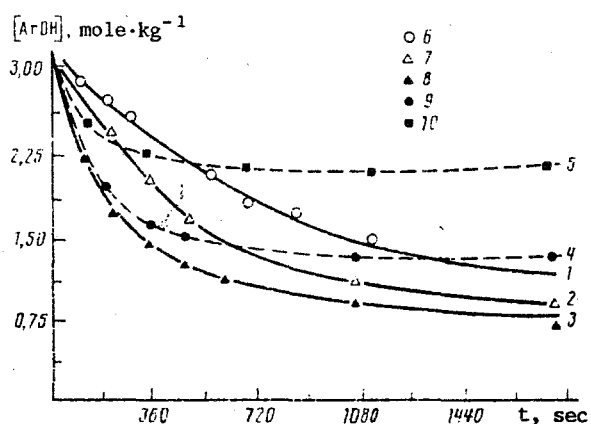
Fig. 2

Fig. 3

Fig. 2. Calculated (1-2) and experimental data (3) for the kinetics of the consumption of ArOH (116°C, $[ArOH]_0$ = 3.29, $[MA]_0$ = 3.75, $[ArOK]_0$ = 0.118, $[H_2O]_0$ = 0.0177 mole·kg^{-1}); 1) calculated from the scheme with the constants for the elementary reactions given in Table 1; 2) calculated as in [1].

Fig. 3. Calculated (1-5) and experimental data (6-10) for the kinetics of the consumption of ArOH (116°C, $[ArOH]_0$ = 3.29, $[MA]_0$ = 3.75, $[ArOK]_0$ = 0.118 mole·kg^{-1}). $[H_2O]$, mole·kg^{-1}: 1) 0.0318, 2) 0.0518, 3) 0.0918, 4) 0.118, 5) 0.16.

the consumption of ArOH calculated from the reaction scheme proposed earlier and from that given here, and also the experimental data. In this example the catalyst employed was ArOK containing 15 mole % H_2O. It will be seen that good agreement between calculation and experiment is achieved by taking into account the additions and changes which have been introduced into the scheme described previously for the kinetics of the reaction of 2,6-di-t-butylphenol with methyl acrylate.

Figure 3 shows the results for the kinetics of the consumption of ArOH in its reaction with MA in the presence of ArOK containing 30, 40, 80, 100, and 135 mole % H_2O. This dependence shows specifically the effect of water on the activity of ArOK over a wide range of water concentrations, the relation observed being close to that which describes the effect of KOH in the catalytic system ArOK—KOH.

Figure 4 shows the dependence of the rate of consumption of ArOH (W) at 160°C on the water content. The form of this dependence, with a maximum in the rate at 80% water, agrees well with the proposed reaction scheme and with the earlier data [1]. Regression analysis of this nonlinear relation gives the analytical expression
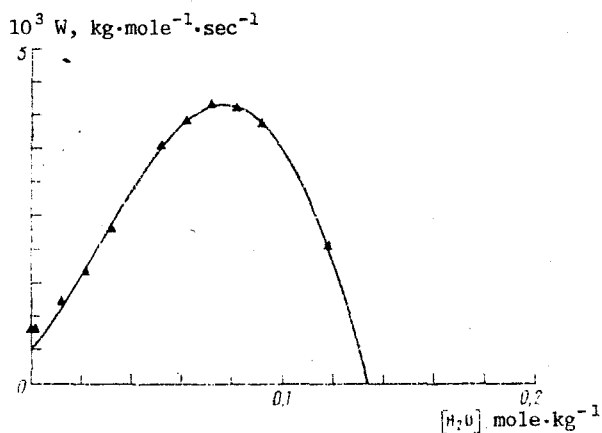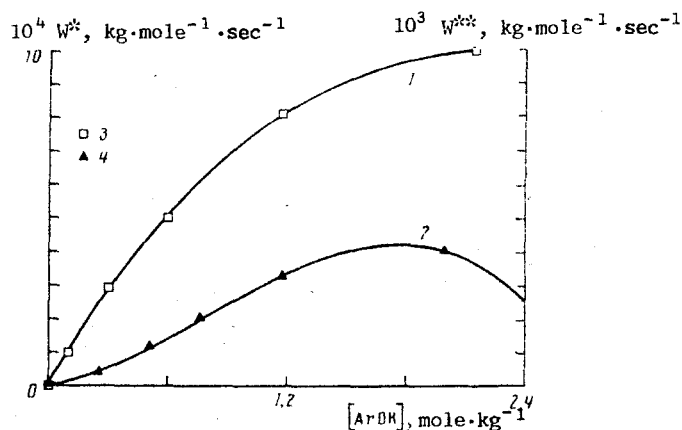
Fig. 4

Fig. 5

Fig. 4. Calculated and experimental dependence of the rate of consumption of ArOH (W at 160°C) on the concentration of H_2O. $[ArOH]_0 = 3.29$, $[MA]_0 = 3.75$, $[ArOK]_0 = 0.118$ mole·kg^{-1}. The curve is calculated and the points experimental.

Fig. 5. Calculated (1, 2) and experimental data (3, 4) for the dependence of the rate of consumption of ArOH (W at 160°C) on the concentration of the catalyst ($[ArOH]_0 = 3.29$, $[MA]_0 = 3.75$ mole·kg^{-1}): 1) $[ArOK]_0 = 0.118$ mole·kg^{-1}; 2) $[ArOK]_0 = 0.118$, $[H_2O]_0 = 0.0413$ mole·kg^{-1}; 3) ArOK; 4) ArOK + 35% H_2O.

$$W_{160} = 8.5 \cdot 10^{-4} + 2.104 \cdot 10^{-3} [H_2O] + 7.406 \cdot 10^{-2} [H_2O]^2 - 0.1902[H_2O]^3 + 0.1096[H_2O]^4$$

Figure 5 shows the experimental and calculated dependence of the rate of reaction W at 160°C on the concentrations of ArOK (curve 1) and of ArOK and H_2O (curve 2). At low concentrations of ArOK, H_2O has an inhibiting effect, apparently due to the existence of a critical concentration of ArOK in the presence of H_2O. It should be pointed out that at low ArOK concentrations these dependences are considerably different. Regression analysis leads to the following results: for the rate of the reaction of ArOH with MA in the presence of ArOK (W*): W* = $1.457 \cdot 10^{-5} + 2.483 \cdot 10^{-2} [ArOK] - 1.975 \cdot 10^{-2} [ArOK]^2 + 4.987 \cdot 10^{-3} [ArOK]^3$, and for the rate of reaction of ArOH with MA in the presence of ArOK and 35 mole % H_2O (W**): W** = $-1.571 \cdot 10^{-6} + 2.838 \cdot 10^{-4} [ArOK] + 1.575 \cdot 10^{-3} [ArOK]^2 - 1.606 \cdot 10^{-3} [ArOK]^3$.

There is also good agreement between the experimental and calculated results for the effect of CH_3OH on this reaction. It is found that concentrations of CH_3OH comparable with those of ArOH have practically no effect on the kinetics of the consumption of the latter.

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Thus, the set of results obtained make it possible to interpret the mechanism of the alkylation of 2,6-di-t-butylphenol by methyl acrylate in terms of the view adopted previous- ly (a catalytic chain mechanism) by allowing for features of catalysis by ArOK in the pres- ence of various substances with proton-donating properties (ArOH, H_2O, CH_3OH) and the effect of these components on the kinetics of the reaction as a whole.

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PROTONATING POWER OF AQUEOUS AND AQUEOUS-ALCOHOLIC
SOLUTIONS OF HCl IN THE PRESENCE OF INORGANIC SALTS

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The indicator method has been used to obtain a scale of protonating power of the medium H_0^S for solutions of HCl in the solvents of constant composition H_2O–EtOH–KCl and H_2O–NH_4Cl at 25°C. It is shown that in the solvents investi- gated the value of H_0^S in HCl is the same as H_0 in aqueous solution for the same ratios of the concentrations of HCl and of the basic solvents H_2O and EtOH. A method is worked out for estimating the value of $pK_{BH^+}^S$ of an organic base in aqueous and aqueous-alcoholic solutions of HCl in the presence of inorganic salts.

The position of equilibrium in the protonation of an organic base is determined by the value of its basicity constant and the acidity function H_0 [1]. Industrial syntheses cata- lyzed by acids are carried out with high concentrations of the reactants, aqueous-organic or organic solvents being used, and also in the presence of inorganic salts. In such pro- cesses the prediction of the effect of solvent composition on reactivity and on H_0 is an im- portant practical problem.

The object of the present investigation was to study the effect of solvent composition on protonating power in the systems H_2O–EtOH–KCl–HCl and H_2O–NH_4Cl–HCl.

EXPERIMENTAL

Spectrophotometry (Specord UV-VIS apparatus) was used to measure the extent of ioniza- tion of 4- and 2-nitroanilines (I and II) at 25°C and the ratio of the concentrations of the unionized (B) and ionized (BH^+) forms of the indicators, $I = C_B/C_{BH^+}$, was calculated. The measurements were carried out at different HCl concentrations in solvents of constant composition: H_2O– 16.5% EtOH–1.18 m KCl for (I) and (II), H_2O–34.45% EtOH–1.027 m KCl for (I), and also H_2O– NH_4Cl for (I) with NH_4Cl contents of 1, 2, 3, and 6.64 m. The concentrations of HCl and NH_4Cl are expressed in the relative molar scale m, i.e., the number of moles of the electro- lyte dissolved in 55.5 moles of the principal solvent. All the solutions of the required