Synergistic effects of alkali metals in the alkylation of naphthalene and toluene with ethene in the ArH–alkali metal systems in THF (ArH – naphthalene, phenanthrene)

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ABSTRACT

The use of mixtures of metallic lithium and sodium in the naphthalene–alkali metal systems in THF leads to a synergistic acceleration of the naphthalene alkylation with ethene at room temperature and atmospheric pressure. The greatest synergistic effect is observed at a Li:Na molar ratio of 2:1. Under these conditions, the overall conversion of naphthalene into alkylation products (linear 1-alkylnaphthalenes and their dihydro derivatives) attains 88% after 24 h (a (Li + Na):$C_{10}H_8$ ratio is 2:1). The use of mixtures of metallic lithium and potassium in such systems results, however, in a synergistic retardation of the alkylation process. The strongest retarding effect is observed at a Li:K molar ratio of 1:1. The efficiency of the toluene alkylation with ethene in the naphthalene–alkali metal systems in THF is also increased on the replacement of lithium or sodium by their mixtures. The best results are obtained at a Li:Na molar ratio of 1:3. With this Li:Na ratio, toluene is almost quantitatively converted into linear and α-branched higher monoalkylbenzenes (24 h, (Li + Na):$C_{10}H_8$ = 2:1). The rate of the naphthalene alkylation with ethene in the presence of toluene is enhanced as well on an introduction of mixtures of lithium and sodium into the system. However the maximum of the activity is shifted here towards higher lithium content (Li:Na = 1:1). A similar synergistic effect of lithium and sodium was found on studying the toluene alkylation with ethene in the phenanthrene–Li–Na systems in THF (a (Li + Na):phenanthrene ratio is 3:1). An addition of potassium to sodium also considerably increases the efficiency of the toluene and naphthalene alkylation with ethene in the naphthalene-based systems. The possible mechanism of the alkali metal synergism in the above-mentioned alkylation reactions is discussed.

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1. Introduction

Adducts of aromatic hydrocarbons with alkali metals play an important role in chemistry. They are excellent reagents for electron transfer to various organic and inorganic substrates, which is used successfully in organic and organometallic synthesis and catalysis (for reviews, see, e.g. [1–5]). One of the outstanding achievements in this area was the discovery of a remarkable ability of radical-anion adducts of alkali metals with naphthalene and other arenes to induce the "living" polymerization of 1,3-dienes and some monoenes.

As part of our ongoing research into C−H bond activation by non-transition metal compounds [6–11], we have previously reported on a high catalytic activity of systems, derived from naphthalene and metallic sodium in THF, in the hydrogen–deuterium exchange of hydrocarbons (naphthalene, benzene, toluene, ethene, methane) at room temperature [8]. A detailed examination of this novel reaction has shown that the rate of the H/D exchange is strongly increased in the presence of the solid phase of the alkali metal in a mixture and drops practically to zero on the replacement of THF by 1,2-dimethoxyethane (DME) as well as on an addition of [15]crown-5 to the system. Subsequently, it has been established that similar systems based on naphthalene and alkali metals (Li, Na, K) in THF are able to introduce naphthalene and toluene into the alkylation reactions with ethene under ambient conditions yielding linear 1-alkylnaphthalenes (together with small quantities of their dihydro derivatives) and linear and α-branched higher monoalkylbenzenes, respectively [10,11]. Here too, the process was strongly accelerated when the solid phase of the alkali metal was present in a mixture, whereas the use of DME instead of THF as well as an addition of [15]crown-5 led again to a sharp decrease in the reaction rate, thus indicating on the possible similarity of mechanisms of the H/D exchange and the alkylation. Systems formed on the treatment of a number of other aromatic hydrocarbons (biphenyl, phenanthrene, trans-stilbene, pyrene, anthracene) with alkali metals in THF proved also to be active in the toluene alkylation with ethene at 22 °C [11].

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In the present article, we report on unusual synergistic effects of alkali metals in the above-mentioned alkylation reactions with ethene in the ArH–alkali metal systems (ArH – naphthalene, phenanthrene) in THF. The discovery of these synergistic effects not only allows one to increase substantially the efficiency of the alkylation but is also of great importance for elucidation of the mechanism of activation of C–H bonds in hydrocarbons by systems of such a type.

For a short preliminary account of a part of this study, see [12,13].

2. Results and discussion

The reactions were carried out at room temperature and atmospheric pressure for 24 h by the standard procedure. In all experiments with the naphthalene-containing systems, the amount of naphthalene (3 mmol) and its initial concentration in THF (2 M) was maintained constant. The relative amounts of alkali metals in a mixture were varied but overall (Li + Na):$C_{10}H_8$, (Na + K):$C_{10}H_8$ and (Li + K):$C_{10}H_8$ molar ratios were kept equal to 2:1. On using such a ratio of the reagents, a part of the taken quantity of the alkali metals remained undissolved and thus was present in the systems in the form of the solid state. In the case of phenanthrene, mixtures of lithium with sodium were tested in the alkylation with ethene. The content of phenanthrene in these experiments was 3 mmol whereas its initial concentration in THF was 2.67 M. A (Li + Na):phenanathrene molar ratio was maintained equal to 3:1. The experiments on the toluene alkylation with ethene were conducted at an equimolar PhCH$_3$:ArH ratio. The products were analyzed by GLC and GLC/MS.

In Table 1, data on the naphthalene alkylation with ethene in the $C_{10}H_8$–Li–Na systems in THF are presented. As it has been shown previously [11], the interaction of ethene with the $C_{10}H_8$–Na system in THF affords 1-ethylnaphthalene (**1**) (35%) together with small quantities (2%) of its two dihydro derivatives (**2** and **3**) in a total yield of 37% based on naphthalene. It turned out, however, that if metallic lithium is added to this system the rate of ethene uptake and the efficiency of the naphthalene alkylation are strongly enhanced, reaching a maximum at a Li:Na molar ratio of 2:1 (Table 1). Under these conditions, a mixture of **1**–**3** (23% of **1**, 3% of **2** and **3**) together with 1-*n*-butylnaphthalene (**4**) (28%), 1-*n*-hexylnaphthalene (**5**) (17%), 1-*n*-octylnaphthalene (**6**) (7%), two dihydro derivatives (**7** and **8**) of **5** (4%), two dihydro derivatives (**9** and **10**) of **6** (3%) and 1-*n*-decylnaphthalene (**11**) (3%) are produced in a total yield of 88%. Further increase in the lithium content leads, however, to a decrease in the rates of ethene uptake and the naphthalene alkylation, and when lithium alone is used the naphthalene conversion into the alkylation products diminishes to 60% (**1** – 26%, **4** – 15%, **5** – 9%, **6** – 5%, **7** + **8** – 3%, **9** + **10** – 2%). Thus, the presence of Li and Na in the system results in a synergistic acceleration of the alkylation of naphthalene with ethene.

It is of interest that at all tested Li:Na ratios, the amount of absorbed ethene in these experiments noticeably exceeds its consumption for the formation of alkylation products (Table 1), thus suggesting the involvement of ethene in some other reactions, for example, with the alkali metal(s) (activated by naphthalene) to give aliphatic organolithium and/or organosodium compounds [14] and also (in the case of lithium) with the corresponding naphthalene dianion to afford products of the ethene carbolithiation [15,16].

The efficiency of the toluene alkylation with ethene is also sharply enhanced in the presence of lithium–sodium mixtures. As a result of these reactions, linear and α-branched higher monoalkylbenzenes are produced. As seen from Table 2, when

the $C_{10}H_8$–Li system in THF is used, the interaction of toluene with ethene results in the formation of *n*-propylbenzene (**12**) (30%), *n*-pentylbenzene (**13**) (5%), 3-phenylpentane (**14**) (8%) and 3-phenyl-heptane (**15**) (5%) in a total yield of 48% based on toluene. However, if metallic sodium is introduced into this system, the rate of the toluene alkylation increases, and at a Li:Na molar ratio of 1:3 the toluene conversion into the alkylation products reaches 97% (**12** – 46%, **13** – 3%, **14** – 44%, **15** – 4%). Still further enhancement in the sodium content lowers the reaction rate, and with sodium alone the toluene conversion amounts to only 18% (**12** – 15%, **14** – 3%). On carrying out the reaction at a Li:Na ratios of 2:1, 1:1 and 1:2, small quantities of 5-phenylnonane (**16**) are formed along with **12**–**15**. Importantly, when **12** instead of toluene is introduced into the alkylation reaction with ethene in the $C_{10}H_8$–Li–Na system in THF (Li:Na = 1:3), exclusively α-branched higher monoalkylbenzenes, viz., **14** and **15**, are produced in an overall yield of 70% (**14** – 68%, **15** – 2%). This means that only more acidic α-C–H bonds of the side alkyl chain in monoalkylbenzenes are able to be activated by alkali metal-based systems of such a type.

The naphthalene alkylation with ethene in the presence of toluene is accelerated as well on the use of mixtures of lithium with sodium (Table 3). The greatest acceleration is observed here at a Li:Na ratio of 1:1. Under such conditions, naphthalene is converted into **1**–**8** in a total yield of 84% (**1** – 45%, **2** + **3** – 9%, **4** – 16%, **5** – 3%, **6** – 6%, **7** + **8** – 5%). If the reaction is conducted in the absence of sodium the naphthalene conversion decreases to 55% (**1** – 34%, **2** + **3** – 2%, **4** – 13%, **5** – 3%, **7** + **8** – 3%) and in the absence of lithium it does not exceed 35% (**1** – 33%, **2** + **3** – 2%). On using a Li:Na ratio of 1:3, small amounts of two dihydro derivatives (**17** and **18**) of **4** are produced together with **1**–**5**, **7** and **8**. As in all of the above-described reactions, the quantity of absorbed ethene is considerably larger than its overall consumption for the alkylation (Table 4).

A similar lithium–sodium synergism is observed in systems based on phenanthrene (Table 5). For example, when a Li:Na molar ratio is 1:2, the yield of products of the toluene alkylation under the action of the phenathrene-containing system reaches 91% of the theoretical value with respect to toluene (**12** – 43%, **14** – 45%, **15** – 3%). Both an increase and a decrease in this ratio diminish the rate of the process. In the absence of sodium, the toluene conversion into higher monoalkylbenzenes drops to 36% (**12** – 27%, **13** – 4%, **14** – 3%, **15** – 2%), and without lithium it is only 11% (**12** – 10%, **14** – 1%). If the reaction is carried out at a Li:Na ratio of 5:1, *n*-heptylbenzene (**19**) is formed in a small quantity along with **12**–**15**. According to GLC/MS, phenanthrene is also alkylated with ethene in such systems but the exact nature of resulting products could not be established here.

In contrast to lithium–sodium mixtures, an introduction of a mixture of lithium with potassium into the naphthalene-containing system in THF leads to a synergistic retardation of the naphthalene alkylation with ethene (Table 6). The strongest retarding effect is observed at a Li:K molar ratio of 1:1. On using such a ratio, the reaction gives **1**, **4** and **5** in a total yield of 19% based on naphthalene. In the absence of potassium, the naphthalene conversion into the alkylation products increases to 60% (see above) while in the absence of lithium it reaches 85% (**1** – 83%, **2** + **3** – 2%). The rate of ethene uptake also passes through a minimum on changing the Li:K ratio but the position of this minimum is shifted here towards higher potassium contents in the system (K:Li = 2–3:1). In all experiments, the amount of absorbed ethene is again noticeably greater than the ethene quantity consumed for the alkylation. It should be noted that when the reaction of ethene with the $C_{10}H_8$–Li–K system is carried out in the presence of toluene, no lithium–potassium synergism is observed in both the naphthalene and toluene alkylation.

The behavior of sodium–potassium mixtures in the toluene alkylation with ethene is analogous to that of lithium–sodium ones

Table 1
Alkylation of naphthalene with ethene in the $C_{10}H_8$–Li–Na systems in THF.[a]

Alkali metal (mmol)		Absorbed C_2H_4		Yield of alkylation products (%)[b]								C_2H_4 consumption for alkylation		Naphthalene conversion (%)
Li	Na	(mmol)	(mol/mol $C_{10}H_8$)	1	2 + 3	4	5	6	7 + 8	9 + 10	11	(mmol)	(mol/mol $C_{10}H_8$)	
6	0	5.40	1.80	26	–	15	9	5	3	2	–	3.60	1.20	60
4.5	1.5	6.72	2.24	24	–	21	13	7	5	4	3	5.37	1.79	77
4	2	6.95	2.32	23	3	28	17	7	4	3	3	6.00	2.00	88
3	3	6.15	2.05	20	3	25	13	5	3	8	–	5.19	1.73	77
2	4	4.20	1.40	41	4	18	6	2	3	2	–	3.72	1.24	76
1.5	4.5	2.53	0.84	41	8	9	4	–	–	–	–	2.37	0.79	62
0	6	2.19	0.73	35	2	–	–	–	–	–	–	1.11	0.37	37

[a] 22 °C, 1 atm, 24 h, 3 mmol of naphthalene, (Li + Na):$C_{10}H_8$ = 2:1, $[C_{10}H_8]_o$ = 2M.
[b] Based on naphthalene.

Table 2
Alkylation of toluene with ethene in the $C_{10}H_8$–Li–Na systems in THF.[a]

Alkali metal (mmol)		Yield of alkylation products (%)[b]					Toluene conversion (%)
Li	Na	12	13	14	15	16	
6	0	30	5	8	5	–	48
4.5	1.5	35	10	6	8	–	59
4	2	37	10	8	10	2	67
3	3	43	8	9	10	4	74
2	4	47	5	19	8	3	82
1.5	4.5	46	3	44	4	–	97
1	5	38	–	43	5	–	86
0	6	15	–	3	–	–	18

[a] 22 °C, 1 atm, 24 h, 3 mmol of naphthalene, (Li + Na):$C_{10}H_8$ = 2:1, $[C_{10}H_8]_o$ = 2M, a $C_{10}H_8$:PhMe molar ratio is 1.06:1.
[b] Based on toluene.

Table 3
Alkylation of naphthalene with ethene in the $C_{10}H_8$–Li–Na systems in THF in the presence of toluene.[a]

Alkali metal (mmol)		Yield of alkylation products (%)[b]								Naphthalene conversion (%)
Li	Na	1	2 + 3	4	5	6	17 + 18	7 + 8	9 + 10	
6	0	34	2	13	3	–	–	3	–	55
4.5	1.5	43	1	20	4	4	–	3	–	75
4	2	43	3	20	2	3	–	4	3	79
3	3	45	9	16	3	6	–	5	–	84
2	4	43	8	15	5	2	–	5	–	78
1.5	4.5	38	15	9	9	–	2	3	–	76
1	5	52	7	8	3	2	–	2	–	74
0	6	33	2	–	–	–	–	–	–	35

[a] 22 °C, 1 atm, 24 h, 3 mmol of naphthalene, (Li + Na):$C_{10}H_8$ = 2:1, $[C_{10}H_8]_o$ = 2M, a $C_{10}H_8$:PhMe molar ratio is 1.06:1.
[b] Based on naphthalene.

Table 4
Comparison of the amount of absorbed ethene with its consumption for the formation of products of toluene and naphthalene alkylation in the $C_{10}H_8$–Li–Na systems in THF.[a]

Alkali metal (mmol)		Absorbed C_2H_4 (mmol)	Ethene consumption for alkylation				Total (mmol)
			Toluene		Naphthalene		
Li	Na		(mmol)	(mol/mol PhMe)	(mmol)	(mol/mol $C_{10}H_8$)	
6	0	7.25	2.01	0.71	2.40	0.80	4.41
4.5	1.5	9.42	2.58	0.91	3.63	1.21	6.21
4	2	8.81	3.14	1.11	3.84	1.28	6.98
3	3	9.05	3.48	1.23	4.02	1.34	7.50
2	4	8.48	3.71	1.31	3.57	1.19	7.28
1.5	4.5	8.80	4.30	1.52	3.33	1.11	7.63
1	5	7.03	3.93	1.39	2.94	0.98	6.87
0	6	2.77	0.59	0.21	1.05	0.35	1.64

[a] 22 °C, 1 atm, 24 h, 3 mmol of naphthalene, (Li + Na):$C_{10}H_8$ = 2:1, $[C_{10}H_8]_o$ = 2M, a $C_{10}H_8$:PhMe molar ratio is 1.06:1.

(Table 7). It was found that when potassium metal is added to the $C_{10}H_8$–Na system in THF the conversion of toluene into **12** and **14** first increases from 18% to 43% (**12** – 26%, **14** – 17%) at a Na:K ratio of 1:1 but then starts to decrease. If sodium is absent in a mixture the yield of the reaction products does not exceed 9% (**12** – 8%, **14** – 1%).

To elucidate the possible role of the sodium–potassium alloy in the observed synergism, we carried out special control experi-

Table 5
Alkylation of toluene with ethene in the phenanthrene–Li–Na systems in THF.[a]

Alkali metal (mmol)		Absorbed C_2H_4 (mmol)	Yield of alkylation products (%)[b]					C_2H_4 consumption for toluene alkylation		Toluene conversion (%)
Li	Na		**12**	**13**	**19**	**14**	**15**	(mmol)	(mol/mol PhMe)	
9	0	5.41	27	4	–	3	2	1.33	0.47	36
7.5	1.5	9.63	38	6	2	7	5	2.41	0.85	58
6	3	8.38	47	5	–	12	5	2.72	0.96	69
4.5	4.5	8.20	51	4	–	18	–	2.69	0.95	73
3	6	9.34	43	–	–	45	3	4.02	1.42	91
1.5	7.5	8.32	49	–	–	18	–	2.41	0.85	67
0	9	5.29	10	–	–	1	–	0.34	0.12	11

[a] 22 °C, 1 atm, 24 h, 3 mmol of phenanthrene, (Li + Na):phenanthrene = 3:1, [phenanthrene]$_o$ = 1.67 M, a phenanthrene:PhMe molar ratio is 1.06:1.
[b] Based on toluene.

Table 6
Alkylation of naphthalene with ethene in the $C_{10}H_8$–Li–K systems in THF.[a]

Alkali metal (mmol)		Absorbed C_2H_4		Yield of alkylation products (%)[b]							C_2H_4 consumption for alkylation		Naphthalene conversion (%)
Li	K	(mmol)	(mol/mol $C_{10}H_8$)	**1**	**2 + 3**	**4**	**5**	**6**	**7 + 8**	**9 + 10**	(mmol)	(mol/mol $C_{10}H_8$)	
6	0	5.40	1.80	26	–	15	9	5	3	2	3.60	1.20	60
4.5	1.5	4.09	1.36	25	–	16	7	4	–	–	2.82	0.94	52
4	2	3.28	1.09	16	–	12	5	3	–	–	2.01	0.67	36
3	3	2.08	0.69	9	–	8	2	–	–	–	0.93	0.31	19
2	4	1.60	0.53	18	–	6	–	–	–	–	0.90	0.30	24
1.5	4.5	1.61	0.54	38	–	–	–	–	––	–	1.14	0.38	38
0	6	2.70	0.90	83	2	–	–	–	–	–	2.55	0.85	85

[a] 22 °C, 1 atm, 24 h, 3 mmol of naphthalene, (Li + K):$C_{10}H_8$ = 2:1, [$C_{10}H_8$]$_o$ = 2M.
[b] Based on naphthalene.

Table 7
Alkylation of toluene and naphthalene with ethene in the $C_{10}H_8$–Na–K systems in THF.[a]

Alkali metal (mmol)		Yield of alkylation products (%)					
		Toluene[b]			Napnthalene[c]		
Na	K	**12**	**14**	**12 + 14**	**1**	**2 + 3**	**1 + 2 + 3**
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	1	9	7	–	7

[a] 22 °C, 1 atm, 24 h, 3 mmol of naphthalene, (Na + K):$C_{10}H_8$ = 2:1, [$C_{10}H_8$]$_o$ = 2M, a $C_{10}H_8$:PhMe molar ratio is 1.06:1.
[b] Based on toluene.
[c] Based on naphthalene.

ments on the interaction of toluene with ethene in THF at 22 °C in the presence of an authentic sodium–potassium alloy (K:Na = 1.77:1). It turned out, however, that no alkyaltion occurs under such conditions. Thus, for the sodium–potassium synergism to be manifested in the toluene alkylation, naphthalene must be present in the system.

The rate of the naphthalene alkylation in the presence of toluene also increases on the use of sodium–potassium mixtures but the synergistic effect observed in this case is noticeably less pronounced than that in the toluene alkylation (Table 7). The highest activity in the alkylation of naphthalene is exhibited here by the system with a Na:K molar ratio of 5.1:0.9. The reaction of ethene with naphthalene in this system gives rise to **1**–**3** in a total yield of 50% (**1** – 42%, **2 + 3** – 8%). When sodium alone is present in the mixture, the yield of **1**–**3** lowers to 36%, and with potassium alone only **1** is formed in a very low yield (7%). The amount of ethene absorbed by these toluene-containing $C_{10}H_8$–Na–K systems passes through a maximum at a Na:K ratio of 3:1 (Table 8). At all ratios used, the quantity of absorbed ethene significantly exceeds its con-

Table 8
Comparison of the amount of absorbed ethene with its consumption for the formation of products of toluene and naphthalene alkylation in the $C_{10}H_8$–Na–K systems in THF.[a]

Alkali metal (mmol)		Absorbed C_2H_4 (mmol)	Ethene consumption for alkylation				Total (mmol)
			Toluene		Naphthalene		
Na	K		(mmol)	(mol/mol PhMe)	(mmol)	(mol/mol $C_{10}H_8$)	
6	0	2.77	0.59	0.21	1.05	0.35	1.64
5.1	0.9	3.25	1.13	0.40	1.50	0.50	2.63
4.5	1.5	4.44	1.36	0.48	1.23	0.41	2.59
4	2	4.22	1.56	0.55	1.14	0.38	2.70
3	3	3.66	1.70	0.60	1.05	0.35	2.75
2.5	3.5	2.55	1.22	0.43	0.81	0.27	2.03
2	4	2.38	0.96	0.34	0.57	0.19	1.53
1	5	1.41	0.42	0.15	0.24	0.08	0.66
0	6	1.21	0.28	0.10	0.21	0.07	0.49

[a] 22 °C, 1 atm, 24 h, 3 mmol of naphthalene, (Na + K):$C_{10}H_8$ = 2:1, [$C_{10}H_8$]$_o$ = 2M, a $C_{10}H_8$:PhMe molar ratio is 1.06:1.
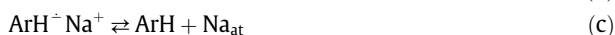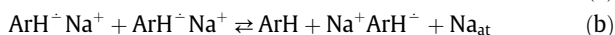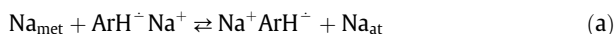
sumption for the toluene and naphthalene alkylation. Interestingly, no sodium–potassium synergism is observed in the case of the naphthalene alkylation with ethene in the absence of toluene.

3. Conclusion

The results of this study revealed the remarkable synergistic effects of alkali metals in the alkylation of toluene and naphthalene with ethene in the ArH–alkali metal systems (ArH – naphthalene, phenanthrene) in THF. In the case of the naphthalene-containing systems, the use of mixtures of lithium and sodium or sodium and potassium leads, as a rule, to a synergistic acceleration of the process. The only exception is the naphthalene alkylation in the $C_{10}H_8$–Na–K systems in the absence of toluene, wherein no sodium–potassium synergism is observed. The use of mixtures of lithium and potassium in the naphthalene-based systems, not containing toluene, results in a synergistic retardation of the naphthalene alkylation, but when toluene is present no lithium–potassium synergism occurs in both the naphthalene and toluene alkylation.

Earlier, for interpreting experimental data on the hydrogen–deuterium exchange of hydrocarbons under the action of the naphthalene–sodium system in THF, it has been suggested that this process proceeds via the following main steps [8]:

(1) Generation of atomic sodium in the $C_{10}H_8$–Na system due to the reactions (a), (b), (c):

$$Na_{met} + ArH^{\cdot-}Na^+ \rightleftarrows Na^+ArH^{\cdot-} + Na_{at} \qquad (a)$$

$$ArH^{\cdot-}Na^+ + ArH^{\cdot-}Na^+ \rightleftarrows ArH + Na^+ArH^{\cdot-} + Na_{at} \qquad (b)$$

$$ArH^{\cdot-}Na^+ \rightleftarrows ArH + Na_{at} \qquad (c)$$

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 of hydrocarbons on the surface of sodium clusters, resulting in the hydrogen–deuterium exchange.

A similar "cluster" mechanism has been proposed [11] for the reactions of the naphthalene and toluene alkylation with ethene in the ArH–alkali metal systems (ArH – naphthalene, biphenyl, phenanthrene, trans-stilbene, pyrene, anthracene) in THF. According to this mechanism, the formation of the alkylation products occurs here through the step of the ethene insertion into the alkali metal–carbon bonds [M]–R, arising on the surface of clusters as a result of the above-mentioned reversible cleavage of the reactive C–H bonds of a hydrocarbon substrate (RH).

$$2[M] + RH \rightleftarrows [M] - R + [M] - H \qquad M = Li, Na, K$$

From the proposed mechanism, it follows that the corresponding heteronuclear lithium–sodium, sodium–potassium and lithium–potassium clusters could form in the bimetallic ArH–Li–Na, ArH–Na–K and ArH–Li–K systems, respectively, in THF. Such heteronuclear clusters might be responsible for the observed synergism of alkali metals in the above-described alkylation reactions.

Similar synergistic effects have previously been observed in the reactions of catalytic olefin oligomerization induced by dispersions of alkali metals in the absence of aromatic promoters (see review [17]). One may assume that the active species ensuring the synergistic acceleration of these reactions (occurring at elevated temperatures) are also heteronuclear clusters, present in the dispersions.

For the naphthalene and toluene alkylation, an alternative mechanism with the participation of the naphthalene dianion as

the active species was also discussed [11]. Within the framework of this mechanism, the observed alkali metal synergism could be due to the formation of the mixed lithium–sodium, sodium–potassium and lithium–potassium salts of the naphthalene dianion differing in their stability and reactivity from the corresponding homonuclear dilithium, disodium and dipotassium derivatives. Note, however, that the use of the above dianionic mechanism for an explanation of the alkylation reactions found meets with considerable difficulties because metallic sodium, in contrast to lithium, does not form the dianion with naphthalene in THF at room temperature in any detectable amounts [18], and for potassium metal no unambiguous evidences for the formation of the naphthalene dianion in THF at 22 °C are available as well.

Further studies are required for the elucidation of the nature of these synergistic effects of alkali metals.

4. Experimental

The experiments were carried out in an Ar atmosphere with careful exclusion of air oxygen and moisture using standard Shlenk techniques. THF and toluene were purified in the usual manner and freshly distilled prior to use from sodium/benzophenone (THF) or over sodium (toluene) under Ar. Commercial naphthalene and phenanthrene were used without further purification. Metallic lithium, sodium and potassium were introduced into the reactions in the form of the particles of the size: ca. $3 \times 2 \times 0.3$ mm in the case of lithium and ca. $4 \times 3 \times 0.5$ mm in the case of sodium and potassium. The reaction products were analysed by GLC with temperature programming (160 °C, 10 min; 160–300 °C, 10 °C/min; 300 °C, 40 min) on a Crompack CP 9001 chromatograph equipped with a flame ionization detector and a DB5 MS (30 m × 0.25 mm) capillary column (the internal standard – dodecane). The GLC/MS analyses were performed on a Trio 1000, FISONS instrument. The most part of the experiments was duplicated or triplicated showing reasonably good reproducibility. On using the naphthalene–potassium system in THF for the naphthalene alkylation in the absence of toluene, the reproducibility was somewhat worse and here the results obtained were averaged for five runs (**1** – 83 ± 6%), **2** + **3** – 2 ± 1%).

4.1. Product identification

Compounds **1**, **4**, **5**, **12**, **13** and **19** were identified by GLC and GLC/MS using authentic samples of these compounds. Products **14** and **15** were identified on the basis of coincidence of their mass spectra with the corresponding literature data [19]. The conclusion on the nature of other products is based on the analysis of their mass spectra. The most important characteristics of the mass spectra recorded for these products are given below. Compound **2**, m/z: 158 ($[M]^+$, 53%), 129 ($[M-Et]^+$, 100%), 128 ($[C_{10}H_8]^+$, 65%). Compound **3**, m/z: 158 ($[M]^+$, 63%), 129 ($[M-Et]^+$, 100%), 128 ($[C_{10}H_8]^+$, 92%). Compound **6**, m/z: 240 ($[M]^+$, 12%), 142 ($[M-C_7H_{14}]^+$, 28%), 141 ($[M-C_7H_{15}]^+$, 100%), 128 ($[C_{10}H_8]^+$, 14%), 115 ($[M-C_7H_{15}-C_2H_2]^+$, 79%). Compound **7**, m/z: 214 ($[M]^+$, 12%), 185 ($[M-Et]^+$, 30%), 157 ($[M-Bu]^+$, 22%), 129 ($[M-Hex]^+$, 100%), 128 ($[C_{10}H_8]^+$, 80%). Compound **8**, m/z: 214 ($[M]^+$, 8%), 185 ($[M-Et]^+$, 14%), 157 ($[M-Bu]^+$, 16%), 129 ($[M-Hex]^+$, 100%), 128 ($[C_{10}H_8]^+$, 86%). Compound **9**, m/z: 242 ($[M]^+$, 10%), 213 ($[M-Et]^+$, 35%), 185 ($[M-Bu]^+$, 11%), 157 ($[M-Hex]^+$, 31%), 129 ($[M-Oct]^+$, 100%), 128 ($[C_{10}H_8]^+$, 93%). Compound **10**, m/z: 242 ($[M]^+$, 13%), 213 ($[M-Et]^+$, 44%), 185 ($[M-Bu]^+$, 15%), 157 ($[M-Hex]^+$, 42%), 129 ($[M-Oct]^+$, 84%), 128 ($[C_{10}H_8]^+$, 100%). Compound **11**, m/z: 268 ($[M]^+$, 13%), 142 ($[M-C_9H_{18}]^+$, 31%), 141 ($[M-C_9H_{19}]^+$, 100%), 128 ($[C_{10}H_8]^+$, 22%), 115 ($[M-C_9H_{19}-C_2H_2]^+$, 69%). Compound **16**, m/z: 204 ($[M]^+$, 8%), 147 ($[M-Bu]^+$, 9%), 91 ($[C_7H_7]^+$, 100%). Com-

pound **17**, m/z: 186 ([M]$^+$, 23%), 157 ([M−Et]$^+$, 34%), 129 ([M−Bu]$^+$, 98%), 128 ([C$_{10}$H$_8$]$^+$, 100%). Compound **18**, m/z: 186 ([M]$^+$, 21%), 157 ([M−Et]$^+$, 23%), 129 ([M−Bu]$^+$, 100%), 128 ([C$_{10}$H$_8$]$^+$, 89%).

4.2. Alkylation of naphthalene in the C$_{10}$H$_8$–Li–Na system

Naphthalene (0.384 g, 3 mmol), THF (1.5 ml), metallic lithium (0.028 g, 4 mmol), metallic sodium (0.046 g, 2 mmol) and dodecane (0.0521 g) 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 mixture was unfrozen to room temperature. Then ethene was introduced from an attached mercury burette and the reaction mixture was stirred at room temperature on a magnetic stirrer. The course of the reaction was monitored based on ethene absorption. After 24 h, when the amount of absorbed ethene attained 2.32 mol per mol of naphthalene (ca. 156 ml, STP), the mixture was diluted with 1.5 ml of THF and analysed by GLC and GLC/MS. The analyses showed the presence of **1–11** in the reaction solution. The overall conversion of naphthalene is 88% (23% of **1**, 3% of **2** and **3**, 28% of **4**, 17% of **5**, 7% of **6**, 4% of **7** and **8**, 3% of **9** and **10** and 3% of **11**).

4.3. Alkylation of toluene and naphthalene in the C$_{10}$H$_8$–Li–Na system

Naphthalene (0.384 g, 3 mmol), THF (1.2 ml), metallic lithium (0.011 g, 1.5 mmol), metallic sodium (0.104 g, 4.5 mmol), toluene (0.3 ml, 2.84 mmol) and dodecane (0.0492 g) were charged under Ar in the Shlenk tube and, after replacement of the argon atmosphere by ethene (from an attached mercury burette; see above), the mixture was stirred at room temperature on a magnetic stirrer. After 24 h, when the amount of absorbed ethene reached 2.93 mol per mol of naphthalene (ca. 197 ml, STP), the reaction solution was diluted with 1.5 ml of THF and analysed by GLC and GLC/MS for the content of products of the naphthalene and toluene alkylation. The results of the analyses are as follows: the naphthalene conversion is 76% (38% of **1**, 15% of **2** and **3**, 9% of **4**, 9% of **5**, 2% of **17** and **18**, and 3% of **7** and **8**); the toluene conversion is 97% (46% of **12**, 3% of **13**, 44% of **14**, 4% of **15**).

Other experiments on the toluene and naphthalene alkylation were carried out by similar procedures. The results are summarized in Tables 1–8.

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