Alkylation of Alkyl Aromatic Hydrocarbons over Metal Oxide–Alkali Metal Superbasic Catalysts

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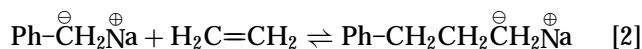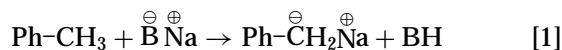
The alkylation of toluene, ethylbenzene, cumene, and xylenes with ethene, propene, and 1,2-diphenylethylene was investigated over superbasic MgO–K and γ-Al$_2$O$_3$–K catalysts and over model systems of the EDA complex type. Metal oxide–alkali metal solid superbases as well as MgO–K polyaromatic hydrocarbon systems exhibited high activity in the transformations carried out under atmospheric and elevated pressure at low temperature. The reaction kinetics, the results of ESR investigations of adsorbed intermediates, and the effects of poisoning using radicals trap TEMPO enabled the identification of F_s^+ sites as catalytically active centres. The proposal of a radical pathway of the reaction was confirmed and illustrated. © 2001 Academic Press
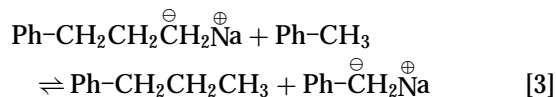
Key Words: alkylbenzenes side-chain alkylation; superbasic catalysts; one-electron donor centre activity; radical reaction pathway.

INTRODUCTION

Only few methods have been proposed for the side-chain alkylation in alkylbenzenes (1–12). The most effective method was the reaction of benzene alkyl derivatives with alkenes as alkylating agents in the presence of extremely strong basic catalysts, largely developed by Pines and co-worker (1, 2). As highly basic catalyst alkali metals, their hydrides and graphite intercalates were used. Especially active catalytic systems were sodium and potassium organic complexes with, e.g., polyaromatic hydrocarbons, alkylchlorides, benzonitrile, or pyridine (1, 2). All these catalysts were assumed to transform alkylbenzenes to benzylic carboanions via a transmetalation reaction. Therefore, the reaction mechanism proposed by Pines and co-worker (13) involves the addition of a benzylic carboanion to the alkene molecule:

$$Ph-CH_3 + \overset{\ominus}{B}\overset{\oplus}{Na} \rightarrow Ph-\overset{\ominus}{C}H_2\overset{\oplus}{Na} + BH \qquad [1]$$

$$Ph-\overset{\ominus}{C}H_2\overset{\oplus}{Na} + H_2C{=}CH_2 \rightleftharpoons Ph-CH_2CH_2\overset{\ominus}{C}H_2\overset{\oplus}{Na} \qquad [2]$$

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$$Ph-CH_2CH_2\overset{\ominus}{C}H_2\overset{\oplus}{Na} + Ph-CH_3$$
$$\rightleftharpoons Ph-CH_2CH_2CH_3 + Ph-\overset{\ominus}{C}H_2\overset{\oplus}{Na} \qquad [3]$$

The same mechanism was adopted by workers in Japan (14) for the alkylation of alkylbenzenes with alkenes over the complex solid three-component superbasic catalyst γ-Al$_2$O$_3$–NaOH–Na.

The results of our studies (1979–1998) on solid superbases of the metal oxide–alkali metal type demonstrated the high activity of superbasic systems in the selective hydrogenation of various alkenes (e.g., ethene, propene, cyclohexene, styrene, and isoprene) and carbon monoxide (15–22). Our superbases are bifunctional systems with extremely strong two-electron donors (Hammett basic strength, $H_- \geq 37$) and one-electron donor (able to ionize molecules with electron affinity values in the range of -0.2 eV) centres on their surface. Even so, it was unequivocally proved by the catalytic poisoning and by the correlation activity vs the concentration of the one-electron donor centres that the extremely strong single-electron donor sites (surface F_s^+ centers—electrons from alkali atoms in anionic vacancies of metal oxides) were responsible for the initiation of the above-mentioned hydrogenation reactions (17). The secondary surface centres of an anion radical type originated from alkenes or CO adsorption on F_s^+ sites were postulated to play the decisive role in the activation of the dihydrogen molecule (19–22). Only recently, the importance of secondary radicals was confirmed by the modelling of surface anion radical centres of differentiated power through the adsorption of various polyaromatics onto F_s^+ centres of the superbasic catalyst γ-Al$_2$O$_3$–K or by the immobilization of the ion radical salt (potassium naphthenide) on the γ-Al$_2$O$_3$ surface (21).

The majority of the basic catalysts used by Pines and co-worker, (1, 2) for side-chain alkylation in alkylbenzenes were EDA (electron donor acceptor) complexes or organo alkali metal reagents, which can produce radicals, according to Morton and co-workers (23, 24). Our superbasic catalysts of the metal oxide–alkali metal type are also the EDA complexes in which electron-deficient surface sites (anionic

vacancies (21, 22)) play the role of acceptors for alkali-metal-derived electrons (the rule of F_s^+ centres formation). Furthermore, reactants such as alkenes or alkylbenzenes form with F_s^+ centres secondary EDA complexes which are of high cata- lytic importance for hydrogenation (of, e.g., alkenes) or dehydrogenation (of, e.g., alkylaromatic hydrocarbons) reactions (21, 22, 26). Finally, the above reactions proceed through radical intermediates. The listed similarities between the catalytic systems used by Pines and solid superbases prompted us to investigate the catalytic activity of superbasic catalysts in the side-chain alkylation of alkyl derivatives of benzene. This work was also intended to be a study of the reaction mechanism. Alkyl aromatics cumene, ethylbenzene, toluene, and *o*-, *m*-, and *p*-xylenes were chosen as a model; the alkylating agents were ethene, propene, and trans stilbene (1,2-diphenylethene). Excellent demonstrations of effects of the appearance of the radical species were achieved by means of the catalyst poisoning and the ESR measurements of the adsorbed states of the reactants. The latter is a special focus of the work of this laboratory.

EXPERIMENTAL

Catalysts

Magnesia was obtained by hydrolysis of $Mg(NO_3)_2 \cdot 6H_2O$ with a concentrated aqueous ammonia solution. After the solution was washed with doubly distilled water, the $Mg(OH)_2$ precipitate was dried at 333, 353, and 393 K for 24 h at each temperature.

γ-Alumina was prepared by hydrolysis of aluminium triisopropoxide (Fluka, pract. dest. $\geq$98% Al), previously purified by distillation under vacuum (bp 413 K, 1.07 kPa). The hydrolysis procedure has been described elsewhere (27, 28). The obtained $Al(OH)_3$ was dried at 313, 353, and 393 K for 24 h at each temperature.

Both hydroxides were calcined before potassium evaporation, first in air at 823 K for 1 h and then in a stream of water-free and deoxygenated nitrogen at the same temperature for 16 h in the case of MgO and for 5 h in the case of γ-Al$_2$O$_3$.

Metallic potassium (Fluka, purum, $\geq$98%) was deposited onto magnesia and γ-alumina surfaces by chemical vapour deposition evaporation under reduced pressure (1.3 Pa) at 573 K. After evaporation the catalysts were evacuated at 623 K and then cooled in a stream of water-free deoxygenated nitrogen.

Reactions

The alkylation reactions under pressure were performed in a stainless steel pressure reactor (250 cm³) according to the following procedure: 0.25 g of catalyst and 8.2 mmol of alkylbenzene (0.78 g for toluene (Aldrich 99%, dest. bp 283–384 K and dried), 0.98 g for cumene (Aldrich 99%, dest. bp 425–427 K and dried), and 0.87 g for ethylbenzene (Aldrich 99%, dest. bp 408–409 K and dried or *o*-, *p*-, *m*-xylenes (Aldrich, >99)) were introduced into a glass ampoule (20 cm³) that had been evacuated and rinsed with dry-deoxygenated N₂. The frozen ampoule was sealed and placed into the evacuated and pure dinitrogen-washed autoclave. The reactor was then rinsed with ethene or propene and filled with a given gas to 1.01 MPa (Aldrich, 99.5+%, ethene) or 0.71 MPa (Aldrich, 99.5+%, propene). The autoclave was thermostatured, the ampoule with catalyst and alkylbenzene was broken, and the remaining mixture was stirred. The reaction products were analyzed by GC using a 5-m column (OV 101/Chromosorb W) and detected by MS (HP 4890 series II).

The reactions under normal pressure were carried out according to a similar procedure in a glass batch reactor (150 cm³) under normal pressure. In this case, 1.64 mmol of corresponding alkylbenzene (0.156 g of toluene, 0.174 g of ethylbenzene, 0.196 g of cumene, or 0.177 g of corresponding xylene) reacted with an excess of ethene or propene over 0.05 g of superbasic catalyst (MgO–K, γ-Al$_2$O$_3$–K, or MgO–K–polyaromatic hydrocarbon).

The reactions with ethylene oxide were carried out in a glass batch reactor at 373 K under normal pressure; 1.64 mmol of corresponding alkylbenzene (0.156 g of toluene, 0.174 g of ethylbenzene, and 0.196 g of cumene) was introduced into the evacuated and then dry-deoxygenated dinitrogen-washed reactor and filled with ethylene oxide (Fluka, purum, >99.8%).

Poisoning of Active Sites

Reactions in the presence of the free radical trap TEMPO (2,2,6,6-tetramethylpiperydynyl-1-oksyl, Aldrich, 99%) were performed at 373 K for 5 h in the glass batch reactor (150 cm³) with the same amounts of reactants as those in reactions under normal pressure described above. Then, 0.001 g of TEMPO was introduced into the reactor together with 0.05 g of a catalyst.

Textural Properties of Studied Catalysts

The specific surface area and pore distribution on the surfaces of the studied catalysts were determined by BET using a Quantasorb IR2 apparatus (Quantachrom) (Table 1).

TABLE 1

Specific Surface Area and Predominant Pore Radius of the Studied Carriers and Superbasic Catalysts

Catalyst	S_{BET} ($m^2 g^{-1}$)	Pore radius Å
MgO	37	74
MgO–K	31	71
γ-Al$_2$O$_3$	92	38
γ-Al$_2$O$_3$–K	90	37

ESR Measurements

The ESR spectra were registered at room temperature using a Brooker ESP 300E spectrometer. Alkylbenzenes and alkenes (1.33×10^{-3} Pa) were adsorbed at room temperature on the surface of the catalysts previously evacuated to 1.33×10^{-2} Pa.

RESULTS

Alkylation of Toluene, Ethylbenzene, and Cumene

Pure magnesia and γ-alumina were inactive in the studied transformations. Both investigated superbasic catalysts, the MgO–K and the γ-Al$_2$O$_3$–K system, exhibited high activity in all the ethylation and propylation reactions of monoalkylbenzenes (Tables 2 and 3). The MgO–K catalyst was found to be considerably more active than the γ-Al$_2$O$_3$–K system in the ethylation of toluene, ethylbenzene, and cumene under elevated pressure. The propyla-

tion of alkyl aromatics, however, gave a higher yield over γ-Al$_2$O$_3$–K.

The only products formed in the ethylation or propylation of the studied alkylbenzenes under alkylation conditions were their respective mono-, di-, or trialkyl derivatives. The amount of the formed unidentified high-temperature boiling fraction did not exceed 0.1%. No oligomerization products of the alkylating alkenes formed in the reactant solution (liquid phase) or in the gas phase. Only in the case of reactions of alkyl aromatics, carried out with ethene at the highest reaction temperature (423 K), did the surface of the catalyst turn the characteristic yellow. IR spectra of the outgassed catalyst samples (1.03 Pa) revealed the presence of characteristic bands at 2935 to 2830 cm^{-1} and 1480 to 1430 cm^{-1} attributed by us (21) to the formed polymeric residue. Such a residue did not form in reactions performed at lower temperature ($\leq$373 K) and was therefore not observed.

It is noteworthy that the catalysts used at temperatures $\leq$373 K maintained their activity after the reaction

TABLE 2

Reaction Products in the Alkylation of Aromatics with Ethene and Propene [Reaction Time: 5 h (Ethene), 10 h (Propene); Pressure: 1.01 MPa (Ethene), 0.71 MPa (Propene)]

| | | | Product (mol%) | | | | | |
| | | | Ethylation | | | Propylation | | |
Reactant	Catalyst	T (K)	Monoalkyl derivative[a]	Dialkyl derivative[b]	Indane[c]	Monoalkyl derivative[d]	Dialkyl derivative[e]	Indane[f]
Toluene	MgO–K	323	2.6	0.0	0.0	5.4	0.0	0.0
		373	26.8	3.0	0.0	5.9	0.0	0.0
		423	34.6	1.4	0.0	23.0	2.4	0.0
	γ-Al$_2$O$_3$–K	323	0.5	0.0	0.0	1.2	0.0	0.0
		373	0.7	0.0	0.0	7.0	0.0	0.0
		423	0.8	0.0	0.0	37.4	0.0	0.0
Ethylbenzene	MgO–K	323	33.0	1.8	2.0	3.2	0.0	0.0
		373	39.6	4.4	0.0	33.0	0.0	0.0
		423	48.7	0.6	0.0	51.0	0.0	0.0
		473	41.5	10.1	2.5	60.0	0.0	0.0
	γ-Al$_2$O$_3$–K	323	21.2	6.1	0.0	7.2	0.0	0.0
		373	23.3	3.8	0.0	48.8	0.0	0.4
		423	32.6	5.6	1.0	45.7	0.0	0.3
		473	40.0	4.6	3.5	53.4	0.0	0.6
Cumene	MgO–K	323	75.8	4.3	0.0	0.0	0.0	0.0
		373	77.7	7.6	0.0	5.3	0.0	0.6
		423	89.8	7.4	0.0	10.0	0.0	0.3
	γ-Al$_2$O$_3$–K	323	69.5	4.0	0.3	0.0	0.0	0.0
		373	48.3	1.7	0.0	10.6	0.0	0.0
		423	39.6	0.0	0.0	16.7	1.1	0.0

[a] Monoalkyl derivative of toluene: 1-phenylpropane; of ethylbenzene: 2-phenylbutane and traces of 1-phenylbutane; of cumene: 2-methyl-2-phenylbutane and traces of 3-methyl-3-phenylhexane.

[b] Dialkyl derivative of toluene: 3-phenylpentene; of ethylbenzene: 3-methyl-3-phenylpentane; of cumene: 3-methyl-3-phenylhexane.

[c] Indane: 1-methylindane for ethylbenzene ethylation; 1,2-dimethylindane for cumene ethylation.

[d] Monoalkyl derivative of toluene: 2-methyl-1-phenylpropane and traces of 1-phenylbutane; of ethylbenzene: 2-methyl-3-phenylbutane and traces of 2-phenylpentane; of cumene: 2,3-dimethyl-2-phenylbutane and traces of 2-methyl-2-phenylpentane.

[e] Dialkyl derivative of toluene: 3-phenylpentene; of ethylbenzene: 3-methyl-3-phenylpentane; of cumene: 3-methyl-3-phenylhexane.

[f] Indane: 1,2-dimethylindane for ethylbenzene propylation; 1,1,2-trimethylindane for cumene propylation.

TABLE 3

Reaction Products in the Alkylation of Equimolar Mixtures of Alkyl Aromatics over MgO–K Catalyst
[Reaction Time: 5 h, Temperature: 373 K, Normal Pressure]

	Starting composition (mol%)	Composition of reagents after reaction (mol%)					
		Toluene	Ethylbenzene	Cumene	A	B	A/B
Toluene–Ethylbenzene	49.3 50.7	46.2	33.8	—	3.1	16.9	0.18
Toluene–Cumene	48.7 51.3	45.2	—	25.1	3.5	26.2	0.13
Ethylbenzene–Cumene	48.5 51.5	—	35.6	35.4	12.9	16.1	0.80

Note. A, monoalkyl derivative of hydrocarbon possessing benzyl carbon atom of lower order. B, monoalkyl derivative of hydrocarbon possessing benzyl carbon atom of higher order. Monoalkyl derivatives: 1-phenylpropane for toluene, 2-phenylpentane for ethylbenzene, and 2-methyl-2-phenylbutane for cumene.

run. In the event of subsequent use of the catalysts, while maintaining the water and oxygen-free conditions of all the operations, the decrease in the rate of a particular reaction did not exceed 12 to 15%.

The reaction of toluene with ethene proceeded according to Eq. [4] with the formation of the mono- and dialkyl derivatives, 1-phenylpropane (**II**) or 3-phenylpentane (**III**):
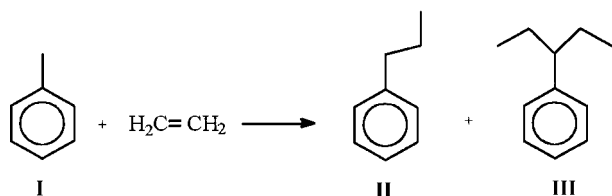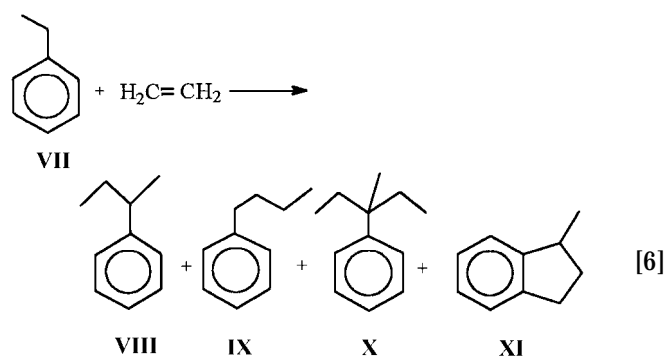

[4]

The products of toluene alkylation with propene were 2-methyl-1-phenylpropane (**IV**), 1-phenylbutane (**V**), and 2,4-dimethyl-3-phenylpentane (**VI**):
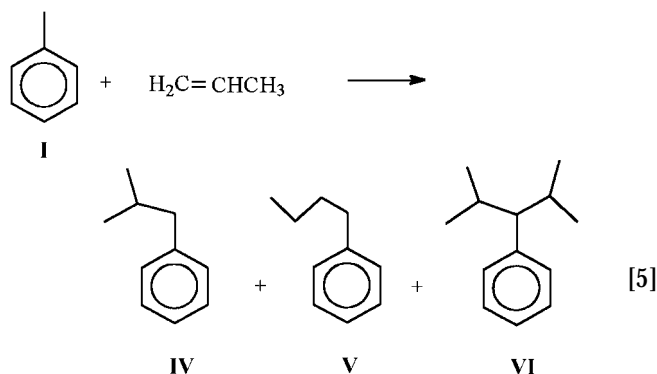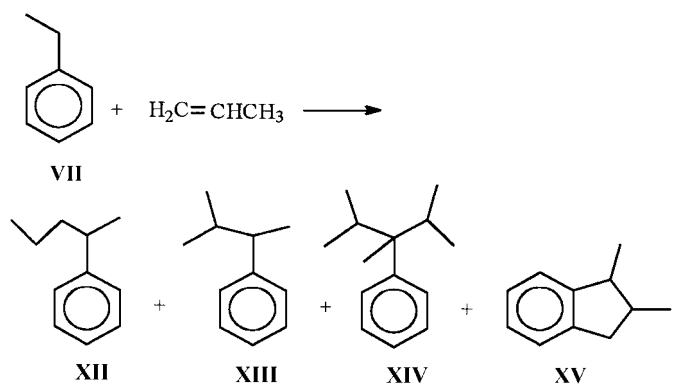

[5]

During ethylbenzene ethylation, monoalkyl derivatives (2-phenylbutane (**VIII**) and traces of 1-phenylbutane (**IX**)) and a dialkyl derivative (3-methyl-3-phenylpentane (**X**)) were accompanied by 1-methylindane (**XI**):
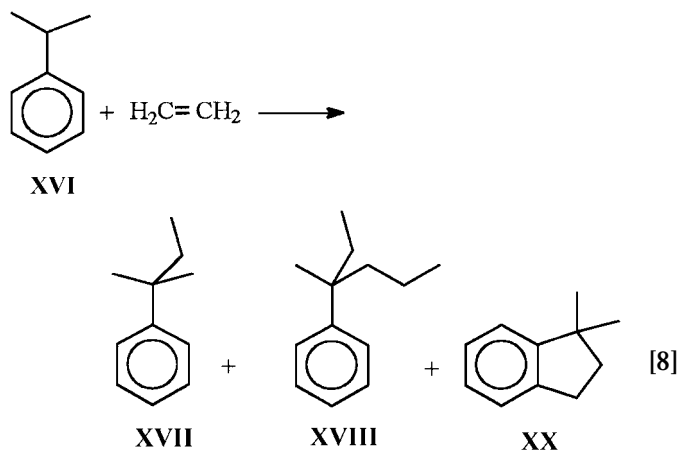

[6]

Ethylbenzene propylation led to 2-phenylpentane (**XII**), 2-methyl-3-phenylbutane (**XIII**), 2,3,4-trimethyl-3-phenylpentane (**XIV**), and 1,2-dimethylindane (**XV**):


[7]

The products of cumene alkylation with ethene were a monoalkyl derivative (2-methyl-2-phenylbutane (**XVII**)), a dialkyl derivative (3-methyl-3-phenylhexane (**XVIII**)), and a cyclization product (1,1-dimethylindane (**XX**)):

[8]

The only products of the cumene propylation were a monoalkyl derivative, 2,3-dimethyl-2-phenylbutane (**XXI**), a dialkyl derivative, 2-methyl-2-phenylpentane (**XXII**), and 1,1,2-trimethylindane (**XXIII**):

[9]
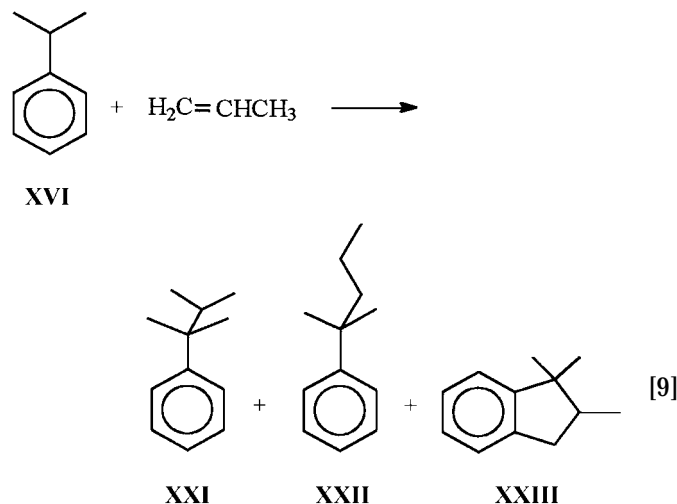
The reactivity of alkyl aromatics in the reaction with ethene changed in the order cumene > ethylbenzene > toluene over both the studied catalytic systems, whereas for the reaction with propene the reactivity order was as follows: ethylbenzene > toluene > cumene. The reactivity sequence of the reactants toward ethene was confirmed by the results of the ethylation of almost equimolar mixtures of hydrocarbon pairs performed under normal pressure (Table 3). According to these results, the relative activity (measured as the corresponding alkyl aromatics conversion ratio) would be established as follows: toluene:cumene = 0.13; toluene:ethylbenzene = 0.18; ethylbenzene:cumene = 0.80. It should be emphasised that the reactivity diminished with the formation of intermediates from a polyaromatic molecule during activation on the superbasic surface.

Alkylation of Xylenes

The superbasic systems were found to be effective catalysts for the alkylation of xylenes as well (Table 4).

The γ-Al$_2$O$_3$–K system exhibited remarkably higher activity than the MgO–K catalyst in the xylene ethylation reaction under elevated pressure. In the propylation process, the conversion of xylenes was insignificantly higher over the alumina–potassium system than over the MgO–K catalyst.

The products of the o-xylene alkylation with ethene were the monoalkylation product, 2-methyl-1-(1-propyl)benzene (**XXIV**), the product of the double alkylation of one methyl group, 2-methyl-1-(3-pentyl)benzene (**XXV**), and the product of the dialkylation of both methyl groups,

TABLE 4

Reaction Products in the Alkylation of Xylenes with Ethene and Propene [Reaction Time: 5 h (Ethene), 10 h (Propene); Pressure: 1.01 MPa (Ethene), 0.71 MPa (Propene)]

| | | | Product (mol%) | | | | | |
| | | | Ethylation | | | Propylation | | |
Reactant	Catalyst	T (K)	A	B	C	A	B	C
o-Xylene	MgO–K	323	1.6	1.6	0.0	0.0	0.0	0.0
		373	32.4	9.0	0.0	6.4	0.6	0.0
		423	30.7	18.0	5.0	33.2	3.8	0.5
	γ-Al$_2$O$_3$–K	323	57.4	1.9	5.8	0.3	0.0	0.0
		373	51.3	11.4	11.2	2.5	0.0	0.0
		423	33.8	17.8	35.8	40.0	3.2	0.0
m-Xylene	MgO–K	323	4.2	0.0	0.0	0.0	0.0	0.0
		373	25.4	1.9	0.0	6.3	0.5	0.0
		423	31.2	43.4	9.1	31.5	4.0	1.2
	γ-Al$_2$O$_3$–K	323	40.4	0.9	1.9	0.2	0.0	0.0
		373	50.3	12.0	9.5	1.6	0.0	0.0
		423	32.7	31.5	29.6	38.2	3.3	0.0
p-Xylene	MgO–K	323	2.4	0.0	0.0	0.0	0.0	0.0
		373	31.4	4.9	2.3	7.0	0.7	0.0
		423	35.4	32.8	11.4	34.3	3.7	0.5
	γ-Al$_2$O$_3$–K	323	63.3	2.6	6.4	0.4	0.0	0.0
		373	40.1	11.1	25.5	3.2	0.0	0.0
		423	36.3	12.9	36.1	44.4	3.2	0.0

Note. A, product of monoalkylation of one methyl group: 1-methyl-2-propylbenzene for o-xylene ethylation, 1-methyl-3-propylbenzene for m-xylene ethylation, and 1-methyl-4-propylbenzene for p-xylene ethylation; 1-methyl-2-isobutylbenzene for o-xylene propylation, 1-methyl-3-isobutylbenzene for m-xylene propylation, and 1-methyl-4-isobutylbenzene for p-xylene propylation. B, product of double alkylation of one methyl group: 1-methyl-2-(3-pentyl)benzene for o-xylene ethylation, 1-methyl-3-(3-pentyl)benzene for m-xylene ethylation, and 1-methyl-4-(3-pentyl)benzene for p-xylene ethylation; 1-methyl-2-[3-(2,4-dimethyl)pentyl]benzene for o-xylene propylation, 1-methyl-3-[3-(2,4-dimethyl)pentyl]benzene for m-xylene propylation, and 1-methyl-4-[3-(2,4-dimethyl)pentyl]benzene for p-xylene propylation. C, product of double alkylation of both methyl groups: 1,2-bis(3-pentyl)benzene for o-xylene ethylation, 1,3-bis(3-pentyl)benzene for m-xylene ethylation, and 1,4-bis(3-pentyl)benzene for p-xylene ethylation; 1,2-diisobutylbenzene for o-xylene propylation, 1,3-diisobutylbenzene for m-xylene propylation, and 1,4-diisobutylbenzene for p-xylene propylation.

1,2-bis(3-pentyl)benzene (**XXVI**):

XXIII + $H_2C=CH_2$ ⟶

XXIV + **XXV** + **XXVI**   [10]
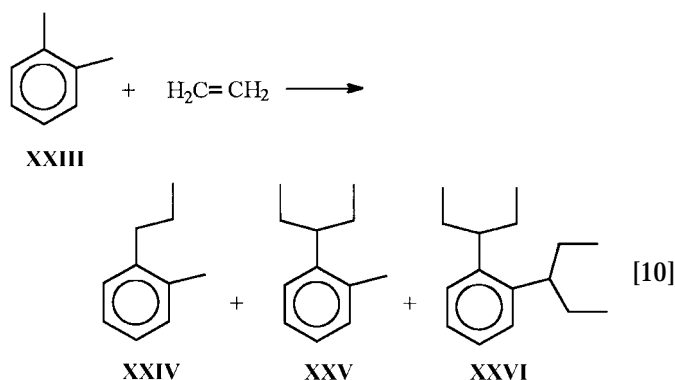
The analogous products 3-methyl-(3-methyl-1-(1-propyl)benzene (**XXVIII**), 3-methyl-1-(3-pentyl)benzene (**XXIX**), and 1,3-bis(3-pentyl)benzene (**XXX**) were obtained during the ethylation of *m*-xylene:

XXVII + $H_2C=CH_2$ ⟶

XXVIII + **XXIX** + **XXX**   [11]
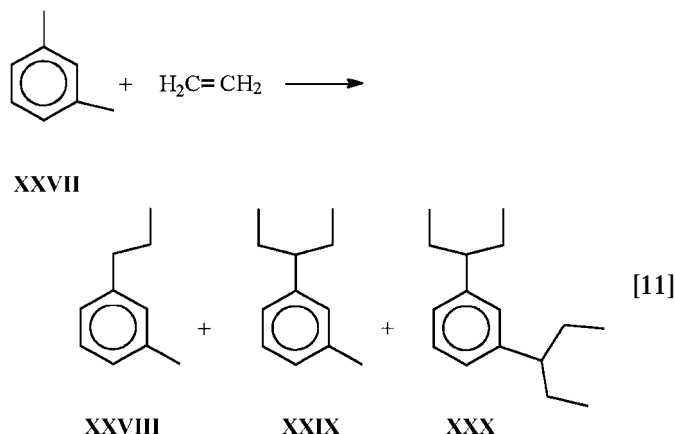
Furthermore, the ethylation of *p*-xylene resulted in the formation of the monoalkylation and dialkylation products of a single methyl group, 4-methyl-1-(1-propyl)benzene (**XXXII**) and 4-methyl-1-(3-pentyl)benzene (**XXXIII**), and the product of the double alkylation of both methyl groups, 1,4-bis(3-pentyl)benzene (**XXXIV**):

XXXI + $H_2C=CH_2$ ⟶

**XXXII** + **XXXIII** + **XXXIV**   [12]
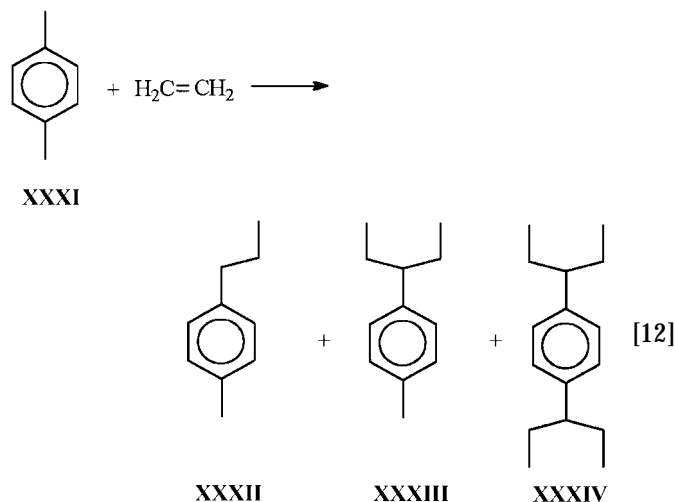
At temperatures below 423 K, the ethylation of all xylenes led to the formation of corresponding monoalkylates as the main products, whereas at higher temperatures they were accompanied by comparable or even larger amounts of the dialkylation products (Table 4).
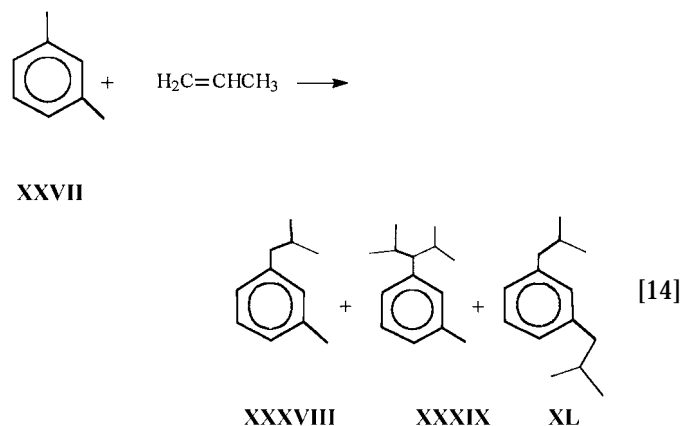
The catalysts under study demonstrated different selectivity behaviour during the introduction of further ethylenic groups into the xylene molecule; the products of the double alkylation of a single CH_3 group dominated the MgO–K catalysts, while over γ-Al_2O_3–K larger amounts of the double alkylation products of both methyl groups were observed.

Similarly, in the ethylation reaction, the propylation of xylenes led to the products of the monoalkylation, the dialkylation of a single methyl group, and the double alkylation of both methyl groups in the alkylbenzene molecule.

o-Xylene alkylation with propene led to 2-methyl-1-(1-(2-methyl)propyl)benzene (**XXXV**) as a main product and to 2-methyl-1-(3-(2,4-dimethyl)pentyl)benzene (**XXXVI**). The product of the double alkylation of both methyls (**XXXVII**) appeared only at the highest reaction temperatures and only over the MgO–K catalyst:

XXIII + $H_2C=CHCH_3$ ⟶

XXXV + **XXXVI** + **XXXVII**   [13]
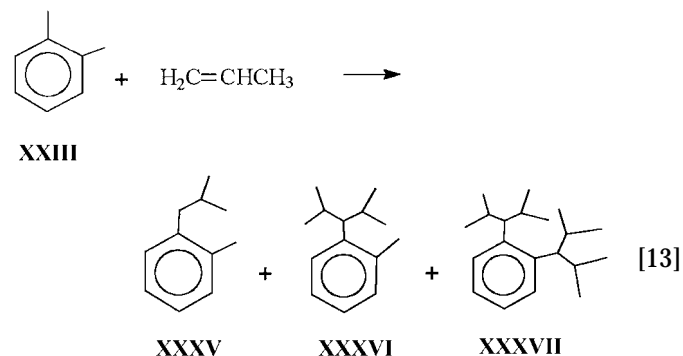
m-Xylene propylation products were 3-methyl-(1-(1-(2-methyl)propyl)benzene (**XXXVIII**) and 3-methyl-1-(3-(2,4-dimethyl)pentyl)benzene (**XXXIX**). At 423 and 473 K over the MgO–K catalyst they were accompanied by remarkable amounts of 1,3-bis(3-(2,4-dimethyl)pentyl)benzene (**XL**):

XXVII + $H_2C=CHCH_3$ ⟶

**XXXVIII** + **XXXIX** + **XL**   [14]

The propylation of *p*-xylene led to the formation of 4-methyl-1-(1-(2-methyl)propyl)benzene (**XLI**) and 4-methyl-1-(3-(2,4-dimethyl)pentyl)benzene (**XLII**); at 473 K it was accompanied by 1,4-bis(3-(2,4-dimethyl)pentyl)benzene (**XLIII**):

XXXI

$$[15]$$

XLI   XLII   XLIII
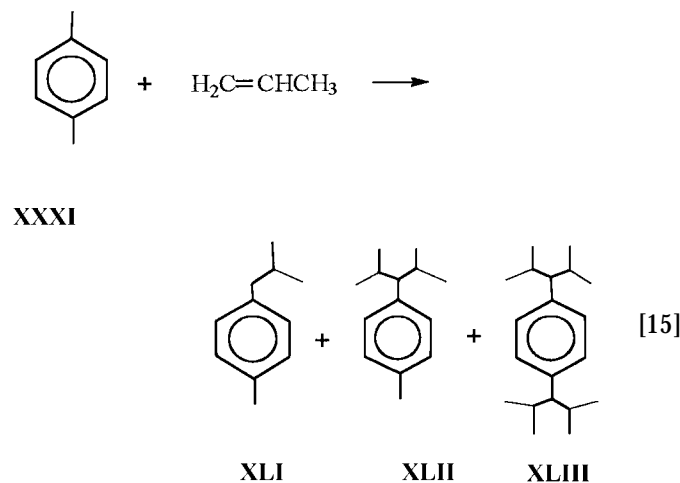
The catalyst under study demonstrated different selectivity behavior when the second ethyl group was introduced into the side chain in the corresponding xylenes. The products of the double alkylation of the same methyl group dominated in the reaction over the MgO–K catalyst, while monoalkylation of both methyl groups in a reactant molecule was the preferred direction of the reaction in the presence of the γ-Al$_2$O$_3$–K system.

Alkylation of Alkyl Aromatics with Stilbene

The alkylation of alkyl aromatics with 1,2-diphenylethylene was strongly affected by steric hindrance. Sterical effects determined the selectivity: for all the alkylated alkylbenzenes, the only reaction product was the corresponding monoalkyl derivative (i.e., 1,2,3-triphenylpropane (**XLVI**) from toluene, 1,2,3-triphenylbutane (**XLVII**) from ethylbenzene, and 2-methyl-2,3,4-triphenylbutane (**XLVIII**) from cumene, Eqs. [16]–[18]), as well as the yield of particular reactions; over the more active MgO–K catalyst the conversion of the reactant reached 100% in the case of the toluene and ethylbenzene reactions, while during the reaction of cumene with the crowded benzyl atom it did not exceed 40% (Table 5).

I   XLV   XLVI

$$[16]$$

VII   XL V   XL VII $[17]$

XVI   XLV   XL VIII

$$[18]$$
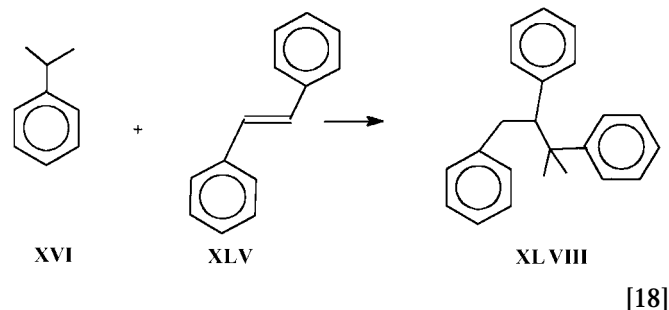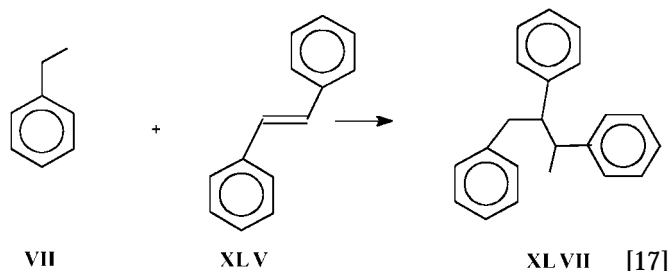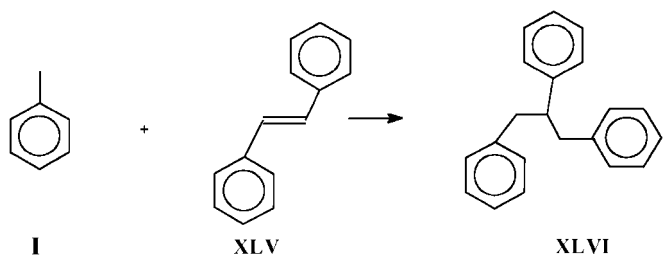
The MgO–K system was found to be a significantly more active catalyst than the γ-Al$_2$O$_3$–K system in the alkylation with stilbene.

TABLE 5

Products in the Alkylation of Alkyl Aromatics with Stilbene [Reaction Time: 5 h, Normal Pressure]

Reactant	Catalyst	T (K)	Product (mol%) Monoalkyl derivative[a]
Toluene	MgO–K	323	100
		373	100
		423	100
		473	100
	γ-Al$_2$O$_3$–K	323	80.0
		373	85.0
		423	90.0
		473	92.0
Ethylbenzene	MgO–K	323	95.0
		373	100
		423	100
		473	100
	γ-Al$_2$O$_3$–K	323	60.0
		373	80.0
		423	83.0
		473	85.0
Cumene	MgO–K	323	25.8
		373	31.8
		423	35.0
		473	40.0
	γ-Al$_2$O$_3$–K	323	20.0
		373	22.0
		423	25.3
		473	30.1

[a] Monoalkyl derivative: 1,2,3-triphenylpropane for toluene reaction, 1,2,3-triphenylbutane for ethylbenzene reaction, and 2-methyl-2,3,4-triphenylbutane for cumene reaction.

Alkylation over EDA-Type Catalysts

According to the procedure described in detail earlier (21), the series of model catalysts possessing extremely strong one-electron donor centres was prepared. These catalysts had the structure of the electron donor–acceptor (EDA) complexes and were synthesized by evaporation of the electron acceptors: naphthalene (electron affinity, $E_A = -0.02$ eV (29)), anthracene ($E_A = 0.64$ eV (30)), or perylene ($E_A = 1.12$ eV (31)) onto the primary catalytic system, MgO (metallic potassium). The specific complex forms between the F_s^+ centres on the catalyst surface (electron donor) and on an adsorbed polyaromatic molecule (electron acceptor). Table 6 lists the results of ethylation and propylation of alkyl aromatics over EDA complex type catalysts.

With one exception, all the catalysts of the MgO–K polyaromatic hydrocarbon type exhibited higher activity in the alkylation reactions than the conventional nonmodified MgO–K catalyst.

It is noteworthy that, as in the case of unmodified superbasic systems, the reactivity of alkyl aromatics in the alkylation reaction changed in the sequence cumene > ethylbenzene > toluene. The monoalkyl ethylation products of all the studied hydrocarbons were accompanied by dialkyl derivatives, while the propylation reactions led selectively to monoalkyl derivatves. The electron affinity of an acceptor in the EDA complex, formed by a polyaromatic hydrocarbon with F_s^+ centres on the MgO–K surface, remarkably influenced catalyst activity. As was previously observed (21), the importance of the strength of the acceptor of the adsorbed polycondensed molecule lay in the mobility of a single electron in the surface complex, changing according to the rule the higher the E_A value of an acceptor, i.e., the higher the mobility of an electron, the higher the one-electron donor power of the complex-type catalyst. The above was clearly supported by the results of our earlier studies of alkene hydrogeneration over catalytic systems of the EDA complex type (21). The order of the catalytic activity in the ethylation of the studied alkyl aromatics was as follows: MgO–K–perylene > MgO–K–anthracene > MgO–K–naphthalene > MgO–K. The activity of the MgO–K–naphthalene system in the ethylation of cumene was even lower than the activity of the original MgO–K system. The same activity sequence (without exception) was established for the alkylation of alkylbenzenes with propene. It is noteworthy that the order of the activity parallelled that of the one-electron donor power of the studied surfaces.

Kinetic Studies

The ethylation and propylation of ethylbenzene under normal pressure were studied over MgO–K and γ-Al$_2$O$_3$–K catalysts in several independent tests to determine the alkyl aromatic conversion and its monoalkyl derivative yield vs the time. The obtained profiles are depicted in Figs. 1 and 2.

As shown in Fig. 1, the maximum yield of the monoalkyl derivative (2-phenylbutane) produced in the alkylation of ethylbenzene with ethene appeared after 8 h for both catalytic systems under study. At longer times further alkylation of the primary reaction product resulted in a decrease in yield with steadily increasing conversion of ethylbenzene. Therefore, 8 h was chosen as the optimum reaction time

TABLE 6

Reaction Products in the Alkylation of Alkyl Aromatics with Ethene and Propene in the Presence of EDA-Type Catalysts at 323 K [Reaction Time: 5 h (Ethene), 10 h (Propene); Pressure: 1.01 MPa (Ethene), 0.71 MPa (Propene)]

|		Products (mol%)					
		Ethylation			Propylation		
Reactant	Catalyst	Monoalkyl derivative[a]	Dialkyl derivative	Others products	Monoalkyl derivative	Dialkyl derivative	Other products
Toluene	MgO–K–perylene	35.2	14.0	0.0	29.3	0.0	0.6
	MgO–K–anthracene	34.8	14.2	0.0	29.1	0.0	0.4
	MgO–K–naphthalene	17.7	0.9	0.0	20.1	0.0	0.0
	MgO–K	2.6	0.0	1.2	5.4	0.0	0.0
Ethylbenzene	MgO–K–perylene	60.7	1.8	5.4	39.0	0.4	0.0
	MgO–K–anthracene	53.9	5.6	7.6	36.5	0.0	0.0
	MgO–K–naphthalene	48.5	4.4	0.0	28.1	0.0	0.0
	MgO–K	37.5	3.1	0.0	7.2	0.0	0.0
Cumene	MgO–K–perylene	90.9	1.1	8.0	32.0	0.0	0.6
	MgO–K–anthracene	85.8	8.5	2.8	31.1	0.0	0.5
	MgO–K–naphthalene	59.9	0.5	0.0	21.6	0.0	0.0
	MgO–K	77.7	0.6	0.0	2.0	0.0	0.0

[a] The same compounds as in Table 1.
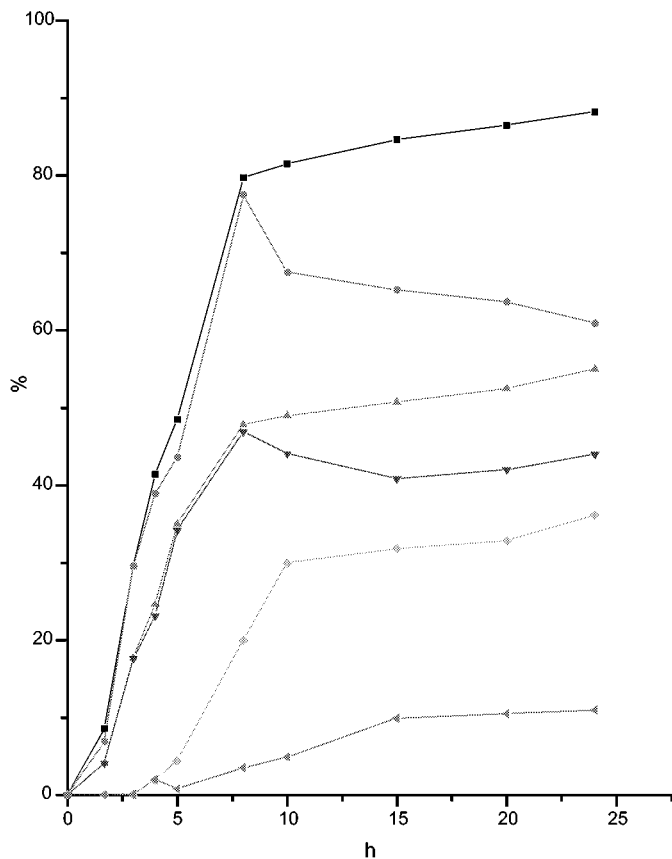
FIG. 1. The profile of ethylbenzene conversion and yields of mono- and dialkyl derivatives vs time in ethylation reaction over MgO–K and γ-Al$_2$O$_3$–K at 373 K and 0.7 MPa. ■, Conversion of ethylbenzene over MgO–K; ●, yield of 2-phenylbutane over MgO–K; ▲, conversion of ethylbenzene over γ-Al$_2$O$_3$–K; ▼, yield 2-phenylbutane over γ-Al$_2$O$_3$–K; ◆, yield of dialkyl derivatives of ethylbenzene over MgO–K; ◀, yield of dialkyl derivatives of ethylbenzene over γ-Al$_2$O$_3$–K.

from the catalytic tests carried out at 373 K under normal pressure (Table 7). The *turnover number* values were established by relating the initial rate values of the reaction to the concentration of the strongest one-electron donor centers, i.e., the F_s^+ centers on the two studied catalyst surfaces. The concentration of the F_s^+ centers, determined by ESR spectroscopy, was equal to 2.4×10^{16} spin g^{-1} for the MgO–K system and 1.5×10^{16} spin g^{-1} for the γ-Al$_2$O$_3$–K system.

Over the MgO–K catalyst, the initial reaction rate of cumene alkylation with ethene was ca. 1.5 times higher than the rate of ethylation of ethylbenzene and 14 times higher than the rate of toluene alkylation. Similar regularity was observed for the reaction carried out in the presence of the γ-Al$_2$O$_3$–K system; however, over this catalyst, the rate of ethylbenzene alkylation was only 7 times higher than the ethylation of toluene. The determined initial reaction rates of the alkylaromatic alkylation with propene were remarkably lower than those for alkylation with ethene. For the studied catalysts, the difference in reactivity between ethene and propene was in the same range: the
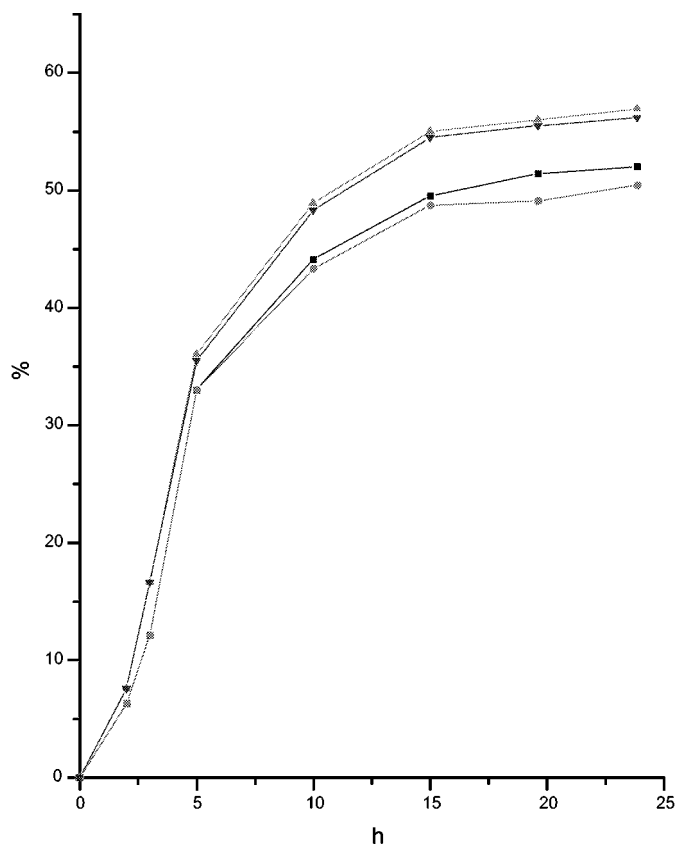
for the reactions of all the studied alkyl aromatic hydrocarbons with ethene. The comparison of the slopes of the kinetic profiles corresponding to the shortest reaction times revealed the remarkably higher activity of the MgO–K as compared with that of the γ-Al$_2$O$_3$–K system.

In the case of alkylation with propene, the yield vs time profiles the conversion of ethylbenzene and the monoalkyl derivative (2-phenylpentane) differed from those noted for the ethylation process (Fig. 2). For the two studied catalysts, the propylation reaction was much slower than the alkylation reaction with ethene, and the yield of 2-phenylpentane increased simultaneously with the conversion of the reactant over the whole range of reaction times. Ten hours was optimum from the point of view of yield and selectivity of the monoalkyl derivative. Therefore, all the propylation reactions under study were carried out for 10 h.

Reactions performed under pressure were too rapid for the precise measurement of the initial rate values of the reactions. The kinetic reaction parameters were calculated

FIG. 2. The profile ethylbenzene conversion and yield of monoalkyl derivative vs time in the propylation reaction over MgO–K and γ-Al$_2$O$_3$–K at 373 K and 1 Mpa. ▲, Conversion of ethylbenzene over MgO–K; ▼, yield of 2-phenylpentane over MgO–K; ■, conversion of ethylbenzene over γ-Al$_2$O$_3$–K; ●, yield of 2-phenylpentane over γ-Al$_2$O$_3$–K.

TABLE 7

The Kinetic Parameters in the Alkylation of Alkylbenzenes with Ethene and Propene [Temperature: 373 K, Normal Pressure]

		Ethylation		Propylation	
Reactant	Catalyst	$r_o{}^a$ (mol g^{-1} h^{-1})	Turnover number (molecule centre^{-1} s^{-1})	r_o (mol g^{-1} h^{-1})	Turnover number (molecule centre^{-1} s^{-1})
Cumene	MgO–K	5.5×10^{-3}	29	4.9×10^{-5}	5
Ethylbenzene		3.86×10^{-3}	19	6.6×10^{-5}	6
Toluene		0.39×10^{-3}	5	1.3×10^{-4}	3
Cumene	γ-Al$_2$O$_3$–K	4.1×10^{-3}	21	1.2×10^{-4}	4
Ethylbenzene		2.7×10^{-3}	12	6.6×10^{-5}	4
Toluene		0.65×10^{-3}	11	4.9×10^{-5}	1

$^a r_o$, initial reaction rate.

rate of ethylation was 6 times higher over MgO–K and 4 times higher over γ-Al$_2$O$_3$–K catalysts. As in the reaction with ethene, toluene exhibited the lowest reactivity of the studied alkylbenzenes.

The kinetics of o-, m-, and p-xylene alkylation with ethene and propene was studied at 573 K under normal pressure. The obtained results (Table 8) confirmed the different selectivity of MgO–K and γ-Al$_2$O$_3$–K catalysts in the ethylation of xylenes as observed in the pressure reactions (Table 4). Initially formed monoalkyl derivatives of the corresponding xylene underwent further ethylation over the two studied catalysts. Over magnesia containing the catalyst, the secondary product was formed by the subsequent ethylation of both CH$_3$ groups in the starting xylene, while in the case of the γ-alumina-derived catalytic system two products (1,1-diethyl derivate and 1,n (n = 1, 2, or 3) diethyl derivate) of dimethylation formed at almost identical rates (Fig. 3). The initial ethylation rates of all xylenes were insignificantly higher over the MgO–K catalyst than over the γ-Al$_2$O$_3$–K system.

Similarly, as in the experiments under pressure, the only propylation product of xylenes was the monoalkyl derivative (Fig. 4). Over the two catalysts studied, the reaction with propene proceeded at a remarkably lower rate than did the ethylation process.

The above-mentioned results of the kinetic measurements indicate that the rate of alkyl aromatic alkylation depends on the nature of the two reactants, alkylbenzene and the alkylating agent.

Electron Spin Resonance (ESR) Studies

The ESR method was used to investigate the surface adsorption states formed during the alkylation reaction on the surfaces of the MgO–K and MgO–K perylene catalysts. The ESR signals derived from the recorded paramagnetic surface states are shown in Fig. 5, and their parameters are listed in Table 9.

In the case of the MgO–K catalyst, the characteristic ESR line (g = 2.0025, ΔH_{max} = 1.665 Gs) of the F_s^+ centre was observed, while in the case of the MgO–K catalyst modified by the adsorption of perylene, the new signal appeared (g = 2.0023, ΔH_{max} = 2.724 Gs) with a slightly resolved hyperfine structure. The intensity of the new signal was close to
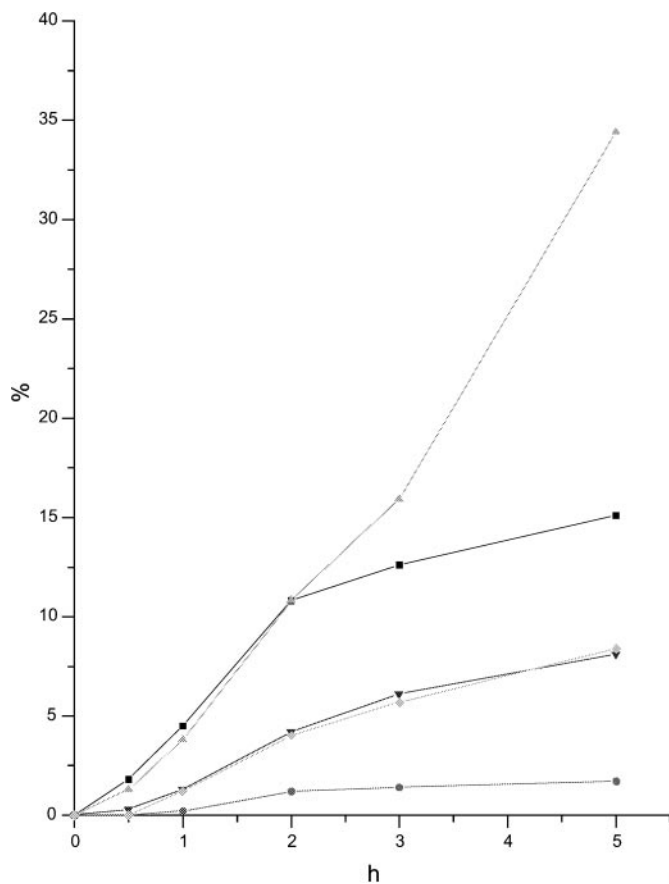

FIG. 3. The yield of mono- and dialkyl derivatives vs time profile in the ethylation of m-xylene at 373 K and normal pressure. ■, Yield of m-xylene monoalkyl derivative of one methyl group ethylation over MgO–K; ●, yield of m-xylene dialkyl derivative of one methyl group ethylation over Mgo–K; ▲, yield of m-xylene monoalkyl derivative of one methyl group ethylation over γ-Al$_2$O$_3$–K; ▼, yield of m-xylene dialkyl derivative of one methyl group ethylation over γ-Al$_2$O$_3$–K; ◆, yield of m-xylene dialkyl derivative of both methyl group ethylation over γ-Al$_2$O$_3$–K.

TABLE 8

The Kinetics of Xylene Alkylation at 373 K and Normal Pressure

			Products (mol%)					
			Ethylation				Propylation	
Time (h)	Reactants	Catalyst	A[a]	B	C	Initial reaction rate (mol g^{-1} h^{-1})	A	Initial reaction rate (mol g^{-1} h^{-1})
0	o-Xylene	MgO–K	0.0	0	0	2.05×10^{-3}	0	1.03×10^{-4}
0.5			2.5	0	0		0	
1			5.8	0.8	0		0	
2			11.0	1.7	0		0.5	
3			15.4	3.6	0		1.5	
5			18.1	4.5	0		2.0	
10			—	—	—		5.8	
24			—	—	—		7.2	
0		γ-Al$_2$O$_3$–K	0.0	0	0	1.31×10^{-3}	0	0.12×10^{-3}
0.5			1.4	0.2	0		0	
1			4.5	1.4	1.5		0	
2			11.4	3.3	2.9		0.6	
3			16.3	5.4	6.1		0.9	
5			35.0	7.7	6.9		1.3	
10			—	—	—		3.0	
24			—	—	—		4.8	
0	m-Xylene	MgO–K	0.0	0.0	0	1.48×10^{-3}	0	0.41×10^{-4}
0.5			1.8	0.0	0		0	
1			4.5	0.2	0		0	
2			10.8	1.2	0		0.2	
3			12.6	1.4	0		1.9	
5			15.1	1.7	0		2.9	
10			—	—	—		5.6	
24			—	—	—		6.8	
0		γ-Al$_2$O$_3$–K	0.0	0	0	1.31×10^{-3}	0	1.10×10^{-4}
0.5			1.3	0.3	0		0	
1			3.8	1.3	1.2		0	
2			10.8	4.2	4.0		0.5	
3			15.9	6.1	5.7		0.7	
5			34.4	8.1	8.4		1.8	
10			—	—	—		2.9	
24			—	—	—		4.4	
0	p-Xylene	MgO–K	0.0	0	0	1.84×10^{-3}	0	1.12×10^{-3}
0.5			2.2	0	0		0	
1			4.7	0.3	0		0	
2			9.8	1.2	0		0.6	
3			13.6	1.5	0		2.2	
5			15.7	1.8	0		3.1	
10			—	—	—		6.0	
24			—	—	—		7.4	
0		γ-Al$_2$O$_3$–K	0.0	0	0	1.48×10^{-3}	0	1.14×10^{-3}
0.5			1.4	0.4	0		0	
1			4.5	1.4	1.3		0	
2			11.4	4.8	3.5		0.7	
3			16.5	5.4	4.5		1.2	
5			34.2	7.9	7.5		2.5	
10			—	—	—		3.2	
24			—	—	—		4.7	

[a] Symbols as in Table 4.

that established for the F_s^+ on the primary catalyst surface.

ESR spectroscopy revealed the presence of paramagnetic surface states of a radical or ion-radical nature, formed after the adsorption of cumene, or propene, or the co-adsorption of cumene and propene on MgO–K and on the MgO–K perylene surfaces. The newly recommended signals were shifted slightly toward higher g *factor* values. The
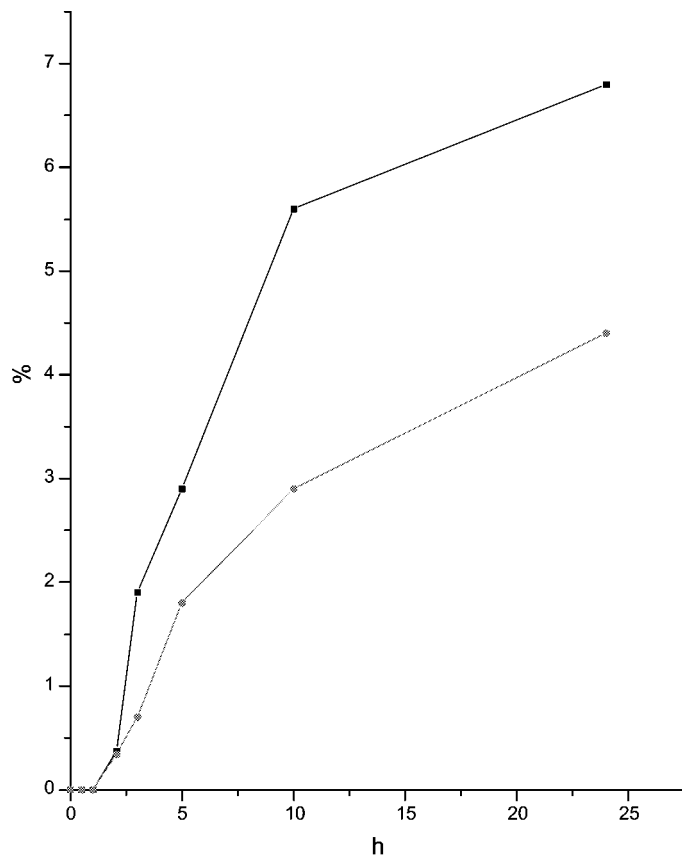
FIG. 4. The yield of 3-methylisobutylbenzene vs time profiles in *m*-xylene propylation at 373 K and normal pressure. ■, Yield of 3-methyl-isobutylbenzene over MgO–K; ●, yield of 3-methylisobutylbenzene over γ-Al$_2$O$_3$–K.

ΔH_{max} width values were also enlarged compared with the values measured for the signals of paramagnetic species on fresh catalyst surfaces (Table 9). Hyperfine resolution of the ESR derived from the adsorbed hydrocarbons was not observed. The results of the ESR spectroscopic investigations were in good agreement with our earlier observation

TABLE 9

The Parameters of ESR Signals Observed after Adsorption of Reactants on Superbasic Catalysts Surfaces

Catalyst	g_{max}	ΔH_{max} (G)	Intensity (arbitrary unit)
MgO–K	2.0025	1.665	26
MgO–K + cumene	2.0027	3.255	17
MgO–K + propene	2.0027	2.643	13
MgO–K + cumene + propene	2.0027	7.741	20
MgO–K–perylene	2.0023	2.724	26
MgO–K–perylene + cumene	2.0024	7.011	11
MgO–K–perylene + propene	2.00248	2.278	14
MgO–K–perylene + cumene +propene	2.0044	2.872	13

related to the formation of radical intermediates (16, 21, 26) from alkenes and alkyl aromatics during adsorption (26) on catalyst surfaces rich in F_s^+ centres. The presence of surface radical states after the adsorption of the reactants on the catalyst surfaces is considered to be the next step to proving the radical nature of the studied alkylation process.

Poisoning Experiments

The trapping of transient carbon-centered radicals with 2,2,5,5-tetramethylpiperidin-1-oxyl (TEMPO) leading to stable adducts has proven to be a valuable mechanistic probe for radical-induced polymerization (32–34), radical rearrangements (35–38), and homolytic dissociations (39–41).

Four reasons suggest the radical type of the studied transformations:

First, the radical type of earlier observed activity exhibited by superbasic catalysts of the metal oxide–alkali metal type in various reactions of hydrocarbons (16, 21, 23, 26).

Second, the high activity of EDA-type superbases in the ethylation and propylation of alkyloaromatic compounds studied in the present work.

Third, the presence of radical species after adsorption of alkylation reactants on the superbasic surfaces.

Finally, the characteristic order of reactivity of benzylic carbons in the alkylated molecules (tertiary > secondary > primary).

Therefore, the use of TEMPO to poison the active surface centres was designed as a convenient test to confirm the expected radical nature of the catalytic process. The ethylation and propylation reactions of cumene, ethylbenzene, and toluene were carried out over MgO–K and MgO–K perylene catalysts at 373 K under normal pressure in the presence of 1 mg of TEMPO in the reactant solutions (see Experimental).

The use of TEMPO, the strong trap of a single electron as a poison in the ethylation and propylation reactions, led to the complete deactivation of both superbasic catalysts. Ethylation and propylation of cumene, ethylbenzene, and toluene in the presence of TEMPO was not successful under the reaction conditions. Simultaneously, the ESR spectra of MgO–K and MgO–K perylene catalysts suspended in the cumene–TEMPO solution did not show the characteristic intensive signals derived from F_s^+ centres or their EDA complexes with perylene (Fig. 6). The only signals in both spectra were the those derived from 2,2,5,5-tetramethylpiperidin-1-oxyl.

Reaction of Alkyl Aromatics with Epoxyethylene

Parallel to the radical centre poisoning experiments, an experiment was conducted to exclude the eventual participation of carboanion-type intermediates in the studied alkylation reaction. With this in mind, the reaction of
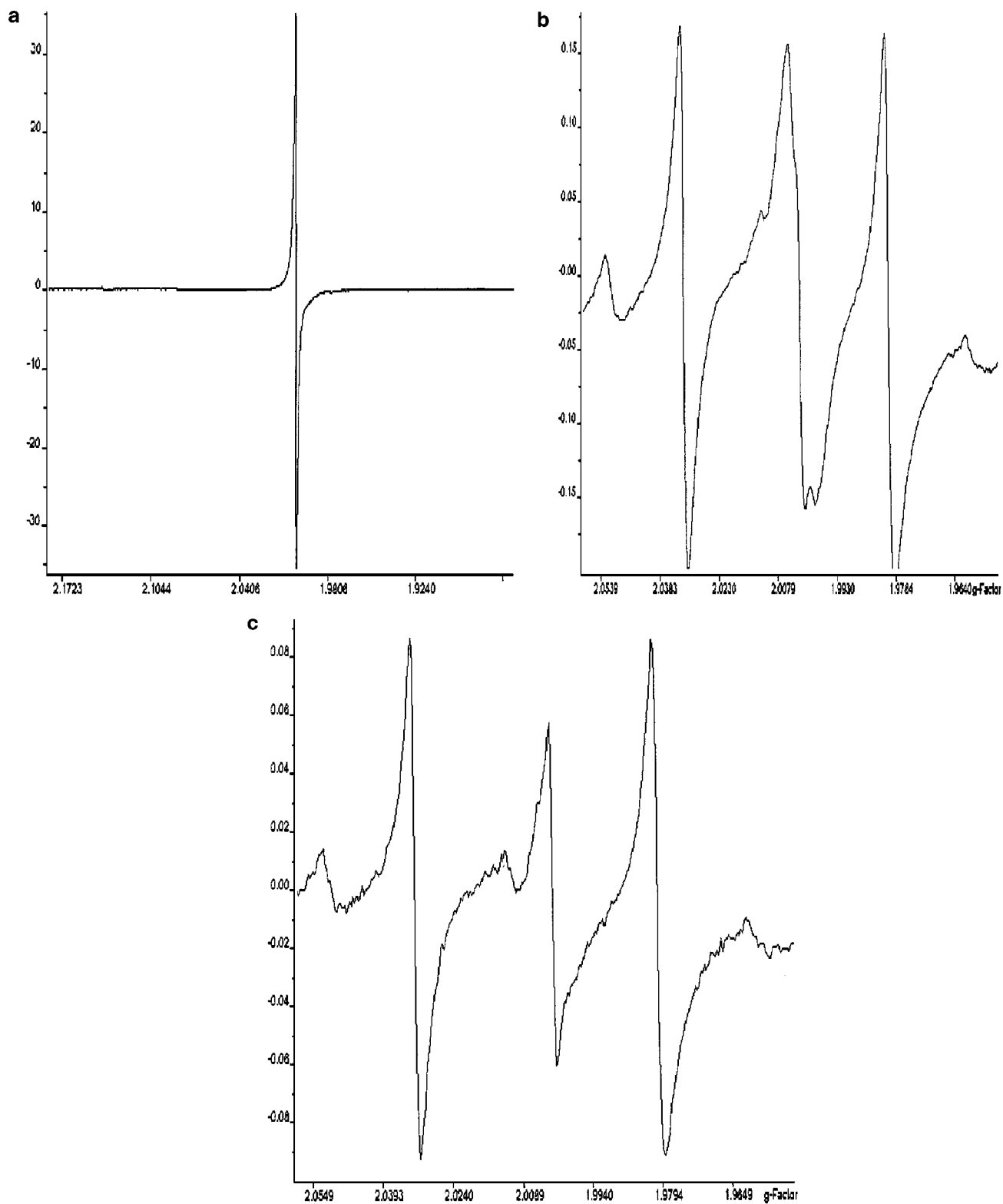
FIG. 5. ESR spectra of MgO–K catalyst and paramagnetic states of reactants adsorbed on the MgO–K surface. (a) ESR spectrum of MgO–K catalyst; (b) ESR spectrum of MgO–K catalysts after cumene adsorption; (c) ESR spectrum of MgO–K catalyst after propene adsorption.
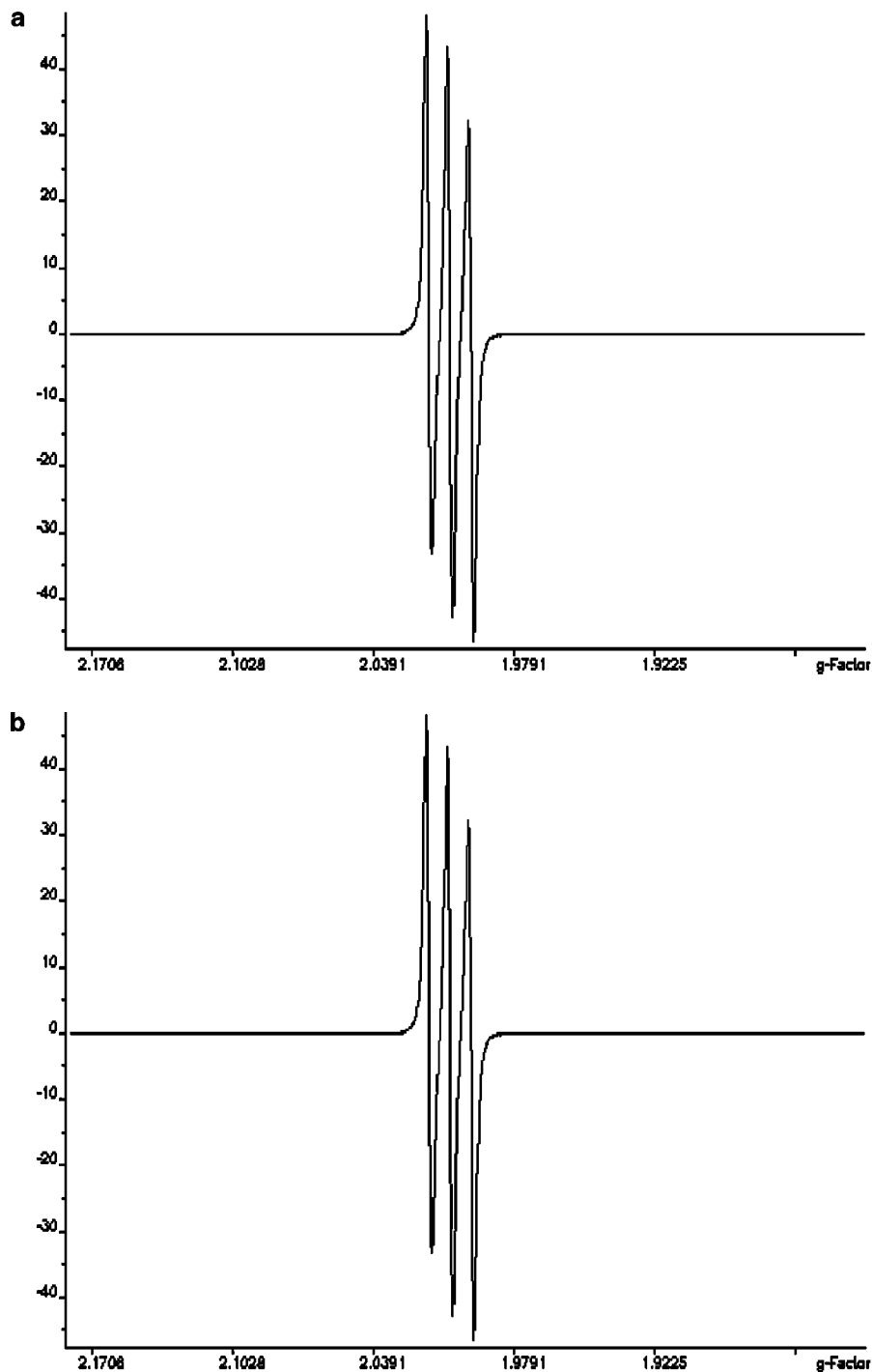
FIG. 6. ESR spectra: (a) MgO–K catalyst in cumene–TEMPO solution; (b) TEMPO in cumene solution.

cumene, ethylbenzene, and toluene was performed over the MgO–K catalyst at 373 K under normal pressure. Epoxides are well known to polymerize easily with ring opening to polyethers according to the cationic, anionic, or coordinative mechanism of polyaddition (42–46). Because of the susceptibility of anionic transformations, epoxyethylene was used as a specific trap of carboanion species. It was

assumed that carbanionic species from adsorbed alkylbenzenes, if present on the superbasic surfaces, must react with the ethylene oxide molecule to form addition products.

The contact of the alkyl aromatic with epoxyethylene under the reaction conditions did not lead to reaction involving the alkylbenzene molecules, independent of which reactant, ethylene oxide or alkylbenzene, was first introduced

into the reactor. In both cases the only reaction proceeding over the superbasic surface was polymerization of epoxide. IR spectroscopy of the MgO–K catalyst covered with polymer revealed the presence of ethylene oxide monomers as the only units in the polyaddition product chain (Fig. 7).

The results of the above experiment proved the lack of anionic-type reactivity of the alkylbenzenes adsorbed on the superbasic surface. The two-electron donor sites on the surface are probably not strong enough to produce anionic-type intermediates during adsorption of alkyl aromatic molecules. Even if such intermediates were formed on the superbasic surfaces, their reactivity would be too low to take part in an addition-type reaction as alkylation or polyaddition processes. The low reactivity of the carbanionic intermediates would result from the fact that the complex formed by the alkyl aromatic carbanion and the two-electron donor surface centre is an inseparable, coupled ion pair. Such limitation of the reactivity of carboanions have been observed for solutions (46).

Regardless of the reasons, carboanion type species do not participate in transformations of a very strong anion acceptor such as epoxyethylene. Thus, they will not be present in the reaction with weak anion acceptors as alkenes during the alkylation process.

Alkylation of Alkyl Aromatics over a Strongly Basic MgO–10%NaOH Catalyst

To prove the importance of strong one-electron donor (F_s^+) centres for the alkylation over a superbasic catalyst and to demonstrate the inactivity of strong two-electron donor centres, the ethylation of cumene, ethylbenzene, and toluene was performed over an MgO–10%NaOH catalyst at 373 K under normal pressure. Strong basic two-electron donor centres ($27 \leq H_- < 33$) were found on the surface of this catalyst, together with the coexisting one-electron donor centres, which exhibited significantly lower donor power than F_s^+ centres on the superbasic surface. The one-electron donor centres on the surface of MgO–10%NaOH were able to reduce acceptor molecules with an E_A value of at least 1.3 eV. None of the studied alkylbenzenes underwent alkylation over the MgO–10%NaOH catalyst. Furthermore, the ESR spectra recorded after reactant adsorption on the studied catalyst surface did not reveal radical or ion-radical activation of the adsorbed molecules. The obtained results support the necessity of the extremely strong one-electron donor sites participating in the reaction path. Simultaneously, they confirm that it is impossible to activate alkylation reactants ionically (i.e., involving two electrons).

Differences in the Activity and Selectivity of the Catalysts

We have demonstrated that the F_s^+ centres on the surfaces of MgO–K and γ-Al$_2$O$_3$–K systems were the source of the activity in the performed alkylation processes. These centres are similar in character (one electron in the anion

vacancy) but differ in the donor strength of the single electron. The MgO–K system is a remarkably stronger single-electron donor than the γ-Al$_2$O$_3$–K system.

Our results of the ethylation and propylation of alkylbenzenes showed that the donor power and the concentration of the F_s^+ centres were not the only factors which determined the activity (depicted by the initial reaction rate, turnover number, or alkylbenzene conversion) and selectivity of the catalytic system. In the series of reactions, a higher total conversion of alkyl aromatic hydrocarbons to their ethylation or propylation products was achieved over γ-Al$_2$O$_3$–K systems. This is the case especially in processes carried out under elevated pressure when propene was used as an alkylating agent or in the alkylation of xylenes. The latter process clearly differed in stereoregularity: over alumina-based catalysts many products of double alkylation of both methyl groups formed, in contrast to reactions over the magnesia-based catalyst. However, in reactions of alkyl aromatics with the huge stilbene molecule, the activity of the MgO–K system was considerably higher than that of the γ-Al$_2$O$_3$–K system (Table 5).

We have not found a simple explanation for the observed difference in the activity of the superbasic catalysts. In the alkylation processes investigated by us, there is no doubt that, apart from electronic factors, steric hindrance plays an important role. The catalyst obtained by potassium vaporization on γ-alumina (γ-Al$_2$O$_3$–K) had a specific surface area 3 times larger than that of the catalyst prepared by potassium vaporization on magnesia (MgO–K). Hence, F_s^+ centres were much more widely distributed on the larger γ-Al$_2$O$_3$–K surface than on MgO–K: concentration ratio per unit area equaled 8×10^{15} (MgO–K) and 0.16×10^{15} spin/m^2 (γ-Al$_2$O$_3$–K).

The arrangement and accessibility of alkyl aromatic molecules adsorbed on these surfaces for alkylating agents are not similar and probably explain the differences in the stereoregularity of the reaction. As far as the effect of pressure on the overall reaction rate is concerned (usually higher activity of γ-Al$_2$O$_3$–K in reactions carried out under elevated pressure exhibited as compared with that of MgO–K), we propose the following explanation: in the processes performed under elevated pressure, the large carrier surface acts as a reservoir for the condensed alkene molecules which in turn results in an increase in the chemisorption rate. The chemisorbed alkene species are postulated to be the reaction intermediates.

Proposal of a Reaction Mechanism

An attempt was made to propose the mechanism of alkylbenzene alkylation over superbasic catalysts of metal oxide–alkali metal type.

The factors governing the activity of the studied catalysts were analyzed, the first of which was the mode of adsorption of the reactants. ESR spectroscopy revealed the
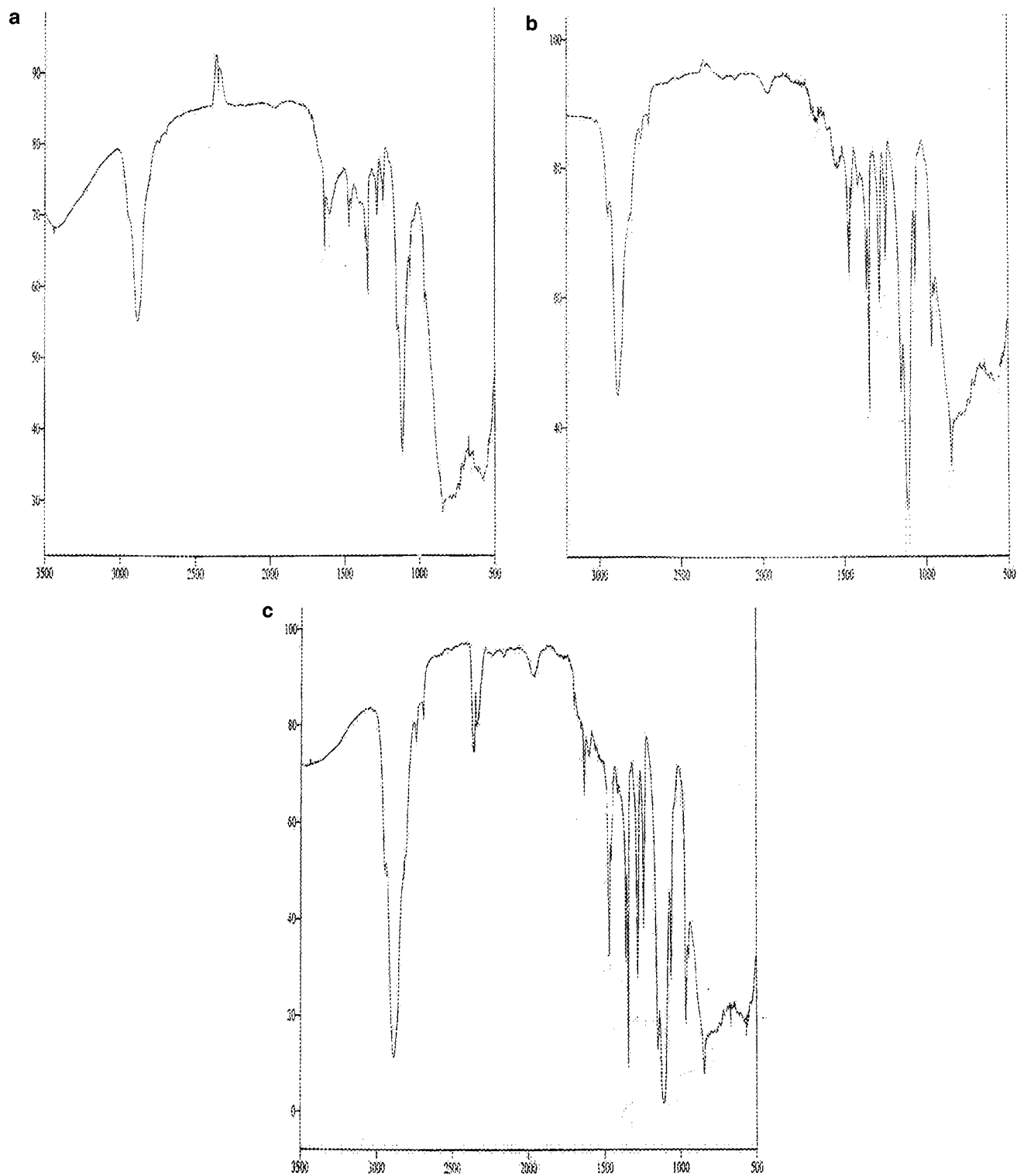
FIG. 7. IR spectra: (a) Polythelene oxide according to (48); (b) after absorption of ethylene oxide on the MgO–K surface; (c) after contacting of ethylene oxide with cumene on the MgO–K surface.

presence of paramagnetic surface states of radical or ion-radical character after adsorption of alkylation reactants on the superbasic surfaces. The appearance of an ESR signal of the radical organic species was accompanied by the disappearance of the signals derived from the intrinsic paramagnetism of the catalysts (F_s^+ centres). This proved the role of the strongest one-electron donor centres as adsorption sites of radical-type forms of alkyl aromatics and alkenes. A similar observation was made for the MgO–K perylene catalyst, the model system of the EDA complex type. The presence of a strong radical trapping agent, TEMPO, in the reaction mixture completely poisoned the alkylation process. Simultaneously, the reaction of alkyl aromatics with ethylene oxide, carried out over the studied superbasic catalysts, did not lead to addition products, which suggests the lack of anionic forms of alkylbenzene on the catalyst surface or the complete inactivity of such possible species toward such a strong anion acceptor as an epoxide molecule. Therefore, we showed that carboanion individuals probably do not exist on the surface of catalysts and were not involved in the studied reaction. This is supported by the observed lack of transformation of reactants over MgO–10%NaOH, a strongly basic but moderately strong catalyst acting as a one-electron donor.

The structure of the molecules of the reactants was also an important factor for the reaction path. As pointed out above, the order of the reactivity of the studied alkyl aromatic hydrocarbons was cumene > ethylbenzene > toluene. This sequence corresponded to the sequence of stability of the corresponding benzyl radicals and, which is very important, was the reverse of the order of stability of hypothetically formed benzylic carboanions. Hence, the activation of the alkylated alkylbenzenes was considered to proceed in a radical manner. Such a conclusion fits well with the concept of an activation step in dehydrogenation of alkyl aromatics over superbasic catalysts (26). This reaction involved the formation of a benzylic radical as a result of the abstraction of a hydrogen atom by a one-electron donor centre:
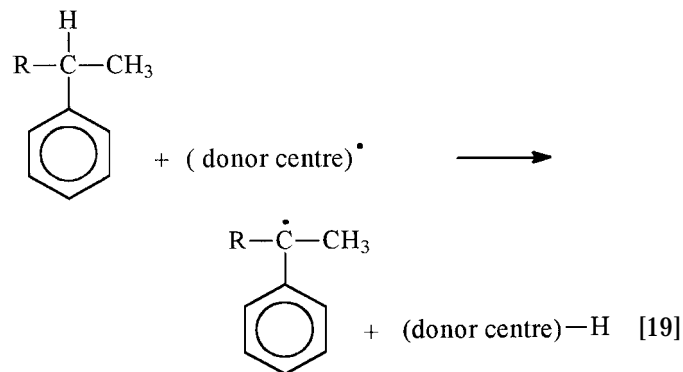

The activation of ethene and propene would occur via ion-radical or radical intermediates. The formation of anion

radical types of alkenes on the F_s^+ centres of superbasic catalysts has been demonstrated (15). This process is illustrated below:

$$(\text{donor centre})^{\bullet} + H_2C{=}CH_2 \longrightarrow (\text{donor centre})^+ H_2C{=}CH_2^{\bullet-} \quad [20]$$
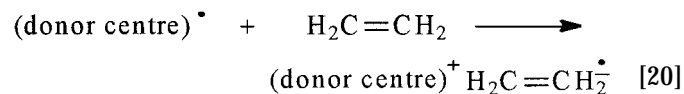
It is proposed that the radical of the alkylbenzene, which originated in the reaction [19], would, in a next step, join with the alkene anion radical to lead to the formation of a terminal radical of alkylated hydrocarbon, thus recovering the one-electron donor centre:
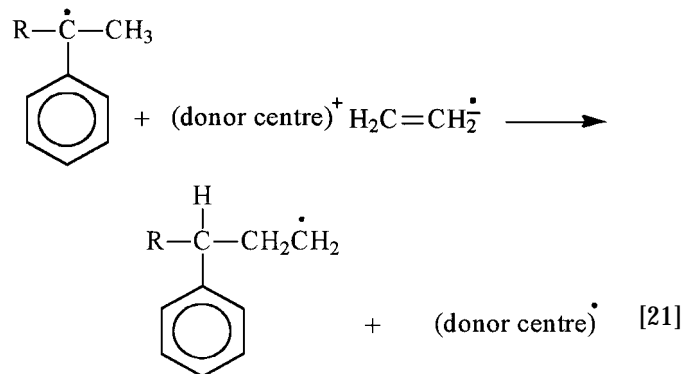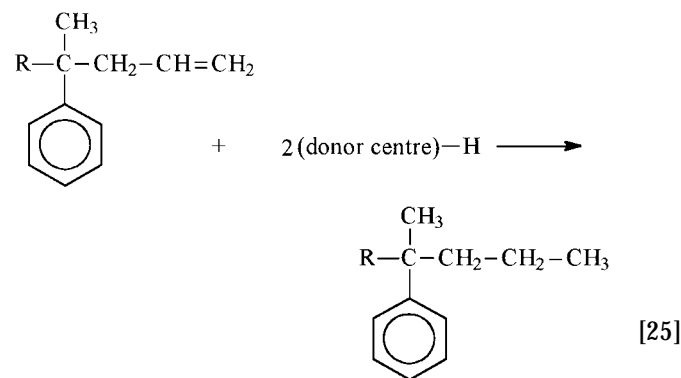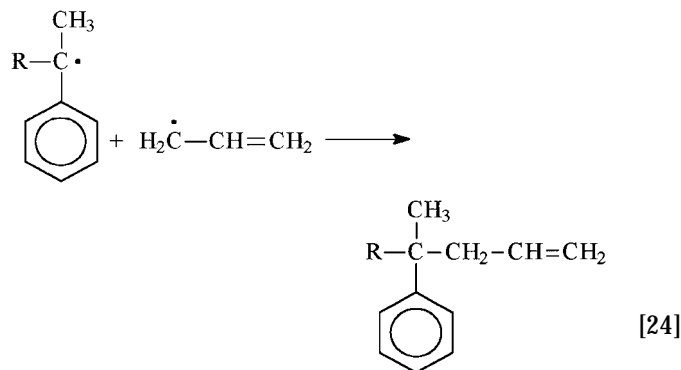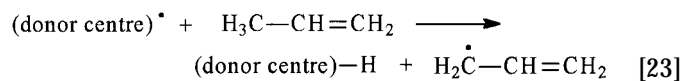

The reaction of the final form of the hydrocarbon radicals with the hydrogen atom bound to the donor centre (Eq. [22]) terminates the process and gives the products of alkylation and reproduces the active site:
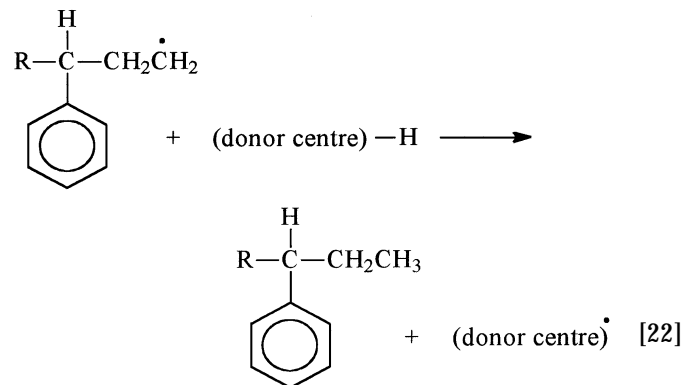
Because of the similarity of the ESR signals of anion radicals to those of radicals of the corresponding alkenes, we cannot offer clear proof of the lack of participation of the said radicals in the alkylation path.

Such individuals are more likely to be involved in the reaction of alkylbenzenes with propene than with ethene. The former alkene can be transformed into the relatively stable allyl radical. Nevertheless, replacing the alkene anion radical with the corresponding alkene radical in the proposal of the reaction pathway would require taking into consideration an additional stage in the process—the reduction of alkenylbenzene:

$$(\text{donor centre})^{\bullet} + H_3C-CH=CH_2 \longrightarrow$$
$$(\text{donor centre})-H + H_2\overset{\bullet}{C}-CH=CH_2 \quad [23]$$

$$\begin{array}{c} CH_3 \\ | \\ R-C\cdot \\ | \\ \text{(phenyl)} \end{array} + H_2\overset{\bullet}{C}-CH=CH_2 \longrightarrow$$

$$\begin{array}{c} CH_3 \\ | \\ R-C-CH_2-CH=CH_2 \\ | \\ \text{(phenyl)} \end{array} \quad [24]$$

$$\begin{array}{c} CH_3 \\ | \\ R-C-CH_2-CH=CH_2 \\ | \\ \text{(phenyl)} \end{array} + 2(\text{donor centre})-H \longrightarrow$$

$$\begin{array}{c} CH_3 \\ | \\ R-C-CH_2-CH_2-CH_3 \\ | \\ \text{(phenyl)} \end{array} \quad [25]$$

It should be emphasized that no traces of alkenylbenzenes with an unsaturated side chain were detected in the reaction mixture, which lowers the probability of the *alkenyl radical* pathway of the reaction.

CONCLUSIONS

i. The solid superbasic systems, MgO–K and γ-Al$_2$O$_3$–K, as well as the model systems of the EDA complex type are active catalysts of side-chain alkylation in alkylbenzenes using ethene, propene, or diphenylethene as alkylating agents.

ii. The reaction chemoselectivity (mono- or difunctionalization of alkylbenzenes) depends on the nature of the alkyl aromatic reactant and alkylating alkene, on the reaction temperature, and on the used catalyst.

iii. The established reactivity sequence of the studied alkylbenzenes, the very high activity exhibited by model catalysts with extremely strong electron donor properties, the appearance of paramagnetic surface species during adsorption of alkylation reactants on the surfaces of the studied catalysts evidenced by ESR, the complete lack of activity shown by catalysts poisoned with TEMPO, and the lack of reactivity of the adsorbed alkyl aromatics toward ethylene oxide prove the decisive role played by the strong one-electron donor centres (F_s^+ sites) in the studied reactions.

iv. The radical or ion-radical mode of alkylbenzene and alkene adsorption on the studied catalyst surfaces and the lack of influence of the adsorption sequence of the reactants on the composition of the alkylation products suggest that alkylbenzenes and alkenes adsorb on independent surface centres in radical and/or ion-radical (less probably) forms, which determine the reaction pathway.

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