Sodium—potassium synergism in the alkylation of toluene and naphthalene with ethene in $C_{10}H_8$—Na—K systems in THF

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Sodium—potassium synergism in the alkylation of toluene and naphthalene with ethene in naphthalene—alkali metal systems in THF was discovered. In the case of toluene, the maximum synergistic effect is observed at an Na : K molar ratio of 1 : 1. With this Na : K molar ratio, the yields of the products of toluene alkylation with ethene considerably increase. The efficiency of naphthalene alkylation (in the presence of toluene) is also markedly enhanced on replacement of sodium or potassium by their mixture.

Key words: naphthalene, toluene, ethene, alkylation, alkali metals, synergism.

Recently we showed that the systems formed upon treatment of naphthalene with alkali metals (Li, Na, K) in THF induce alkylation of toluene and naphthalene with ethene under mild conditions.[1] As a result of these reactions, occurring at room temperature, toluene is converted into monoalkylbenzenes and naphthalene is converted into alkylnaphthalenes and their dihydro derivatives. The phenomenon of lithium—sodium synergism was also discovered; this substantially increased the reaction efficiency.[2] Especially strong synergistic effects were observed in the alkylation of toluene, which was converted almost quantitatively into higher monoalkylbenzenes at a Li : Na ratio of 1 : 3. The degree of conversion of naphthalene into the alkylation products was also enhanced substantially when a mixture of lithium and sodium was used.

In this work, we report on the synergistic effect of Na and K in the alkylation of toluene and naphthalene with ethene.

Results and Discussion

The reactions were carried out at room temperature and atmospheric pressure for 24 h by the standard procedure. In all experiments, the amount of naphthalene (3 mmol) and its initial concentration (2 mol L^{-1}) were maintained constant. The relative amounts of sodium and potassium were varied but the overall (Na+K) : $C_{10}H_8$ molar ratio was maintained at 2 : 1. The experiments with toluene were carried out at an equimolar $PhCH_3$: naphthalene ratio. The products were analyzed by GLC and GC/MS.

It was shown previously[1] that alkylation of toluene with ethene under the action of the $C_{10}H_8$—Na system in THF affords *n*-propylbenzene (**1**) and 3-phenylpentane (**2**) in a low total yield (16%: 12% of **1** and 4% of **2**). Equally low yields of **1** and **2** in this reaction were also observed in the present study (Table 1).

Table 1. Alkylation of toluene and naphthalene with ethene in $C_{10}H_8$—Na—K systems in THF

N/mmol[a]		Yield of alkylation products (%)					
		toluene[b]			naphthalene[c]		
Na	K	**1**	**2**	**1**+**2**	**3**	**4**+**5**	**3**+**4**+**5**
6	0	15	3	18	33	3	36
5.1	0.9	24	8	32	42	8	50
4.5	1.5	26	11	37	37	4	41
4	2	25	15	40	38	—	38
3	3	26	17	43	35	—	35
2.5	3.5	21	11	32	27	—	27
2	4	16	9	25	19	—	19
1	5	9	3	12	8	—	8
0	6	8	—	8	7	—	7

[a] *N* is the quantity of the alkali metal added.
[b] Based on toluene.
[c] Based on naphthalene.

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Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 11, pp. 2107—2109, November, 1999.

1066-5285/99/4811-2083 $22.00

However, we found that, if even a small amount of potassium metal is added to the $C_{10}H_8$—Na system in THF, the degree of conversion of toluene into the alkylation products substantially increases. As the proportion of potassium in the mixture increases, the efficiency of toluene alkylation is further enhanced, reaching a maximum at a Na : K ratio of 1 : 1 (Table 1). Under these conditions, toluene and ethene react to give compounds **1** and **2** in a total yield of 43% (26% of **1** and 17% of **2**), which is ~2.5 times as high as that in the reaction carried out without potassium. When the amount of potassium further increases, the system activity starts to decrease; when potassium alone is used, the reaction gives **1** in only 8% yield. Thus, sodium and potassium, like lithium and sodium,[2] exert a synergistic effect on the alkylation of toluene with ethene.

To elucidate the possible role of the sodium—potassium alloy in the observed synergism, we carried out special control experiments in which toluene was made to react with ethene in THF at 20 °C in the presence of an authentic sodium—potassium alloy (K : Na = 1.77 : 1). However, the results of these experiments showed that alkylation does not occur under these conditions. Thus, for the sodium—potassium synergism to be manifested in the alkylation of toluene, naphthalene must be present in the system.

The efficiency of alkylation of naphthalene with ethene also increases in the presence of a mixture of sodium with potassium, but the synergistic effect observed in this case is noticeably less pronounced than that in the alkylation of toluene. It can be seen from Table 1 that the reaction of ethene with naphthalene in the $C_{10}H_8$—Na system in THF (in the presence of toluene) affords 1-ethylnaphthalene (**3**) and minor amounts of its dihydro derivatives **4** and **5** in a total yield of 36% based on naphthalene (33% of **3** and 3% of **4**+**5**). If potassium metal is added to the system, the degree of conversion of naphthalene into the alkylation products increases to 50% at the ratio Na : K = 5.1 : 0.9; however, further increase in the content of potassium decreases the efficiency of the process and the use of the $C_{10}H_8$—K system in THF gives **3** in only a very low yield (7%). It is of interest that no sodium—potassium synergism is observed when naphthalene is alkylated with ethene in the absence of toluene.

Previously, a mechanism was proposed for interpreting the features of deuterium—hydrogen exchange in hydrocarbons under the action of the $C_{10}H_8$—Na system in THF[3]; the mechanism included the following main steps:

(1) generation of atomic sodium in the $C_{10}H_8$—Na system in THF due to reactions (1)—(3)

$$\mathrm{Na}(met) + \mathrm{ArH}^{\cdot-}\mathrm{Na}^+ \rightleftharpoons \mathrm{Na}^+\mathrm{ArH}^{\cdot-} + \mathrm{Na(at)}, \qquad (1)$$

$$\mathrm{ArH}^{\cdot-}\mathrm{Na}^+ + \mathrm{ArH}^{\cdot-}\mathrm{Na}^+ \rightleftharpoons \mathrm{ArH} + \mathrm{Na}^+\mathrm{ArH}^{\cdot-} + \mathrm{Na(at)}, \qquad (2)$$

$$\mathrm{ArH}^{\cdot-}\mathrm{Na}^+ \rightleftharpoons \mathrm{ArH} + \mathrm{Na(at)}, \qquad (3)$$

ArH — naphthalene;

(2) agglomeration of atomic sodium into sodium clusters $[Na_n]$, stabilized by the formation of surface complexes with naphthalene;

(3) reversible cleavage of C—H and C—D bonds in hydrocarbons on the surface of sodium clusters, resulting in the hydrogen—deuterium exchange.

It follows from this mechanism that the corresponding mixed sodium—potassium and lithium—sodium clusters could form in the $C_{10}H_8$—Na—K and $C_{10}H_8$—Li—Na systems in THF. These mixed clusters might be responsible for the synergism of alkali metals in the above-described alkylation reactions.

Similar synergistic effects have been observed previously (see the review[4]) in catalytic oligomerization of olefins induced by dispersions of alkali metals in the absence of aromatic promoters. Apparently, the active species ensuring the synergistic acceleration of these reactions (occurring at elevated temperatures) are also mixed clusters of alkali metals, present in the dispersions.

Experimental

The experiments were carried out under argon with careful exclusion of atmospheric oxygen and moisture. THF and toluene were purified by standard procedures and distilled prior to use over sodium and sodium benzophenone ketyl (THF) or over sodium (toluene) in an Ar atmosphere. Naphthalene was used without additional purification. The reaction products were analyzed by GLC with temperature programming (160 °C, 10 min; 160—300 °C, 10 °C min^{-1}; 300 °C, 40 min) on a Chrompack CP 9001 chromatograph equipped with a flame ionization detector and a DB5 MS (30 m × 0.25 mm) capillary column; dodecane was used as the internal standard. GC/MS analyses were carried out on a FISONS Trio 1000 instrument.

Product identification. Compounds **1** and **3** were identified by GLC and GC/MS using standard samples of **1** and **3**. Compound **2** was identified based on the fact that its mass spectrum coincided with the corresponding published data for **2** (see Ref. 6). The conclusion on the nature of **4** and **5** was based on analysis of their mass spectra. The most important characteristics of the mass spectra recorded for the products are presented below, m/z (I_{rel} (%)): **1**: 120 $[M]^+$ (20), 91 $[C_7H_7]^+$ (100); **2**: 148 $[M]^+$ (31), 119 $[M - C_2H_5]^+$ (70), 91 $[C_7H_7]^+$ (100); **3**: 156 $[M]^+$ (65), 141 $[M - CH_3]^+$ (100), 115 $[M - CH_3 - C_2H_2]^+$ (19); **4**: 158 $[M]^+$ (53), 129 $[M - C_2H_5]^+$ (100), 128 $[M - C_2H_5 - H]^+$ (65), 127 $[M - C_2H_5 - 2\ H]^+$ (33); **5**: 158 $[M]^+$ (63), 129 $[M - C_2H_5]^+$ (100), 128 $[M - C_2H_5 - H]^+$ (92), 127 $[M - C_2H_5 - 2\ H]^+$ (41).

Alkylation of toluene and naphthalene with ethene in $C_{10}H_8$—Na—K systems. Naphthalene (0.384 g, 3 mmol), sodium (0.069 g, 3 mmol), potassium (0.117 g, 3 mmol), toluene (0.3 mL, 3 mmol), dodecane (internal standard, 0.0484 g), and 1.2 mL of THF were placed in the Schlenk tube under Ar. The content of the Schlenk tube was cooled with liquid dinitrogen and, after removal of the argon by evacuation, the content was unfrozen to ~20 °C. Then ethene was introduced from an attached mercury burette and the reaction mixture was stirred at 20—23 °C on a magnetic stirrer; the course of the reaction was monitored based on ethene absorption. After 24 h, when the amount of ethene absorbed was ~1.22 moles per mole of naphthalene (~82 mL under standard conditions), the mixture was diluted with 1.5 mL of THF and analyzed by GLC and GC/MS. The reaction of toluene with ethene gave compounds **1** and **2** in 26 and 17% yields, respectively (based on toluene); the reaction of naphthalene with ethene afforded **3** in 35% yield (based on naphthalene).

Other experiments on the toluene and naphthalene alkylation were carried out by similar procedures. The results are summarized in Table 1.

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Received April 12, 1999