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Promoting Alkylation of Non-Transition Metals with Organic Halides in the Presence of Binary Systems Based on Organometallic Compound and Transition Metal Compound: II.[1] Comparative Study of Efficiency of Various Agents in the Course of Destruction of Passivating Film on the Surface of Alkylated Metal

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Abstract—It has been demonstrated that alkylzinc halides efficiently destroy the passivating film on the zinc–copper pair in the course of its alkylation with ethyl bromide to give ethylzinc bromide. The alkylzinc halides efficiency is comparable to that of ethyl iodide and exceeds that of salts of transition or non-transition metals as well as of ultraviolet irradiation. Addition of alkylzinc halides or metal salts as well as ultraviolet irradiation have practically no effect on the developed reaction. The results have demonstrated that the organometallic component of the binary systems is polyfunctional; this permits a generalization of known features of a number of known methods promoting direct synthesis of organometallic compounds.

Keywords: zinc, ethyl bromide, alkylation, promoting, mechanism

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According to concepts discussed in [1], the direct synthesis of organometallic compounds via alkylation of metals with organic halides occurs with an induction period. The induction period is due to the presence of passivating film on the surface of alkylated metal. During the induction period the passivating film is destroyed, allowing for direct contact of the organic halide with the metal resulting in the formation of the organometallic target product. It is presumed that the passivating film can be etched under the action of organic halides, organometallic compounds, atomic and molecular halogens, and other compounds capable of the alkylated metal oxidation [1]. In particular, besides the mixed organometallic compounds, salts of transition as well as non-transition metals (potential source of positively charged ions, sufficiently strong oxidizers) may act as the etching agents. The above-listed compounds are either inherently present in the reaction mixture (organic halide), or are purposely added, or are formed in the course of the reaction. For instance, atomic and molecular halogens are formed via the homolytic rupture of the carbon–halogen bond of the organic halide under ultraviolet irradiation during direct synthesis of organometallic compounds. The known experimental facts do not contradict the described mechanism. In particular, UV irradiation as well as addition of organometallic compounds, metal salts, or elemental halogens efficiently promotes zinc–copper pair alkylation with ethyl bromide [1]. If the added oxidizers do not directly inhibit or accelerate the formation of the organometallic product, the observed induction period should be shortened, whereas the rate of the developed alkylation reaction should be independent of the promotor concentration in the mixture.

If the above-assumed behavior would be confirmed experimentally, that would support the previously developed mechanism implying the polyfunctional action of the organometallic components of the binary alkylating systems [1] and would permit generalization

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[1] For communication I, see [1].

of the efficiency of the known agents promoting the direct synthesis of organometallic compounds.

In this study we chose ethyl halides, ethylzinc halides, and salts of transition as well as non-transition metals as the objects.

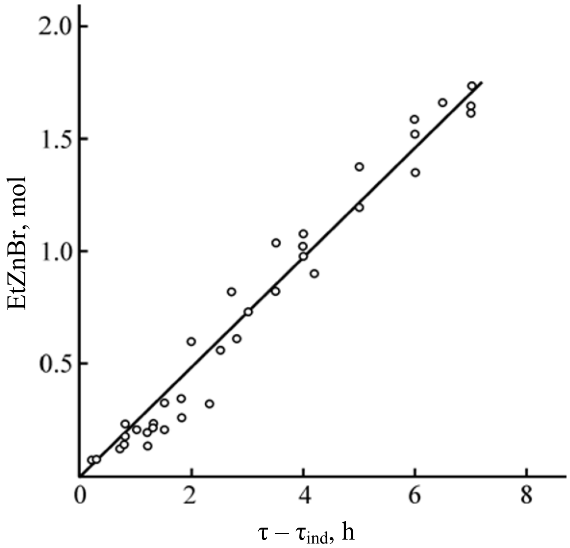
It was presumed that the homolytic rupture of the carbon–bromine bonds in ethyl bromide under UV irradiation could yield atomic and molecular bromine. However, since the commercially available powdered zinc did not react with ethyl bromide under the experimental conditions (UV irradiation in the presence of ethyl iodide, ethylzinc bromide, or metal salts) [1], we used as a test process the smoothly occurring reaction of zinc–copper pair alkylation with ethyl bromide [Eq. (1)].

$$\mathrm{EtHlg} + \mathrm{Zn}\ (\mathrm{Zn{-}Cu\ pair}) \rightarrow \mathrm{EtZnHlg}. \qquad (1)$$

First, we demonstrated that the method of zinc–copper pair preparation affected the induction period duration. This was tested using the metals pair alkylation with ethyl bromide in the presence of ethyl iodide [Eq. (1)] followed by thermal disproportionation of the formed ethylzinc halides [Eq. (2)].

$$2\mathrm{EtZnHlg} \rightarrow \mathrm{Et_2Zn} + \mathrm{ZnHlg_2}. \qquad (2)$$

The results are collected in Table 1. The highest activity was observed in the case of the metal pair prepared following the method *a* from cuttings of zinc and copper(II) oxide (exp. nos. 1–17). The induction periods in the course of such metal pair interaction with a mixture of ethyl bromide and ethyl iodide at 60–70°C was of 10 to 45 min. Taking the result into account, the zinc–copper pair for further experiments was prepared following the method *a*.



Kinetic curves of the developed process of ethylzinc bromide formation in the course of interaction of zinc–copper pair with ethyl bromide in the absence of any additives, in the presence of ethylzinc halides or metal salts, or under UV irradiation. The points are plotted using data of 15 experiments (Table 2); τ, experiment duration; τ_{ind}, induction period.

We determined the effect of various additives and UV irradiation on the course of the studied process, in particular, on the efficiency of destruction of the passivating film on the zinc–copper pair surface (Table 2). In all experiments presented in Tables 1 and 2 the prepared zinc–copper pair was passivated keeping in air for 3–5 min prior to the alkylation.

The oxide film formation on a metal surface is known to be very rapid: the 0.1 nm thick film is formed within fraction of a second [2–5]. When the oxide film thickness is of 2–5 nm, further metal oxidation is usually stopped due to no direct contact of the metal with the oxidizer [2–4]. Therefore, we assumed that the oxide film was formed at the zinc-copper metal pair during the 3–5 min passivating in air.

The efficiency of the oxide film destruction was judged from duration of the induction period during direct synthesis of ethylzinc halides. The highest depassivating efficiency comparable to that of ethyl iodide addition was observed in the presence of ethylzinc halides in the starting reaction mixture (Table 1, exp. nos. 1–17). The induction period observed in the experiments at 38°C was 1.2–7.2 h independent of ethylzinc halide concentration in the mixture (Table 2, exp. nos. 2–5). The induction period was found to be somewhat longer in the presence of iron(III) and cobalt(II) chlorides (Table 2, exp. nos. 6 and 7). The results, however, did not allow an unambiguous conclusion on the relationship between the promotor nature and its efficiency towards destruction of the passivating film. The significant factors were likely the solubility of the tested substances in the organic halide as well as the nature and concentration of the metal-containing and other components present in the solution and on the passivating film surface.

The induction period was shortened at UV irradiation. Efficiency of UV irradiation was comparable to that of addition of cobalt(II) or iron(III) chloride (Table 2, exp. nos. 13–15), being significantly dependent on the distance between the radiation source and the quartz reactor. The longest induction period was observed in the case of the zinc–copper pair

Table 1. Influence of method of zinc–copper pair preparation and the reagents ratio on the organozinc compounds synthesis[a]

Exp. no.	Method of Zn–Cu pair preparation	EtBr : EtI	Induction period (τ_{ind}), min[b]	Duration of the developed process ($\tau - \tau_{ind}$), min[c]	Et_2Zn yield, %
1	*a*	1.0	15	30	82
2	"	1.0	15	35	84
3	"	1.0	25	35	81
4	"	1.0	30	30	84
5	"	1.0	30	35	85
6	"	1.0	35	30	84
7	"	1.0	35	30	84
8[d]	"	1.0	15	35	85
9[e]	"	1.0	15	75	68
10[f]	"	1.0	10	90	62
11[g]	"	1.0	15	150	47
12	"	1.3	20	35	86
13	"	2.0	20	60	85
14	"	3.0	20	120	81
15	"	3.0	15	130	84
16	"	7.0	15	215	76
17	"	10.0	45	170	63
18	*b*	1.0	55	55	77
19	"	1.0	60	85	80
20	"	1.0	65	90	79
21	*c*	1.0	85	120	88
22	"	1.0	90	130	85
23	*d*	1.0	The reaction did not start within 5 h		

[a] Zinc–copper pair: 256 g (3.73 mol Zn), total loading of EtBr and EtI: 2 mol, vigorous stirring during EtZnHlg synthesis, EtZnHlg synthesis temperature: 60–70°C, Et_2Zn synthesis temperature: 150–180°C. [b] Completion of induction period was noticed by appearance of white fume in the reactor. [c] Completion of EtZnHlg synthesis was noticed by ceased evolution of alkyl halides; τ, experiment duration. [d] Zinc–copper pair: 216.6 g (3.15 mol Zn). [e] Zinc–copper pair: 177.2 g (2.58 mol Zn). [f] Zinc–copper pair: 146.7 g (2.14 mol Zn). [g] Zinc–copper pair: 128.0 g (1.86 mol Zn).

refluxing with ethyl bromide in the absence of any additive (Table 2, exp. no. 1). The developed reaction was not affected by the introduction of ethylzinc halides or the salts, by UV irradiation, or by the regularly increasing concentration of ethylzinc bromide product. The kinetic curve shown in the figure was plotted using the results of 15 experiments.

In all cases, the initial charge of zinc–copper pair being 256 g, the developed process occurred at a constant rate of $(67.5\pm1.2) \times 10^{-6}$ mol/s. At the same time, the data reported in Table 1 (exp. nos. 1–11) demonstrated that the process duration increased with decreasing zinc–copper pair content in the initial mixture. The results indicate the low promoting ability (if any) of the salts, ethylzinc halides, and UV irradiation with respect to the developed process, as compared to the analogous action of copper in the zinc–copper pair. Furthermore, we concluded that the passivating film formed on the zinc–copper pair surface under the experimental conditions was thinner than that on the surface of commercially available zinc powder (kept in air during several months prior to the testing). Hence, the shorter induction period (11–50 min, the average duration being 24 min) in the course of alkylation of commercial zinc powder with ethyl bromide in the presence of the ethylzinc bromide–copper(I) iodide binary system [1] as compared to that during alkylation of zinc–copper pair in the presence of ethylzinc bromide (3.8–7.2 h), likely reflected the fact that development of zinc–copper pair alkylation required formation of active zinc surface containing adatoms and small clusters of copper besides mere destruction of the passivating film. In other words, the catalytically active components were adatoms and small clusters of copper rather than microphases;

Table 2. Synthesis of ethylzinc bromide from ethyl bromide and zinc–copper pair in the presence of various additives or under UV irradiation[a]

Exp. no.	Reaction mixture composition		Induction period (τ_{ind}), h[b]		Duration of the developed process ($\tau - \tau_{ind}$), h[c]	EtZnBr yield, % (mol)
	EtBr, g (mol)	additive, g (mol)	38°C	20°C		
1	218 (2.0)	–	35.0	160.0	0	0 (0)
					7.0	87 (1.73)
2	206 (1.89)	1.13 (0.006)	3.8	–	0	0 (0)
		EtZnBr			0.2	4 (0.07)
					0.7	6 (0.12)
					1.2	10 (0.20)
					4.0	57 (1.08)
					5.0	63 (1.20)
					6.0	72 (1.36)
3	204 (1.87)	15.72 (0.090)	7.2	–	0	0 (0)
		EtZnBr			0.3	4 (0.07)
					0.8	10 (0.18)
					1.3	12 (0.23)
					1.8	18 (0.34)
4	172 (1.58)	49.80 (0.286)	7.0	–	0	0 (0)
		EtZnBr			3.5	52 (0.82)
5[d]	202 (1.85)	22.79 (0.103)	1.2	–	0	0 (0)
		EtZnI			0.3	4 (0.08)
					0.8	8 (0.14)
					1.3	12 (0.21)
					1.8	14 (0.26)
					2.3	17 (0.32)
6	218 (2.0)	3.00 (0.011)	9.5	25.5	0	0 (0)
		$FeCl_3 \cdot 6H_2O$			1.2	7 (0.14)
					2.0	30 (0.60)
					3.0	37 (0.73)
					4.2	45 (0.90)
					6.0	80 (1.59)
7	218 (2.0)	4.50 (0.019)	11.8	34.5	0	0 (0)
		$CoCl_2 \cdot 6H_2O$			1.5	16 (0.32)
					2.7	41 (0.82)
					6.5	83 (1.66)
8	218 (2.0)	2.50 (0.010)	14.0	34	0	0 (0)
		$SnCl_4$			5.0	69 (1.38)
9	218 (2.0)	2.65 (0.005)	20.0	50.0	0	0 (0)
		$Bi(NO_3)_3 \cdot 5H_2O$			7.0	82 (1.64)
10	218 (2.0)	2.30 (0.007)	21.0	69.5	0	0 (0)
		ZnI_2			2.5	28 (0.56)
					3.5	52 (1.04)
11	218 (2.0)	0.02 $ZnCl_2$	28.0	161.0	0	0 (0)
					7.0	83 (1.66)
12	218 (2.0)	0.05	27.0	155.0	0	0 (0)
		$MgSO_4 \cdot 7H_2O$			7.0	81 (1.62)

Table 2. (Contd.)

Exp. no.	Reaction mixture composition		Induction period (τ_{ind}), h[b]		Duration of the developed process ($\tau - \tau_{ind}$), h[c]	EtZnBr yield, % (mol)
	EtBr, g (mol)	additive, g (mol)	38°C	20°C		
13[e]	218 (2.0)	–	12.2	18.0	0	0 (0)
					0.8	12 (0.23)
					2.8	31 (0.61)
					6.0	76 (1.53)
14[f]	″	–	23.0	50.0	0	0 (0)
					1.0	10 (0.21)
					4.0	52 (1.03)
15[g]	″	–	30.5	140	0	0 (0)
					1.5	10 (0.21)
					4.0	49 (0.98)

[a] All the experiments except for no. 5 were performed at 38–40°C without stirring. Zinc–copper pair was prepared by method *a*; loading: 256 g (3.73 mol Zn). [b] In the cases of prolonged induction period the mixture was incubated either at ethyl bromide boiling point (38°C) or at room temperature (20°C). [c] τ, experiment duration. [d] Stirring at 180 rpm. [e] UV irradiation; 10 cm distance between the UV source and the reactor. [f] UV irradiation; 20 cm distance between the UV source and the reactor. [g] UV irradiation; 25 cm distance between the UV source and the reactor.

similar assumption was made in the binary systems discussion [1].

To summarize, the introduction of ethylzinc halides and metal salts into the initial reaction mixture as well as the UV irradiation of the mixture noticeably shortened the induction period during the direct synthesis of organometallic compounds but had practically no effect on the rate of the developed process. Hence, the known methods to promote the direct alkylation process (UV irradiation as well as addition of salts, organic derivatives of non-transition metals, elemental halogens, reactive organic halides, or hydrogen halides) are primarily based on the ability of listed agents to remove the passivating film off the alkylated metal surface. Alkylzinc halides were highly reactive in that regard, their efficiency was comparable to that of ethyl iodide and exceeded that of salts of transition or non-transition metals and of UV irradiation. The observation confirmed the hypothetic views on polyfunctional nature of the organometallic component of the binary alkylating systems [1].

The promoting action of the zinc–copper pair was likely primarily caused by the catalysis of the process with adatoms and small clusters of copper present on the zinc surface; the catalytic centers were formed (at least partially) in the course of the direct synthesis of organozinc compounds. The catalytic cycle could be similar to that described in [1] in the case of binary alkylating system. If that is true, the known methods of the alkylation promoting (based on using the alloys or pair of the alkylated metal as well as on introduction of the transition metals or their compounds) can be rationalized as follows: the key stages of the process can involve atoms, small clusters, or subhalides of the transition metal formed on the surface of the alkylated metal.

EXPERIMENTAL

The following chemicals were used as received: zinc powder (PTs-10), copper powder (TsMTU 4451-54), bismuth(III) nitrate pentahydrate (“pure” grade), calcium chloride (“pure” grade), cobalt(II) chloride hexahydrate (“pure” grade), copper(II) oxide (“analytically pure” grade), copper(II) sulfate pentahydrate (“analytically pure” grade), iron(III) chloride hexahydrate (“pure” grade), magnesium sulfate heptahydrate (“analytically pure” grade), sodium hydroxide (“analytically pure” grade), tin(IV) chloride (“pure” grade), zinc(II) iodide (“pure” grade), zinc oxide (“pure” grade), and glycerol (“pure” grade). Zinc cuttings were prepared mechanically from zinc plate (grade 0). Zinc chloride was prepared via dehydration of $ZnCl_2 \cdot 1.5H_2O$ (“pure” grade) [6]. Argon (“pure” grade), ethyl bromide (“pure” grade), and ethyl iodide (“pure” grade) were additionally purified as described elsewhere [1].

Ethylzinc bromide solution in ethyl bromide was prepared as described in [1]. Ethylzinc iodide solution in ethyl bromide was prepared from crystalline ethylzinc iodide that was in turn prepared from zinc–copper pair (see method *a* below) and ethyl iodide.

Preparation of zinc–copper pair. *a.* Prepared from zinc cuttings and copper(II) oxide as described elsewhere [1].

b. Prepared similarly to method *a* from 240 g of zinc cuttings and 20 g of copper powder.

c. Prepared similarly to method *a* from 240 g of zinc powder and 20 g of copper(II) oxide. Uniform grey color reflected the completeness of the pair preparation.

d. An electrolysis cell was filled with an electrolyte [50 g of copper(II) sulfate pentahydrate, 100 g of glycerol, 200 g of sodium hydroxide, 28 g of zinc oxide, and distilled water up to the total volume of 1 L), zinc plates acted as anode. The zinc–copper pair was deposited at steel cathode at the current of 0.26 A/cm^2. In the course of the process, copper(II) sulfate pentahydrate was added to the electrolyte. The so prepared zinc–copper pair was washed with distilled water and vacuum-dried at 80°C. Copper content in the prepared pair was 13–14 wt %.

Ethylzinc halides preparation from zinc–copper pair and ethyl halides was performed in round-bottom glass reactors equipped with reflux condenser and thermometer, similarly to zinc alkylation with ethyl bromide described in [1]. In the experiments performed under forced stirring conditions (Table 1, exp. nos. 1–23 and Table 2, exp. no. 5), the reactor was equipped with a stirrer.

Heat-induced disproportionation of ethylzinc halides into diethylzinc and zinc(II) halides. After zinc alkylation was complete, the stirrer was removed from the reactor, the reflux condenser was exchanged with the Liebig condenser connected with a trap cooled in a Dewar vessel with a mixture of acetone and carbon dioxide ice (–70 to –40°C). The residual alkyl halides were distilled off at 50°C in a vacuum. The trap was exchanged with a clean one, and the heat-induced disproportionation was performed with simultaneous distillation off of the formed diethylzinc. The reaction was performed at 150–180°C and the residual pressure of 10–40 mmHg. Diethylzinc yield was determined from the mass of the isolated product. Diethylzinc boiling point of 118°C coincided with the reference data [7].

Zinc ions in the specimens were quantitatively determined as described elsewhere [1].

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