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Promoting of Non-Transition Metal Alkylation with Organyl Halides in the Presence of Binary Systems Based on an Organometallic Compound and a Transition Metal Compound:

III.[1] Influence of Various Factors on the Rate of Stationary Process

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Abstract—Basing on analysis of the proposed mechanism of promoting of non-transition metals alkylation with organic halides in the presence of binary systems containing an organometallic compound and a transition metal compound, we discuss the possible effects of different factors (the components binary system components and the alkylated metal content in the mixture, hydrodynamic conditions in the reactor, and temperature) on the rate of the stationary process. Alkylation of zinc with ethyl bromide in the presence of ethylzinc bromide–copper(I) iodide mixture has been considered as a model system. The experiments have confirmed the basic analysis results, thus confirming the model validity. The concept of mathematical modeling of direct synthesis of mixed alkyl derivatives of zinc in the presence of the binary systems has been proposed.

Keywords: zinc, ethyl bromide, alkylation, promoting, mathematical model, reaction mechanism

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Validity of all details of the mechanism of promoting of direct synthesis of organometallic compounds in the presence of certain binary systems proposed in [2] can be hardly directly proved experimentally at the current state of the art. However, it is of interest to experimentally investigate the kinetic features of the process reflecting its mechanism. Coincidence with the conclusions derived via the kinetic analysis of the proposed mechanism would then be an argument for validity of the latter. In view of that, in this work we have considered the zinc alkylation with ethyl bromide in the presence of ethylzinc bromide and copper(I) iodide as a model system to investigate the effects of different factors on the stationary process rate. The conclusions made by theoretical consideration of the proposed scheme were further verified experimentally.

The proposed stage-by-stage scheme of direct synthesis of organometallic compounds in the presence of the binary systems and the preliminary experimental results on alkylation of zinc powder with ethyl bromide in the presence of ethylzinc bromide and copper(I) iodide [2] have suggested that the process course can be roughly divided into two parts: a relatively short induction period and the following stationary process. The stationary reaction proceeds at constant rate up to deep conversion of zinc and ethyl bromide. Taking these considerations into account, the following formal kinetic equation (1) has been proposed to describe the stationary process:

$$w = k^{\mathrm{eff}}\alpha\theta_{\mathrm{Cu}}S_{\mathrm{Zn}}, \tag{1}$$

with w, the process rate; k^{eff}, effective specific rate constant; α, a factor equal to the fraction of zinc surface free of the passivating film and transition metal phases; θ_{Cu}, concentration of the catalytically active particles (for example copper adatoms) at zinc surface; and S_{Zn}, surface area of zinc.

The following assumptions have been made to derive the kinetic equation: strong adsorption of the

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organic halide at the surface is required for the process to occur; the θ_{Cu} surface concentration is quasi-stationary, whereas the $\alpha\theta_{Cu}S_{Zn}$ value is approximately constant in the course of the process up to deep conversion of the reactants (zinc and ethyl bromide). The first assumption can be rationalized as follows: if the organic halide attacks the catalytically active particle from the bulk phase, the equation should include its volumetric concentration, significantly decreasing in the course of the process. This scheme contradicts the observed constant rate of the reaction, whereas the condition of strong adsorption of the organic halide at the active surface are not against their known adsorption properties in the case of transition metal surface [3, 4] and high reactivity of atoms, small clustersand metals subhalides towards organic halides [2]. The dimensionless surface concentration of the organic halides at the active surface can then equal to unity in the case of adsorption saturation; hence, the organic halide concentration can be excluded from the kinetic equation coinciding with the experimental observations. The θ_{Cu} quasi-stationarity requires that the sequence of the stages determining the active zinc surface formation is quasi-stationary as well. Such set of the stages can be considered as a branched sequence of irreversible and reversible mono- and bimolecular reactions [2]. Generally, the linear sequence of (ir) reversible stages is quasi-stationary if the rate constant of the first irreversible stage is much less than the rate constants of the other irreversible stages [5]. In the studied case, the first irreversible stage of all the branches of the stages sequence is the reaction of the binary system components (EtZnBr and CuI) at the CuI particles surface to form ethylcopper. This stage (cross-metallation) is reversible; however, since the formed ethylcopper is further subject to fast thermal decomposition to form copper atoms along with molecular products of recombination and disproportionation of ethyl radicals, the ethylcopper formation can be considered almost irreversible. The preliminary experiments [2] have shown that interaction of ethylzinc bromide and copper(I) iodide under conditions of direct synthesis of ethylzinc bromide is extremely slow, the ethylzinc bromide conversion being as low as 2% after 5 h at 38°C. This has confirmed that the cross-metallation stage limits the supply of copper atoms at the zinc surface and the subsequent macroscopic stage of copper phase formation. Then the sequence of stages determining formation of active zinc surface in the course of direct synthesis of ethylzinc bromide is indeed quasi-stationaryand the θ_{Cu} surface concentration can be considered quasi-stationary. The α factor should increase in the course of the process due to gradual elimination of the passivating film at the zinc surface. Therefore, the decrease of zinc surface area (S_{Zn}) during the process is somewhat compensated by the increase of the α factorand the $\alpha\theta_{Cu}S_{Zn}$ product can be varied marginally up to deep conversion of zinc.

The presence of the surface concentration of copper adatoms (θ_{Cu}) term in Eq. (1) practically implies that the active zinc surface is determined by a ratio of the copper crystallization rate at zinc surface and copper supply rate to the surface. Henceall the factors affecting kinetics of the transition metal supply at the surface of the alkylated metal and the crystallization rate (nucleation and growth rates) can potentially determine the value of active surface of the alkylated metal and, therefore, the rate of the target organometallic compound formation. These factors include the content of the alkylated metal and the binary mixture components and hydrodynamic conditions in the reactor, on top of temperature (changing the rate of all the chemical stages according to the exponential law) as well as nucleation and crystal growth rates of the transition metal. Preliminary experiments have revealed that the stationary process rate is almost independent of ethylzinc bromide concentration in the reaction mixture [2]. Hence, the process control by varying the organometallic compound content has been considered inefficient, likely due to adsorption saturation of the transition metal compound (CuI) surface at low concentration of the organometallic component (EtZnBr) of the binary system. Therefore, the EtZnBr concentration has not been further considered as a significant factor.

Effect of copper(I) content in the starting mixture. Concentration of copper adatoms at zinc surface (θ_{Cu}) included in kinetic equation (1) is unknown and should be linked to the known content of CuI in the initial reaction mixture in order to perform the analysis. Rigorous solution of the set of differential kinetic equations corresponding to the stage-by-stage scheme of active zinc surface formation [2] is fairly complicated; let us therefore limit the consideration to a general qualitative level. In particular, it has been established that in the case of homogeneous first-order reactions in the closed system at constant volume-current concentrations of intermediates and products are proportional to the initial concentration of the starting reactant, independently of the complexity of the linear and branched schemes including (ir) reversible stages [5–7]. Addition of the heterogeneous stages into the scheme does not change the general conclusion. Hencecurrent concentrations of all the intermediates of an arbitrary set of first-order stages seem to be proportional to the initial concentration of the starting reactant; this is not necessarily true, however, if the scheme includes the higher-order stages [6]. It has been earlier demonstrated [2] that the stages set determining zinc active surface formation can be considered as a branched sequence of (ir) reversible mono- and bimolecular reaction starting from the interaction of the binary mixture component (CuI and EtZnBr in the model system discussed herein). Hence concentration of copper adatoms at zinc surface should be proportional (or symbate) to the CuI content in the starting reaction mixture; let us consider the direct proportionality case for the sake of simplicity. Heterogeneous character of the process should be accounted for, resulting in the inverse proportionality of the surface concentration of the adatoms to the zinc surface area [Eq. (2)]:

$$\theta_{\mathrm{Cu}} = \beta(S_{\mathrm{sp}})_{\mathrm{CuI}}[\mathrm{CuI}]_0/(\alpha S_{\mathrm{Zn}}), \qquad (2)$$

with β, a factor depending on effective rate constants of the stages determining copper atoms supply at the zinc surface; $(S_{\mathrm{ap}})_{\mathrm{CuI}}$, specific surface of CuI; $[\mathrm{CuI}]_0$, content of CuI in the starting reaction mixture.

Accounting for Eq. (2), the kinetic equation (1) can be reshaped as follows:

$$w = k^{\mathrm{ef}}\beta(S_{\mathrm{sp}})_{\mathrm{CuI}}[\mathrm{CuI}]_0 \approx k_1^{\mathrm{ef}}[\mathrm{CuI}]_0, \qquad (3)$$

with $k_1^{\mathrm{ef}} = k^{\mathrm{eff}}\beta(S_{\mathrm{sp}})_{\mathrm{CuI}}$, effective rate constant.

Equation (3) suggested that the stationary process rate should be approximately proportional to the copper(I) iodide content in the starting mixture and independent of the zinc content under conditions of adsorption saturation of CuI surface with the organometallic component of the binary mixture. In other words, the rate of direct synthesis of the organometallic compound should be determined by the rate of copper adatoms appearance at the zinc surface. It has been assumed that the $(S_{\mathrm{sp}})_{\mathrm{CuI}}$ and $[\mathrm{CuI}]_0$ values were approximately constant in the course of the stationary process. The assumption is based on the very low rate of the binary mixture components interaction as observed experimentally in [2]. However, Eq. (3) can be operative only over the part of the $w = f\{[\mathrm{CuI}]_0\}$ dependence (corresponding to the lowest CuI content) rather than over the whole range of $[\mathrm{CuI}]_0$ values. Enhancement of copper-containing particles supply to zinc surface should end up with the adsorption saturation, when all the zinc surface sites available for binding copper atoms or their precursors are loaded. In other words, the θ_{Cu} value and the process rate should reach the highest value at the given temperatureand further increase of $[\mathrm{CuI}]_0$ will not affect the process rate any more, the latter being exclusively determined by temperature and zinc surface at start [Eq. (4)]:

$$w = k^{\mathrm{eff}}\alpha(\theta_{\mathrm{Cu}})_{\max}(S_{\mathrm{sp}})_{\mathrm{Zn}}[\mathrm{Zn}] \approx k_2^{\mathrm{ef}}[\mathrm{Zn}]_0, \qquad (4)$$

with $\alpha(S_{\mathrm{sp}})_{\mathrm{Zn}}[\mathrm{Zn}] \approx \gamma[\mathrm{Zn}]_0 \approx \mathrm{const}$; γ, a proportionality coefficient; $k_2^{\mathrm{ef}} = k^{\mathrm{eff}}\gamma(\theta_{\mathrm{Cu}})_{\max}$, effective rate constant; $(\theta_{\mathrm{Cu}})_{\max}$, surface concentration of copper atoms under conditions of adsorption saturation of zinc surface; $(S_{\mathrm{sp}})_{\mathrm{Zn}}$, specific surface area of zinc; [Zn], content of zinc in the reaction mixture; $[\mathrm{Zn}]_0$, content of zinc in the starting mixture.

Hence, the $w = f\{[\mathrm{CuI}]_0\}$ plot should in general case contain the initial linear part showing the approximately linear increase of the stationary process rate [Eq. (3)] and a plateau part of the constant stationary process rate [Eq. (4)]. Since zinc alkylation does not occur in the absence of copper(I) iodide [2], the curve should cross the coordinate origin as shown in Fig. 1a.

Effect of zinc content in the starting mixture. At low content of zinc in the starting mixture and constant supply of copper atom to the adlayer at zinc surface adsorption saturation of zinc surface with copper atoms should be attained, the adatoms concentration being the highest possible according to the adsorption isotherm. Under such conditions, only part of copper-containing particles present in the reaction mixture is trapped at zinc surfaceand the rate of the stationary process should be proportional to zinc content in the starting mixtureaccording to Eq. (4). However, if zinc surface area grows sufficiently high, practically all the copper-containing particles supplied at the surface can be trappedand the surface concentration of copper adatoms is then proportionally decreased with the increase of zinc surface area, the active zinc surface are ($S_{\mathrm{act}} \approx \gamma\theta_{\mathrm{Cu}}[\mathrm{Zn}]_0$) being approximately constant, determined by the copper atoms supply at the adlayer and the process temperature. Under such conditions, Eq. (3) is held. Hence, the $w = f\{[\mathrm{Zn}]_0\}$ plot should be represented by a curve with saturation part starting at the coordinate origin as well as shown in Fig. 1a.

Effect of hydrodynamic conditions in the reactor. The rate of copper atoms supply at zinc surface can be

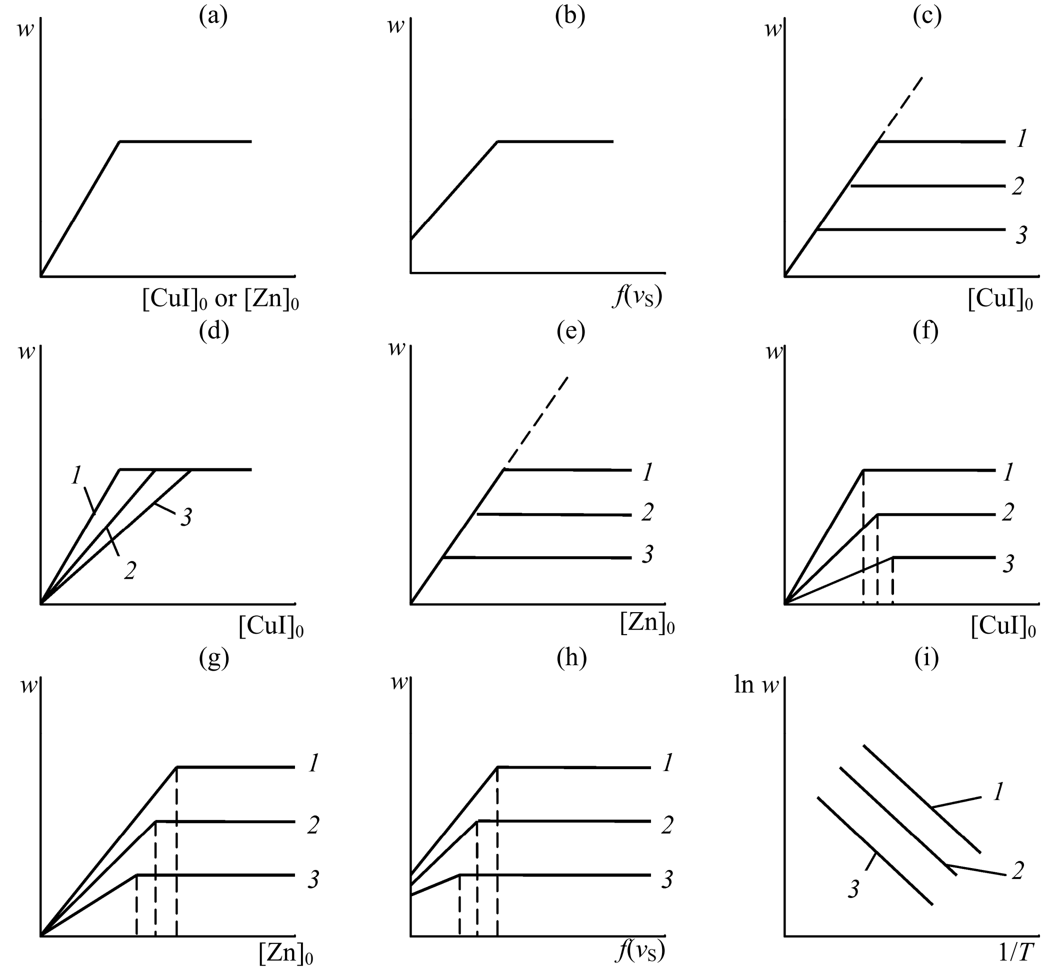

Fig. 1. Rate of stationary alkylation of zinc with ethyl bromide in the presence of ethylzinc bromide and copper(I) iodide as function CuI(I) and zinc content in the starting mixture (a) or the stirring intensity $f(v_S)$ (b); the $w = f\{[CuI]_0\}$ changes upon simultaneous variation of zinc content in the starting mixture (c), the stirring intensity (d), and temperature (f); the $w = f\{[Zn]_0\}$ changes upon simultaneous variation of copper(I) iodide or the stirring intensity (e) and temperature (g); the $w = f[f(v_S)]$ changes upon simultaneous variation of temperature (h); the stationary process rate as function of temperature upon simultaneous variation of the stirring intensity (i). In all the cases the varied factor intensity increases in the *1* > *2* > *3* series.

in general determined by the mass transfer on top of the chemical stages. The active zinc surface is then formed according to the laws of mixed diffusion-chemical or purely diffusion kinetics. Therefore, the active zinc surface area (and consequently, the rate of the stationary alkylation process) can be affected by the conditions of forced mixing of the reaction mixture. In the stirring intensity is varied when the saturation of copper adatoms adsorption at the zinc surface is not attained, the stationary alkylation rate as function of the stirring intensity should show up a plateau at some point, whereas initially the enhanced mixing will accelerate the process due to speeding up the diffusion-limited stages. The transition into the plateau region will presume the change of the active surface formation regime from the diffusion or diffusion-kinetic into the purely kinetic one. The stirring bar rotation speed (v_S) or any derived function [$f(v_S)$] can be utilized as parameter to describe the reaction mixture mixing efficiency. The $w = f[f(v_S)]$ plot does not start at the coordinate origin, since in the absence of the forced mixing the mass transfer is not completely stopped. The corresponding plot is sketched in Fig. 1b. Similarly to the above-discussed cases, the onset of the constant rate of the direct synthesis of organometallic compound as function of the mixing intensity is due to the attained adsorption saturation of zinc surface with copper adatomsbeing possible even outside the purely kinetic regime of the active zinc surface formation. However, independently of the active formation regime (either kinetic or diffusion one), the "saturation" shape of the stationary alkylation rate as function of CuI or Zn content in the starting mixture should be preserved.

Simultaneous variation of a pair of parameters. The above-discussed single-factor plots of the stationary process rate should be somewhat changed when the two factors are varied simultaneously. In particular both the slope of the initial linear part of the curve and the plateau value can be changed in the $w = f\{[\mathrm{CuI}]_0\}$, $w = f\{[\mathrm{Zn}]_0\}$and $w = f[f(v_\mathrm{S})]$ plots. Using Eqs. (3) and (4), it can be demonstrated that the plots should become as shown in Figs. 1c–1h.

The stationary process rate as function of temperature should approximately follow the Arrhenius equation, showing close to linear plots in the $\ln w \sim 1/T$ coordinates (Fig. 1i). The effective activation energy determining the slope of the linear Arrhenius plot is in turn determined by effective activation energies of the stages of catalytic formation of the target organometallic compound as well as of the active surface formation. If the catalytic process gives the major contribution into the overall activation energy, the slope of the plot is expected to be marginally changed as function of the mixing efficiency and the regime of the active zinc surface formation (Fig. 1i). If the process is at least partially diffusion-controlled, its rate should increase with the mixing intensity until the process regime is changed to the kinetic one.

Prior to the investigation of various factors affecting the rate of the stationary alkylation process, we purposefully checked that differences of in the admixtures composition and the particles size of various commercial zinc grades had practically no effect on the kinetics of its alkylation with ethyl bromide in the presence of the EtZnBr–CuI system (Fig. 2a and Table 1). Experimental results demonstrating the effects of the mixing intensity, temperature and content of the mixture components are given in Figs. 2–6 and Tables 1–4.

Similarly to the preliminary trials [2]alkylation of zinc powder with ethyl bromide over the whole range of the varied parameters revealed the induction period and almost constant rate of the developed process. Therefore, the kinetic curves were fitted with a linear equation (5):

$$G_\mathrm{OMC}(\tau) = w(\tau - \tau_\mathrm{ind}), \qquad (5)$$

with G_OMC amount of the formed ethylzinc bromide, mol; w, rate of the stationary process, mol/s; τ and τ_ind, the current experiment time and the induction period, respectively, s.

Kinetics of all the experimental runs was appropriately described by Eq. (5). The process rate and its standard deviation (regarded as the confidence interval) were determined via linear regression analysis of the kinetic curve via standard methods [8]. Validity of the fitting was estimated by the Fisher criterion comparing the experimental (F_exp) and the tabulated (F_tab) values [9]. Dispersion of reproducibility of kinetic experiments required for F_exp calculation was found from the two independent series of experiments including 3 and 7 runs via the usual method [9]. Examples of the achieved reproducibility of kinetic measurements is demonstrated by kinetic curves *1* in Figs. 2b–2e plotted according to the results of several independent runs. The rate of the process was estimated by combined processing of the whole set of experimental points using the ($\tau - \tau_\mathrm{ind}$) values determined individually for each of the runs as the fitting parameter.

The experimental results coincided with the above-discussed expectations derived from qualitative analysis of the process kinetic scheme (cf. Figs. 3a, 3c, 5a, 5c, 5d, and 6a–6c with the corresponding sketches in Fig. 1c–1*h*), thus supporting the mechanism suggested in [2]. Noteworthily, the plots stationary process rate (mol/s) as function of the respective parameters $w = f(v_\mathrm{S})$, $w = f\{[\mathrm{CuI}]_0$ and $w = f\{[\mathrm{Zn}]_0\}$ appeared as curves with saturation, their increasing parts being well fitted with Eqs. (6)–(9) (the confidence intervals are reported equal to the standard deviation).

$$w(38°\mathrm{C}) = [(12.63\pm1.81) + (10.64\pm0.66)v_\mathrm{S}] \times 10^{-6}, \quad (6)$$

with v_S, stirring bar rotation speed, s^{-1}; $S = 1.6 \times 10^{-6}$ mol/s correlation coefficient $r = 0.996$ (Fig. 3a).

$$w(38°\mathrm{C},\ v_\mathrm{S} > 4.5\ \mathrm{s}^{-1}) = k_1^\mathrm{ef}[\mathrm{CuI}]_0 = [(1.71\pm0.09) \times 10^{-3}][\mathrm{CuI}]_0, \qquad (7)$$

with $[\mathrm{CuI}]_0$, copper(I) iodide content in the starting mixture, mol; $S = 6.7 \times 10^{-6}$ mol/s, $r = 0.993$ (Fig. 5a).

$$w(38°\mathrm{C}) = \{[(3.82\pm0.55) + (3.23\pm0.20)v_\mathrm{S}] \times 10^{-4}\}[\mathrm{CuI}]_0, \qquad (8)$$

with v_S, stirring bar rotation speed, s^{-1} ($v_\mathrm{S} \le 4.5\ \mathrm{s}^{-1}$), $S = 0.050 \times 10^{-3}$ mol/s, $r = 0.996$ (Figs. 5a, 5b).

$$w(38°\mathrm{C}) = (5.69\pm0.18) \times 10^{-5}[\mathrm{Zn}]_0, \qquad (9)$$

with $[\mathrm{Zn}]_0$, zinc content in the starting mixture, mol; the physical meaning of proportionality coefficient is determined by Eq. (4) ($S = 3.9 \times 10^{-6}$ mol/s, $r = 1.000$) (cf. Fig. 6a).

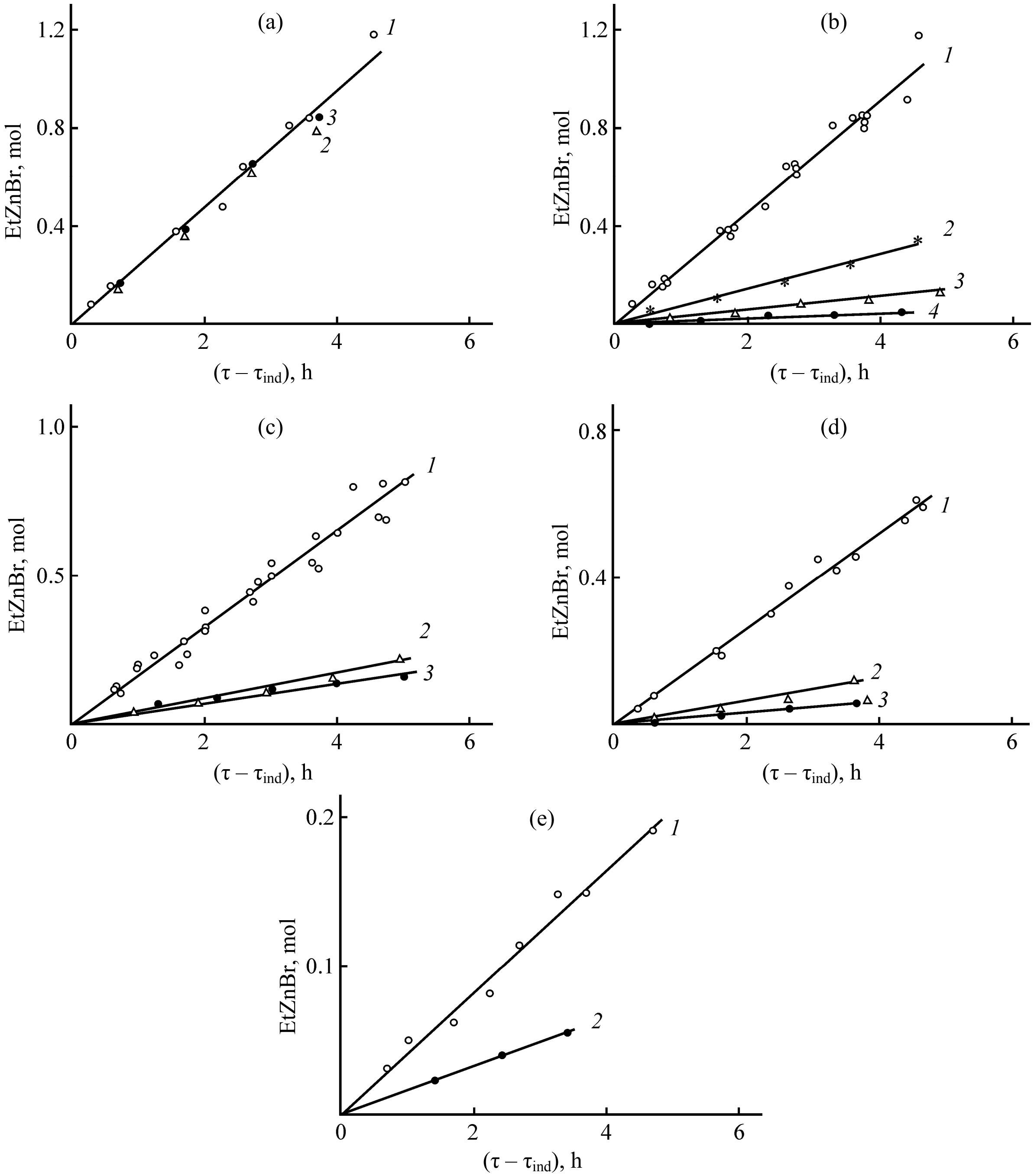

Fig. 2. Kinetics of ethylzinc bromide accumulation in the reaction mixture in the course of zinc powder alkylation with ethyl bromide in the presence of ethylzinc bromide–copper(I) iodide binary mixture for different zinc grades (a), temperature and the stirring bar speed (b–e) (the starting mixtures composition is listed in Table 1). (a) zinc grade: PTs-10 (*1*), PTs-4 (*2*), PTs-3 (*3*), v_S = 500 min^{-1}, T = 38°C; (b) v_S = 500 min^{-1}, T = 38 (7 independent runs) (*1*), 28 (*2*), 18 (*3*), 8°C (*4*); (c) v_S = 180 min^{-1}, T = 38 (7 independent runs) (*1*), 28 (*2*), 20°C (*3*); (d) v_S = 120 min^{-1}, T = 38 (3 independent runs) (*1*), 28 (*2*), 18°C (*3*); (e) v_S = 0 min^{-1}, T = 38 (2 independent runs) (*1*), 28°C (*2*).

In the frame of the suggested mechanism, the plateau in the $w = f\{[\mathrm{CuI}]_0\}$ plot is due to adsorption saturation of zinc surface with catalytically active copper-containing particles (adatoms, small clusters and, possibly copper subhalide) that was attained (38°C and initial zinc loading of 1.84 mol) at $[\mathrm{CuI}]_0$ of 0.060 (v_S = 500 min^{-1}), 0.060 (v_S = 250 min^{-1}), 0.075 (v_S = 180 min^{-1}), 0.094 (v_S = 120 min^{-1}), and 0.295 (no

Table 1. Alkylation of different grades of commercial zinc powder with ethyl bromide in the presence of the ethylzinc bromide–copper(I) iodide binary system[a]

Exp. no.	Zinc grade	Experiment time, h	Induction period, min	Number of points in the kinetic curve	Ethylzinc bromide yield, %	Rate of ethylzinc bromide formation ($w \times 10^6$, mol/s) and standard deviation of the kinetic curve fitting
1	PTs-3	4	17	4	46	64.4±2.5 ($S = 0.016$)
2	PTs-4	4	17	4	44	61.3±2.9 ($S = 0.019$)
3	PTs-10	5	26	5	64	69.3±3.4 ($S = 0.033$)
4	PTs-10	4	44	3	44	65.7±9.2 ($S = 0.051$)

[a] The experiments were performed at 38°C under conditions of forced stirring of the reaction mixture (the stirring bar rotation speed 500 min^{-1}). Starting mixture composition: 120.3 g (1.84 mol) of zinc, 200 g (1.84 mol) of ethyl bromide, 11.89 g (0.07 mol) of ethylzinc bromide, and 6.25 g (0.033 mol) of copper(I) iodide.

forced stirring) mol (Fig. 5a). Since under conditions of the experiment shown in Fig. 5a ($[\mathrm{CuI}]_0 = 0.03$ mol) the adsorption saturation was not attained, the plateau observed in the $w = f(v_\mathrm{S})$ plot was due to the transition from the diffusion or diffusion-kinetic formation of active zinc surface to the purely kinetic one. The onset of the plateau in the $w = f\{[\mathrm{Zn}]_0\}$ plots (38°C, $[\mathrm{CuI}]_0 = 0.033$ mol) was observed at zinc loading $[\mathrm{Zn}]_0$ of 1.112 ($v_\mathrm{S} = 500$ min^{-1}), 0.977 ($v_\mathrm{S} = 250$ min^{-1}), 0.792 ($v_\mathrm{S} = 180$ min^{-1}), 0.632 ($v_\mathrm{S} = 120$ min^{-1}), and 0.200 (no forced stirring) mol (Fig. 6a). The effect of initial CuI loading and temperature on the $w = f\{[\mathrm{Zn}]_0\}$ plot is presented in Figs. 6b, 6c.

The effective activation energy of the stationary process was practically constantclose to 70 kJ/mol, with the stirring bar speed (Fig. 3c): 73.3±4.2 (500 min^{-1}), 66±24 (180 min^{-1}), 78±16 (120 min^{-1}), 72 (no forced stirring) kJ/mol. The high effective activation energy and its independence of the mixing conditions evidenced about kinetic regime of ethylzinc bromide at all the studied stirring speeds. Dependence of the stationary process rate on the stirring intensity was likely due to the effect on the active zinc surface.

The change of ethylzinc bromide content in the starting mixture from 0.48 to 3.24 mol/L had practically no effect on the rate of the direct synthesis (Fig. 3b). The EtZnBr concentration (mol/L) was determined basing of the measured density of ethylzinc bromide solution in ethyl bromide that was satisfactorily fitted with Eq. (10) (8 points, the confidence interval is given by standard deviation $S = 6$ kg/m^3, $r = 0.999$).

$$\rho_{18} = 1456 + (6.335 \pm 0.060)[\mathrm{EtZnBr}], \qquad (10)$$

with ρ_{18}, the solution density at 18°C, kg/m^3; [EtZnBr], ethylzinc bromide concentration in the 0–56 wt % range.

On top of other conclusions, the constant process rate observed up to deep conversion of the starting reagents in the studied systems demonstrated that the increase of ethylzinc bromide in the course of the target reaction should not affect the alkylation kinetics. However, the complete $w = f\{[\mathrm{EtZnBr}]_0\}$ plot should likely be represented by a curve with saturation, starting in the coordinate origin (Fig. 3b). Since the experiments were performed at $[\mathrm{CuI}]_0$ of 0.03 mol, outside the range of adsorption saturation of zinc surface with copper-containing species (Fig. 5a), the observed plateau of the $w = f\{[\mathrm{EtZnBr}]_0\}$ function likely resulted from adsorption saturation of CuI particles with EtZnBr over the whole studied range of the starting ethylzinc bromide loadings. That was natural, since copper(I) iodide was used in catalytic amounts.

Noteworthily, the onset of the $w = f\{[\mathrm{CuI}]_0\}$ and $w = f\{[\mathrm{Zn}]_0\}$ plateaus should be observed at the same incident flux of copper-containing particles onto the zinc surface, other conditions being equal. The incident flux could be characterized by the ratio of initial loadings of copper(I) iodide and zinc: $\{[\mathrm{CuI}]_0/[\mathrm{Zn}]_0\}_\mathrm{op}$, the "op" subscript hereafter denoting "onset of plateau." The typical "saturation" shape of the $w = f\{[\mathrm{CuI}]_0\}$ and $w = f\{[\mathrm{Zn}]_0\}$ plots conditioned the crucial importance of the $\{[\mathrm{CuI}]_0/[\mathrm{Zn}]_0\}_\mathrm{op}$ value (or the value corresponding to other binary systems and alkylating metals) for mathematical modeling of direct synthesis of organometallic compounds in the presence of the binary systems. In particular both Eqs. (3) and (4) should be operative to determine the $w = f\{[\mathrm{CuI}]_0\}$

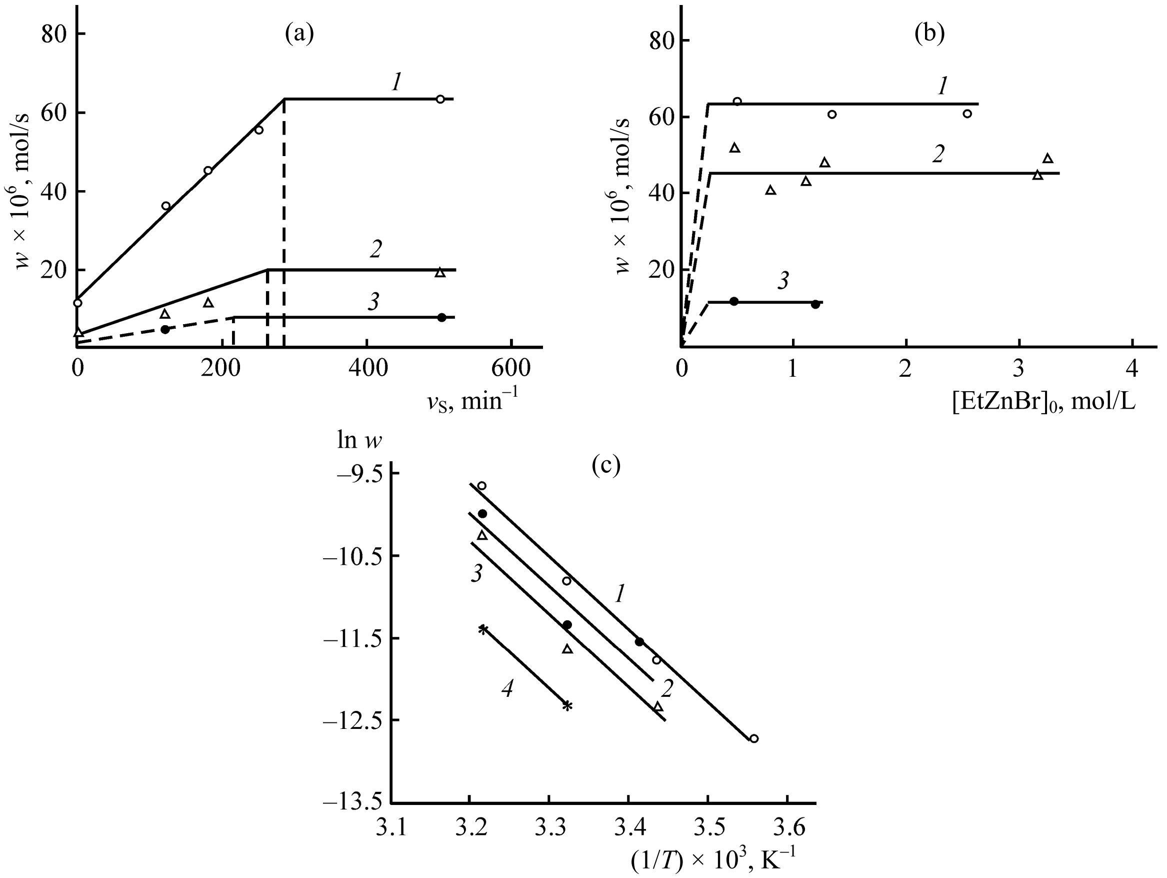

Fig. 3. Rate of zinc powder alkylation with ethyl bromide in the presence of ethylzinc bromide–copper(I) iodide binary system as function of the stirring intensity at different temperatures (a), starting concentration of ethylzinc bromide at different stirring conditions at 38°C (b), and temperature under different stirring conditions (c) (see data in Table 2). (a) *T* 38 (*1*), 28 (*2*), 18°C (*3*); (b) 500 (*1*), 180 (*2*), 0 min^{-1} (*3*); (c) 500 (*1*), 180 (*2*), 120 (*3*), 0 min^{-1} (*4*).

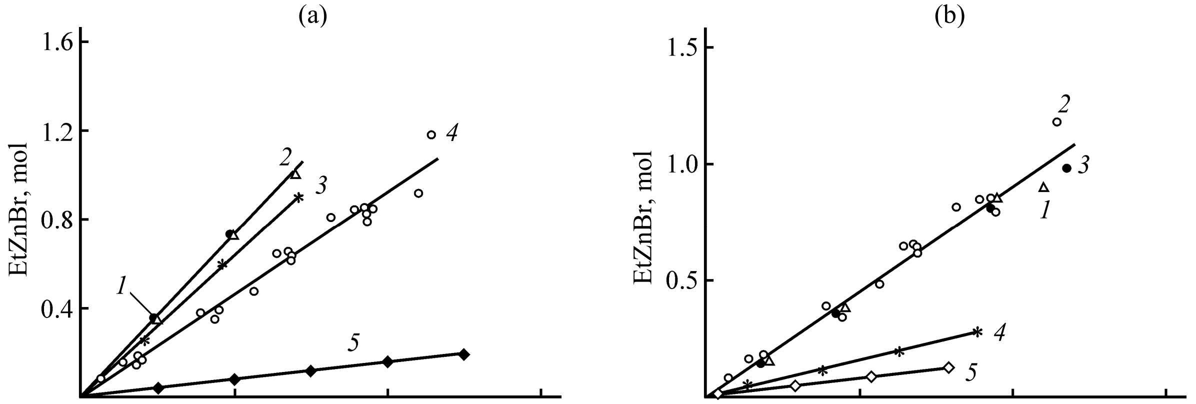

Fig. 4. Kinetics of ethylzinc bromide accumulation in the reaction mixture in the course of zinc powder alkylation with ethyl bromide in the presence of ethylzinc bromide–copper(I) iodide binary system at 38°C, stirring bar speed 500 min^{-1}, and varied content of copper(I) iodide (a) and zinc (b) in the starting mixture. Copper(I) iodide content, mol: (*1*) 0.119, (*2*) 0.079, (*3*) 0.056, (*4*) 0.033, (*5*) 0.003 (Table 3). Zinc content, mol: (*1*) 3.77, (*2*) 1.84, (*3*) 0.98, (*4*) 0.30, (*5*) 0.13 (Table 4).

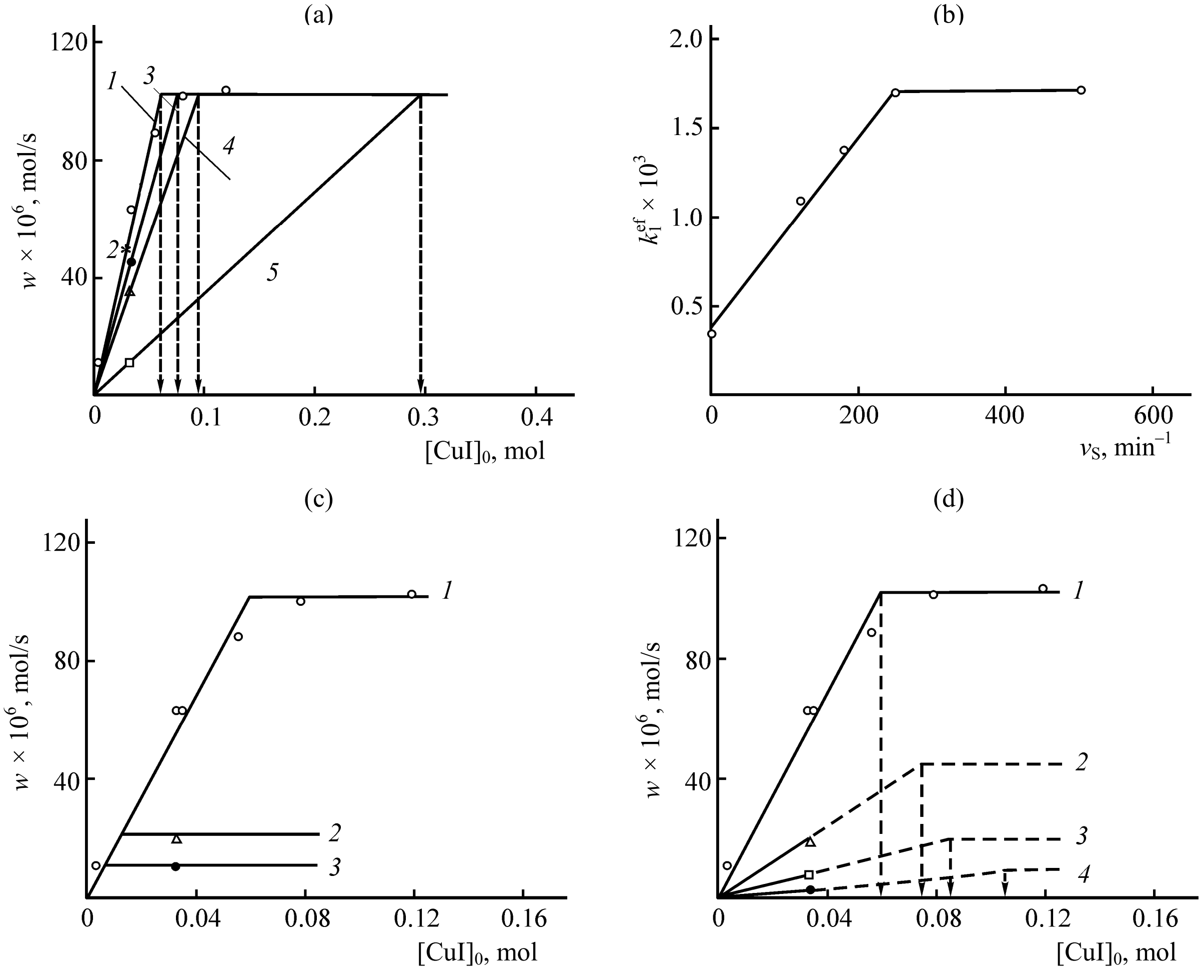

Fig. 5. Rate of zinc powder alkylation with ethyl bromide in the presence of ethylzinc bromide–copper(I) iodide binary mixture as function of copper(I) iodide content in the starting mixture at varied stirring bar speed (a and b), zinc content (c), and temperature (d). (a) $T = 38$°C, $v_S = 500$ (*1*) (Table 3), 250 (*2*), 180 (*3*), 120 (*4*), 0 min^{-1} (*5*) [(arrows) point at the $\{[CuI]_0\}_{if}$ values corresponding to the onset of plateau region (Tables 2 and 3)]; (b) k_1^{ef} in Eq. (7) as function of the stirring bar speed (see data in Fig. 5a); (c) $T =$ 38°C, v_S 500 = min^{-1}, [Zn] = 1.84 (*1*), 0.30 (*2*), 0.13 mol (*3*) (Tables 3 and 4); (d) $v_S = 500$ min^{-1}, [Zn] = 1.84 mol, T 38 (*1*), 28 (*2*), 18 (*3*), 8°C (*4*) (Tables 2 and 3).

and $w = f\{[Zn]_0\}$ values in the region of the plateau onset. Hence, Eq. (11) is held:

$$k_1^{ef}\{[CuI]_0\}_{op} = k_2^{ef}\{[Zn]_0\}_{op}. \qquad (11)$$

Accounting for Eq. (3) and (4), from Eq. (11) it follows:

$$\{[CuI]_0/[Zn]_0\}_{op} = k_2^{ef}/k_1^{ef} \approx \gamma(\theta_{Cu})_{max}/\beta(S_{sp})_{CuI}. \qquad (12)$$

Since factor β is a function of effective rate constants of the stages determining copper atoms supply to the adlayer at zinc surface, it should generally depend on both temperature and the reaction mixture stirring conditions. If factor β is approximately linear with the stirring speed ($\beta = \delta + \varepsilon v_S$, δ and ε being constant at a given temperature), Eq. (12) can be reshaped as follows.

$$\{[CuI]_0/[Zn]_0\}_{op} = (\eta + \zeta v_S)^{-1}, \qquad (13)$$

with $\eta = \delta(S_{sp})_{CuI}/\gamma(\theta_{Cu})_{max}$; $\zeta = \varepsilon(S_{sp})_{CuI}/\gamma(\theta_{Cu})_{max}$.

Equation (13) holds true in the diffusion of diffusion-kinetic regimes of zinc active surface formation, whereas in the purely kinetic regime factor β (and consequently, the $\{[CuI]_0/[Zn]_0\}_{op}$ value) becomes constant with the mixing intensity.

As expected both the $w = f\{[CuI]_0\}$ and $w = f\{[Zn]_0\}$ plots entered the plateau regions at the same value of effective incident flux of copper-containing particles

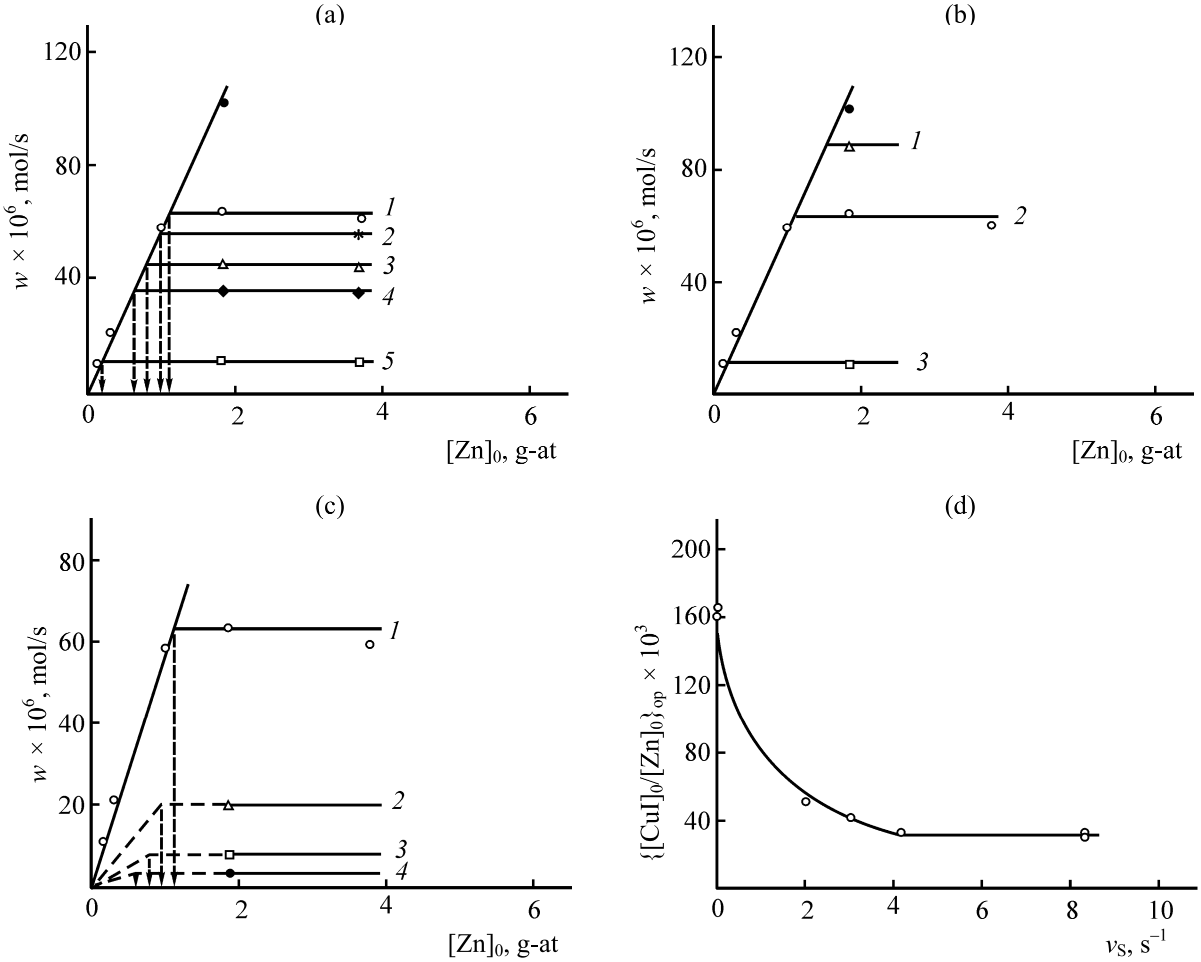

Fig. 6. Rate of alkylation of zinc powder with ethyl bromide in the presence of ethylzinc bromide–copper(I) iodide binary system as function of zinc content in the initial mixture at the varied stirring bar speed (a), content of copper(I) iodide (b), and temperature (c); The effect of stirring on the $\{[\mathrm{CuI}]_0]/\mathrm{Zn}]_0\}_{\mathrm{op}}$ value at 38°C (d). (a) 38ºC, $[\mathrm{CuI}]_0 = 0.033$ mol, $v_\mathrm{S} = 500$ (*1*), 250 (*2*), 180 (*3*), 120 (*4*), 0 min^{-1} (*5*) {Table 4, hereafter (dark circle) corresponds to Exp. 5 and 6 in Table 3; (arrows) point at the $\{[\mathrm{Zn}]_0\}_{\mathrm{op}}$ values corresponding to the plateau onset}; (b) 38°C, $v_\mathrm{S} = 500$ min^{-1}, $[\mathrm{CuI}]_0 = 0.056$ (Exp. 4, Table 3) (*1*), 0.033 (Exp. 1–5, Table 4) (*2*), 0.003 mol (Exp. 1, Table 3) (*3*); (c) $v_\mathrm{S} = 500$ min^{-1}, $[\mathrm{CuI}]_0 = 0.033$ mol, $T = 38$ (Exp. 1–5, Table 4) (*1*), 28 (*2*), 18 (*3*), 8°C (Table 2) (*4*).

(as expressed with the $[\mathrm{CuI}]_0/[\mathrm{Zn}]_0\}_{\mathrm{op}}$ ratio), other conditions (temperature and stirring conditions) being equal (Table 5).

The η and ζ coefficients [Eq. (13)] were determined using Eqs. (8) and (9).

$$\{[\mathrm{CuI}]_0/[\mathrm{Zn}]_0\}_{\mathrm{op}} = \{[(3.82\pm0.55) \times 10^{-4}/(5.69\pm0.18) \times 10^{-5}] + [(3.23\pm0.20) \times 10^{-4} v_\mathrm{S}/(5.69\pm0.18) \times 10^{-5}]\}^{-1} = [(6.71\pm0.99) + (5.68\pm0.39)v_\mathrm{S}]^{-1}. \qquad (14)$$

Equation (14) holds at $v_\mathrm{S} \leq 4.5$ s^{-1} (if $v_\mathrm{S} > 4.5$ s^{-1}, the $v_\mathrm{S} = 4.5$ s^{-1} should be used), the confidence intervals were determined using fundamentals of accuracy calculation [10].

Equation (14) accurately describes the experimental $\{[\mathrm{CuI}]_0//[\mathrm{Zn}]_0\}_{\mathrm{op}}$ values as function of the mixing efficiency over the whole studied range of the stirring bar speed (Table 5 and Fig. 6d). From the practical reasons, the reaction rate should be maximized; such conditions correspond to sufficiently high stirring bar rate when its effect is vanished (4.5 s^{-1} in the studied case) and the highest possible temperature (38°C, ethyl bromide boiling point at atmospheric pressure). Hence, Eq. (7) and the $\{[\mathrm{CuI}]_0/[\mathrm{Zn}]_0\}_{\mathrm{op}}$ value at 38°C (Table 5) are of the most practical importance.

$$\{[\mathrm{CuI}]_0/[\mathrm{Zn}]_0\}_{\mathrm{op}}\,(38°\mathrm{C}) = (31\pm3) \times 10^{-3}, \text{ mol CuI/mol Zn}. \qquad (15)$$

Table 2. Effect of the reaction mixture stirring speed and temperature on the rate of alkylation of zinc powder with ethyl bromide in the presence of ethylzinc bromide–copper(I) iodide binary system[a]

T, ºC	Stirring bar rotation speed, min^{-1}	Number of points in the kinetic curve and zinc grade	Rate of ethylzinc bromide formation ($w \times 10^6$, mol/s)	Standard deviation of the kinetic curve fitting, mol
38	500	27 (PTs-3, 4, 10)	63.3±0.9	0.045
	250	5 (PTs-3)	55.6±1.9	0.052
	180	27 (PTs-3, 4, 10)	45.1±0.8	0.046
	120	12 (PTs-3, 10)	36.0±0.6	0.022
	0	8 (PTs-3, 10)	11.4±0.3	0.008
28	500	5 (PTs-10)	19.9±1.1	0.011
	180	5 (PTs-4)	12.0±0.8	0.008
	120	4 (PTs-10)	9.0±1.1	0.008
	0	3 (PTs-10)	4.5±0.2	0.001
20	180	5 (PTs-4)	9.7±0.5	0.014
18	500	5 (PTs-10)	7.7±0.7	0.007
	120	4 (PTs-10)	4.5±0.1	0.0004
8	500	5 (PTs-10)	3.0±0.2	0.002

[a] Starting mixture composition: 120.3 g (1.84 mol) of zinc, 200 g (1.84 mol) of ethyl bromide, 11.89 g (0.07 mol) of ethylzinc bromide, and 6.25 g (0.033 mol) of copper(I) iodide.

Table 3. Effect of copper(I) iodide content in the starting mixture on the rate of alkylation of zinc powder with ethyl bromide in the presence of ethylzinc bromide–copper(I) iodide binary system[a]

Exp. no.	$[\text{CuI}]_0$, g (mol)	Experiment time, h	Induction period, min	Number of points in the kinetic curve	Ethylzinc bromide yield, %	Rate of ethylzinc bromide formation ($w \times 10^6$, mol/s) and standard deviation of the kinetic curve fitting
1	0.571 (0.003)	5.0	0	5	11	11.0±0.1 (*S* = 0.003)
2	6.250 (0.033)	5.0	11–44	27	64	63.3±0.9 (*S* = 0.045)
3	6.665 (0.035)	4.1	9	3	48	63.1±2.7 (*S* = 0.015)
4	10.665 (0.056)	3.0	10	3	49	89.2±4.2 (*S* = 0.015)
5	15.045 (0.079)	2.8	0	3	55	101.4±0.8 (*S* = 0.010)
6	22.662 (0.119)	2.0	2	2	40	103.6

[a] The experiments were performed at 38°C under conditions of forced stirring of the reaction mixture (the stirring bar rotation speed 500 min^{-1}). Starting mixture composition: 120.3 g (1.84 mol) of powder PTs-10 zinc (PTs-3 and PTs-4 zinc grades were used in Exp. 2 as well), 200 g (1.84 mol) of ethyl bromide, and 11.89 g (0.07 mol) of ethylzinc bromide. The reaction rate at the plateau region of the $w = f\{[\text{CuI}]_0\}$ plot derived via combined processing of Exp. 5 and 6 was of $(102.0\pm0.7) \times 10^{-6}$ mol/s, $S = 0.010$ mol. The τ_{ind} value for Exp. 2 is reported as a range containing all individual τ_{ind} values.

Equations (7) and (15) represent a mathematical model of the process at 38°C and the mixing conditions corresponding to the kinetically controlled process ($v_\text{S} \geq 4.5$ s^{-1}). Having been given the $[\text{Zn}]_0$ initial loading, Eq. (15) allows calculation of the initial $[\text{CuI}]_0$ loading required to reach the $\{[\text{CuI}]_0\}_\text{op}$ plateau value of the $w = f\{[\text{CuI}]_0\}$ function; further increase of copper(I) iodide loading should not affect the process rate. The so determined $\{[\text{CuI}]_0\}_\text{op}$ value can be transformed into the highest zinc alkylation rate in the considered system at 38°C via Eq. (7). The synthesis time required for the desired conversion of the reactants can be estimated using Eq. (5).

The experimental data obtained in this work allowed more detailed mathematical modeling of the processaccounting for the process temperature under conditions of the kinetic rate control (at $v_\text{S} \geq 4.5$ s^{-1}), in addition to the effects of the reactor hydrodynamic regime and the reactants loading [Eqs. (8) and (14)].

$$w = 348.338 \times 10^7 \exp(-73287/RT)[\text{CuI}]_0, \tag{16}$$

with *R*, universal gas constant, J mol^{-1} K^{-1}; *T*, absolute temperature, K.

The above-given equations accurately reproduced the experimental values of the stationary process rate

Table 4. Effect of zinc powder content in the reaction mixture on the rate of its alkylation with ethyl bromide in the presence of ethylzinc bromide–copper(I) iodide binary system at 38°C[a]

Stirring bar rotation speed, min^{-1}	Exp. no.	$[\text{Zn}]_0$, g (mol)	Zinc grade	Experiment time, h	Induction period, min[b]	Number of points in the kinetic curve	Ethylzinc bromide yield, %	Rate of ethylzinc bromide formation ($w \times 10^6$, mol/s) and standard deviation of the kinetic curve fitting	
								individual experiment or series	at the plateau of the $w = f\{[\text{Zn}]_0\}$[c]
500	1	8.50 (0.13)	PTs-10	4.0	50	4	96	10.9±0.6 ($S = 0.004$)	–
	2	19.61 (0.30)	PTs-10	4.0	28	4	92	21.5±0.8 ($S = 0.005$)	–
	3	64.07 (0.98)	PTs-10	5.0	18	4	99	58.6±1.7 ($S = 0.015$)	–
	4	120.3 (1.84)	PTs-3, 4, 10	5.0	14–44	23	64	64.2±1.0 ($S = 0.043$)	63.3±0.9 ($S = 0.045$)
	5	246.48 (3.77)	PTs-10	4.6	11	4	50	59.6±3.2 ($S = 0.027$)	
250	6	240.00 (3.67)	PTs-3	5.0	0	5	50	55.6±1.9 ($S = 0.052$)	55.6±1.9 (S 0.052)
180	7	120.30 (1.84)	PTs-3, 10	5.0	0–46	9	44	45.9±1.9 ($S = 0.057$)	45.1±0.8 (S 0.046)
	8	240.00 (3.67)	PTs-3, 4	5.0	0–19	18	54	44.7±0.9 ($S = 0.040$)	
120	9	120.30 (1.84)	PTs-10	5.0	22–26	8	33	36.5±0.8 ($S = 0.026$)	36.0±0.6 (S 0.022)
	10	240.00 (3.67)	PTs-3	5.0	38	4	31	34.9±0.6 ($S = 0.005$)	
0	11	120.30 (1.84)	PTs-10	5.0	105	3	8	11.8±3.3 ($S = 0.013$)	11.4±0.3 (S 0.008)
	12	240.00 (3.67)	PTs-3	5.0	19	5	11	11.2±0.4 ($S = 0.004$)	

[a] The starting mixture composition was the same in all the experiments: 200 g (1.84 mol) of ethyl bromide, 6.25 g (0.033 mol) of copper(I) iodide, and 11.89 g (0.07 mol) of ethylzinc bromide. [b] In the case of the series of several individual experiments the τ_{ind} is given as a range containing all the individual τ_{ind} values. [c] Determined via combined treatment of Exp. 4 and 5 (500 min^{-1}), 7 and 8 (180 min^{-1}), 9 and 10 (120 min^{-1}), and 11 and 12 (0 min^{-1}).

over the whole studied ranges of temperature, mixing conditions and initial loadings of copper(I) and zinc. In particular, the absolute deviations of the calculates rates from the experimental ones were of (5.4±1.4) × 10^{-6} mol/s [calculated using Eqs. (7) and (15)], (4.3±2.4) × 10^{-6} mol/s [Eqs. (15) and (16)], and (3.3±3.4) × 10^{-6} mol/s [Eqs. (8) and (14)].

Finally, we compared the efficacy of promoting of zinc alkylation with ethyl bromide in the presence of the EtZnBr–CuI and Zn–Cu pairs. In particular, the rate of stationary alkylation of zinc as component of the zinc–copper pair (256 g of the mixture, 3.73 mol of zinc) at 38°C was of (67.5±1.2) × 10^{-6} mol/s; no significant influence of the stirring intensity on the process rate was revealed [1]. The highest rate of stationary alkylation of zinc with the EtZnBr–CuI at the initial zinc loading of 3.73 mol was of 197.7 × 10^{-6} mol/s at 38°C [Eqs. (7) and (15)]. Hence, utilization of the latter binary system significantly decreased the induction period of the process (from tens of hours [1] to 20±20 min according to data of 36 runs) and almost trebled the stationary process rate. Likely, kinetic models of other processes of direct

Table 5. Effective incident flux of copper-containing particles at the zinc surface ($\{[CuI]_0/[Zn]_0\}_{op}$) corresponding to transition of the reaction rate ($w = f\{[CuI]_0\}$) or ($w = f\{[Zn]_0\}$) dependences to the plateau region (T = 38ºC)

Stirring bar rotation speed		$\{[CuI]_0/[Zn]_0\}_{op} \times 10^3$, mol CuI/mol Zn		
min^{-1}	s^{-1}	experiment		calculation according to Eq. (14)
		$w = f\{[CuI]_0\}$ (Fig. 5a)	$w = f\{[Zn]_0\}$ (Fig. 6a)	
500	8.33	33	30	31±3
270	4.50	–	–	31±3
250	4.17	33	34	33±3
180	3.00	41	42	42±4
120	2.00	51	52	55±5
0	0	161	165	149±22

synthesis of mixed organozinc compounds in the presence of binary systems can be built similarly.

To summarize. the experimental results obtained in this work supported validity of the earlier suggested mechanism of the binary systems action [2] and all the studied factors except for initial content of the organometallic component of the binary system were efficient to control the process.

EXPERIMENTAL

Zinc powder of different grades (PTs-3 GOST 12601-76, PTs-4 GOST 12601-76and PTs-10 TU 48-4015-1/0-81) and copper(I) iodide (“pure” grade) were used as received.

Purification of argon and ethyl bromide (both of “pure”), preparation of ethylzinc bromide in ethyl bromideand procedure of the alkylation was described elsewhere [2]. The experiments without forced mixing were performed in a reactor not equipped with any stirrer. Granulometric composition of zinc powder was determined via sedimentation in the gravitation field [11], the total mass of the zinc specimen being of 2 g, the precipitate mass being determined using a torsion balance without fractionation, the cup immersion depth being of 0.24 m and water serving as dispersion medium. Density of ethylzinc bromide solutions in ethyl bromide was determined using a bottle method [12]. No correction for vapor mass was made.

REFERENCES

1. Eremeev, I.V., *Russ. J. Gen. Chem.*, 2014, vol. 84, no. 10, p. 1909. DOI: 10.1134/S1070363214100077.
2. Eremeev, I.V., *Russ. J. Gen. Chem.*, 2014, vol. 84, no. 8, p. 1561. DOI: 10.1134/S1070363214080222.
3. Pochekutova, T.S., Khamylov, V.K., Domracheev, G.A., and Zhuk, B.V., *Metalloorg. Khim.,* 1988, vol. 1, no. 3, p. 561.
4. Zhou, X.L., Solymosi, F., Blass, P.M., Cannon, K.C., and White, J.M., *Surf. Sci.*, 1989, vol. 219, nos. 1–2, p. 294.
5. Rozovskii, A.Ya., *Geterogennye khimicheskie reaktsii (kinetika i makrokinetika)* [Heterogeneous Chemical Reactions (Kinetics and Macrokinetics)}, Moscow: Nauka, 1980.
6. Denisov, E.T., *Kinetika gomogennykh khimicheskikh reaktsii* (Kinetics of Homogeneous Chemical Reactions), Moscow: Vysshaya Shkola, 1988.
7. Rodigin, N.M. and Rodigina, E.N., *Posledovatel'nye khimicheskie reaktsii (Matematicheskii analiz i raschet)* [The Sequence of Chemical Reactions (Mathematical Analysis and Calculation)], Moscow: Akad. Nauk SSSR, 1960.
8. Gordon, A.J. and Ford, R.A., *The Chemist's Companion. A Handbook of Practical Data, Techniques and References*, New York: Wiley, 1972.
9. Lebedev, N.N., Manakov, M.N., and Shvets, V.F., *Teoriya khimicheskikh protsessov osnovnogo organicheskogo i neftekhimicheskogo sinteza* (Theory of Chemical Processes of Basic Organic and Petrochemical Synthesis), Moscow: Khimiya, 1984.
10. Squires, G.L., *Practical Physics,* London: McGraw-Hill, 1968.
11. *Laboratornye raboty i zadachi po kolloidnoi khimii* (Laboratory Works and Objectives of Colloid Chemistry), Frolov, Yu.G. and Grodskii, A.S., Eds., Moscow: Khimiya, 1986.
12. Stepin, B.D., *Tekhnika laboratornogo eksperimenta v khimii* (Equipment Laboratory Experiment in Chemistry), Moscow: Khimiya, 1999.