

Catalytic activation of C–H bonds of alkanes, ethene and aromatic hydrocarbons by the adducts of active carbons with metallic potassium

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Abstract

It has been shown that the adducts of active carbons with metallic potassium are able to activate C–H bonds of alkanes, ethene and aromatic hydrocarbons and introduce these compounds into the hydrogen–deuterium exchange reactions at room temperature. This paper describes the reactions of the redistribution of hydrogen isotopes in CD₃H, C₆H₅CD₃ and C₆D₅CH₃ catalysed by the potassium–carbon adducts as well as the similar isotope exchange reactions in the systems C₂H₄–C₂D₄, C₆H₆–C₆D₆, *n*-C₆H₁₄–*n*-C₆D₁₄ and CD₄–*n*-C₅H₁₂. A study of the isotope exchange between C₆H₆ and C₆D₆ has shown that the efficiency of the process is strongly dependent on the potassium content in the catalyst passing through a maximum at the K:C molar ratio of 1:7.45. © 1998 Elsevier Science B.V. All rights reserved.

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At the present time, a large body of data on catalytic activation of C–H bonds of alkanes by transition metal compounds is available (see, e.g., Refs. [1–3]). Much less is known about the use of non-transition metal compounds for alkane activation. In 1972, Tamaru et al. have shown that lamellar compounds of graphite with metallic potassium exhibit catalytic activity in the reaction of the isotope exchange between

methane-d₀ and D₂ [4]. The reaction starts at 100–130°C, the adduct C₂₄K being about twice as active than C₈K (at 300°C). In another publication by Tamaru et al. [5], the H₂–D₂ equilibration reaction catalysed by graphite–potassium lamellar compounds has been described. According to Ozaki et al. [6], the adducts of active carbon with metallic potassium and sodium are also capable of catalysing this H₂–D₂ exchange reaction under mild conditions. In the present communication, we wish to report on the ability of the potassium–carbon adducts

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Table 1
Redistribution of hydrogen isotopes in CD₃H catalysed by the adduct of active carbon SKT with potassium^a

Reaction time (τ) (min)	Isotope composition of methane (%)					$([d_4]_{\tau}/[d_4]_e) \times 100\%$
	d ₀	d ₁	d ₂	d ₃	d ₄	
0	—	—	0.4	99.6	—	0
6	—	—	8.8	80.0	11.2	34
8	—	1.9	17.9	60.8	19.4	63
30	0.2	3.0	19.8	52.4	24.6	80

^a20°C, 0.14–0.18 g of the catalyst, molar ratio K:C in the catalyst is 1:3.73, initial volume of methane is 7.2–8.3 ml STP; $[d_4]_{\tau}$ is content of methane-d₄ at time τ , $[d_4]_e$ is content of methane-d₄ corresponding to the statistical isotope equilibrium.

to activate C–H bonds of various hydrocarbons (including alkanes) and introduce these compounds into the hydrogen–deuterium exchange reactions even at room temperature.

For preparation of the potassium–carbon adducts, conventional commercial active carbon SKT (1500 m² g⁻¹; 85.86% C, 0.24% H) of the Russian production was employed. In some experiments, the potassium adducts obtained from the original graphite-like active carbon ‘Sibunit’ [7] (500 m² g⁻¹, 99.5% C) were also used. Before the reaction with potassium, SKT carbon was dried at 180–190°C in vacuum for 6–8 h, while ‘Sibunit’ carbon was dried in vacuum at 130°C for 6–8 h. The adducts were prepared by the gradual addition of potassium metal to a vigorously stirred carbon at 120–130°C for 15 min under Ar with subsequent stirring of the resulting material at the same temperature for 1.45 h. Under such conditions, melted potassium smoothly reacted with active carbon to yield dark brown strongly pyrophoric samples which were tested in the hydrogen–deuterium exchange.

In a typical experiment, 0.14–0.18 g of potassium adduct with SKT carbon (molar ratio K:C = 1:3.73) was placed under Ar in a glass ampule ($V = 9$ – 10 ml). Then the ampule was evacuated, filled with CD₃H (600 mmHg) and, after sealing, kept during definite time at room temperature. The results of mass-spectral analysis have shown that in the course of the reaction a rapid formation of a mixture of all five isotopic forms of methane (d₀–d₄) from CD₃H takes place (Table 1). After 8 min the isotope composition of methane corresponds to 63% of the statistical isotope equilibrium and after 30 min the extent of approaching of the reaction to the equilibrium reaches 80% (based on methane-d₄). Under similar conditions, the interaction of ethene-d₀ with an equimolar amount of ethene-d₄ gives (after 8 min) the mixture of five isotopic forms of ethene (d₀–d₄) corresponding to 72% of the equilibrium (based on ethene-d₂). After 40 min, the process of redistribution of hydrogen isotopes in ethene practically attains the equilibrium (Table 2). The potassium metal alone (even in a form of a

Table 2
Hydrogen–deuterium exchange between ethene-d₀ and ethene-d₄ catalysed by the adduct of active carbon SKT with potassium^a

Reaction time (τ) (min)	Isotope composition of ethene (%)					$([d_2]_{\tau}/[d_2]_e) \times 100\%$
	d ₀	d ₁	d ₂	d ₃	d ₄	
0	47.9	—	—	4.8	47.3	0
8	16.2	19.0	26.8	21.0	17.0	72
40	6.3	23.0	35.3	26.3	9.1	95

^a20°C, 0.15–0.17 g of the catalyst, K:C = 1:3.73, initial volume of ethene is 8.3 ml STP.

Table 3

Hydrogen–deuterium exchange in the system benzene- d_0 –benzene- d_6 catalysed by the adducts of active carbon SKT with potassium^a

K:C (mol/mol)	Reaction time (τ) (h)	Isotope composition of benzene (%)							$([d_3]_t/[d_3]_e) \times 100\%$
		d_0	d_1	d_2	d_3	d_4	d_5	d_6	
1:7.45	0	50.1	—	—	—	—	1.9	48.0	0
	0.5	15.5	17.0	12.1	10.1	12.2	17.0	16.1	32
	1.0	2.3	10.4	22.9	28.8	23.3	10.2	2.1	92
1:12	1.0	17.5	16.5	10.5	8.2	10.7	17.1	19.5	26
1:7.45	1.0	2.3	10.4	22.9	28.8	23.3	10.2	2.1	92
1:5.1	1.0	8.8	15.7	17.1	16.4	17.0	15.8	9.2	52

^a20°C, amount of the catalyst \approx 0.3 g, amount of benzene is 0.4 ml.

mirror deposited on glass) displays no activity in the H/D equilibration reaction in methane (20°C, 1 day) and the rate of the H/D exchange in ethene on the potassium mirrors at 20°C is very low. The starting active carbon is unable alone to bring about the H/D equilibration reactions of hydrocarbons under ambient conditions.

Like methane and ethene, aromatic hydrocarbons also undergo the hydrogen–deuterium exchange at room temperature under the action of the potassium adducts with SKT carbon. The reactions were conducted in Schlenk tubes with stirring under Ar. A study of the isotope exchange in the benzene- d_0 –benzene- d_6 system has shown that the efficiency of the process is strongly dependent on the amount of potassium in the catalyst, passing through a maximum at the molar ratio K:C = 1:7.45 (Table 3). On using the catalyst of such composition, the reaction of benzene- d_0 with benzene- d_6 affords even after 30 min the mixture of all seven isotopic forms (d_0 – d_6) of benzene, and after 1 h nearly equilibrium mixture of these d_0 – d_6 species is

produced. Close activity in the H/D exchange in benzene is displayed by the potassium–carbon adduct obtained from the above-mentioned graphite-like active carbon ‘Sibunit.’ As ‘Sibunit’ represents practically pure carbon one may conclude that mineral admixtures presented in SKT carbon are not responsible for the observed activity of its adducts with potassium in the isotope exchange.

In the case of toluene, both the hydrogen atoms of the aromatic ring and of the methyl group are involved in the H/D exchange. This is evidenced by the formation of noticeable amounts of toluene- d_4 , toluene- d_5 and toluene- d_6 (along with the corresponding d_0 – d_2 species) from $C_6H_5CD_3$ in the presence of the potassium–SKT carbon adduct as catalyst (0.35 g, K:C = 1:7.45, 20°C, 12 h, 0.2 ml of $C_6H_5CD_3$). Analogously, toluene- d_6 and toluene- d_7 (along with their d_4 and d_3 isotopomers) are produced from $C_6D_5CH_3$ under the same conditions.

Of especial interest is the ability of potassium adduct with SKT carbon to catalyse the hydrogen–deuterium exchange at room temperature

Table 4

Hydrogen–deuterium exchange between methane- d_4 and n -pentane- d_0 catalysed by the adduct of active carbon SKT with potassium^a

Reaction time (h)	Isotope composition of n -pentane (%)						Deuterium content in n -pentane (at.%)
	d_0	d_1	d_2	d_3	d_4	d_5 – d_{12}	
0	100	—	—	—	—	—	0
1	97.7	1.9	0.4	—	—	—	0.2
96	26.1	34.1	22.8	12.5	4.5	—	11.3

^a20°C, 0.17–0.20 g of the catalyst, K:C = 1:7.45, initial volume of methane is 8.8 ml STP (600 mmHg), amount of n -pentane is 0.05 ml.

even in such inert hydrocarbons as *n*-hexane and *n*-pentane. Thus, on using the adduct with the K:C molar ratio of 1:7.45, the mixture of nine isotopic forms of hexane ($d_0 = 38.2\%$, $d_1 = 9.9\%$, $d_2 = 1.6\%$, $d_3 = 0.3\%$, $d_{10} = 0.5\%$, $d_{11} = 0.7\%$, $d_{12} = 3.2\%$, $d_{13} = 11.1\%$, $d_{14} = 34.5\%$) is obtained after 1 h in the interaction of hexane- d_0 with equimolar amount of hexane- d_{14} (0.38 g of the catalyst, 0.4 ml of hexane) and after 12 h the mixture of hexanes of the following isotope composition is formed: $d_0 = 21.9\%$, $d_1 = 18.8\%$, $d_2 = 7.0\%$, $d_3 = 1.7\%$, $d_4 = 0.3\%$, $d_5 = 0.3\%$, $d_{10} = 1.0\%$, $d_{11} = 2.7\%$, $d_{12} = 8.0\%$, $d_{13} = 17.5\%$, $d_{14} = 20.8\%$ (0.30 g of the catalyst, 0.4 ml of hexane). Another example of C–H bond activation in liquid alkanes by the potassium–carbon adducts is the reaction of cross hydrogen–deuterium exchange between

methane- d_4 and pentane- d_0 (Table 4). In this case the redistribution of deuterium between the gaseous and liquid phases occurs.

References

- [1] A.E. Shilov, Activation of Saturated Hydrocarbons by Transition Metal Complexes, D. Riedel, Dordrecht, 1984.
- [2] R.H. Crabtree, Chem. Rev. 85 (1985) 245.
- [3] C.L. Hill (Ed.), Activation and Functionalization of Alkanes, Wiley, New York, 1989.
- [4] M. Ichikawa, K. Kawase, K. Tamaru, J. Chem. Soc. Chem. Commun., (1972) 177.
- [5] K. Watanabe, T. Kondow, M. Soma, T. Onishi, K. Tamaru, J. Chem. Soc. Chem. Commun. (1972) 39.
- [6] M. Ishizuka, A. Ozaki, J. Catal. 35 (1974) 320.
- [7] Yu.I. Ermakov, V.F. Surovikin, G.V. Plaksin, V.A. Semikolenov, V.A. Likhobolov, L.V. Chuvilin, S.V. Bogdanov, React. Kinet. Catal. Lett. 32 (1987) 435.