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KINETIC ISOTOPE EFFECT IN TRANS-ALKYLATION WITH ETHYLBENEZENE

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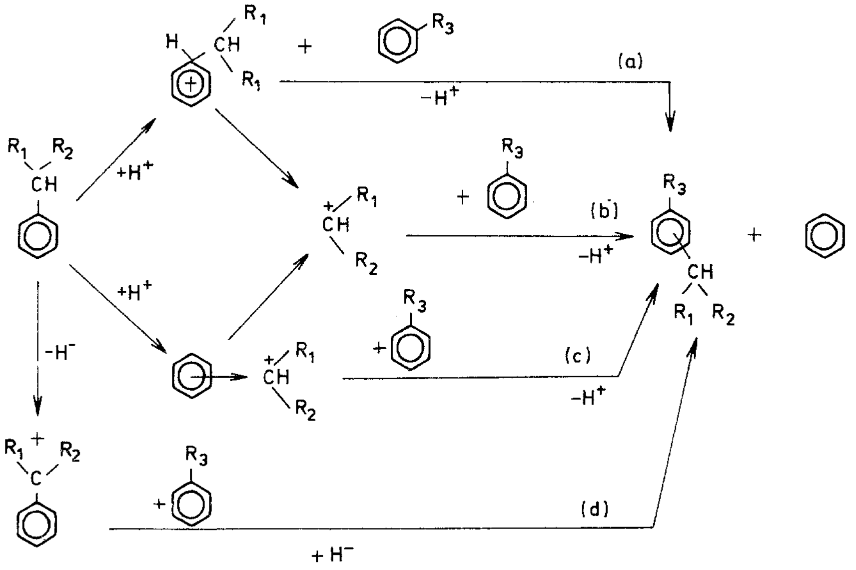
Kinetic isotope effect (KIE) measurements in the trans-alkylation of toluene and benzene with ethylbenzene in hexane in the presence of $AlBr_3$ at 313 K indicate that deuterium in the toluene methyl group causes a small inverse KIE characteristic for a π-complex transiton state. The small direct KIE found for the reaction with $C_2D_5C_6H_5$ does not agree with a mechanism involving alkyl- and α-phenylalkyl cations.

Измерен кинетический изотопный эффект (КИЭФ) в транс-алкилировании толуола и бензола этилбензолом в гексане в присутствии $AlBr_3$ при 313 К. Показано, что дейтерий в метильной группе талуола вызывает небольшой обратный КИЭФ, что свидетельствует о протекании реакции через π-комплексное переходное состояниер В реакции с этильензолом $C_2D_5C_6H_5$ обнаружен небольшой нормальный КИЭФ, что не согласуется с протеканием реакции через алкил- и α-фенилалкилкатионы.

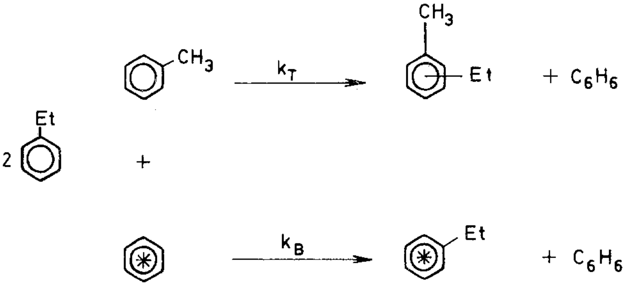
Although trans-alkylation has been extensively used as a process to obtain supplementary quantities of alkylaromatic compounds, its mechanism is still open to debate. As illustrated by the reaction scheme on top of p. 412, the reaction probably occurs via the following alternative routes: (a) a bimolecular mechanism involving a σ-complex transition state /1/; (b) a dealkylation-alkylation mechanism, the alkyl group being detached in the form of an alkyl cation /2/; (c) a bimolecular mechanism involving a π-complex transition state /3/; (d) a mechanism via hydride ion abstraction from the α-carbon atom of the alkylbenzene to form an α-phenylalkyl cation /4/.

The available literature lacks KIE data for trans-alkylation. This was the aim of the present study, together with further refinement of the reaction mechanism on their basis.



(R_1, R_3: alkyl (H); R_2: alkyl)

For this purpose the ethylbenzene-benzene-1-6^{14}C-toluene system was used. $AlBr_3$ and hexane served as catalyst and solvent, respectively.



Experimental data are listed in Table 1.

As is seen from Table 1 (exps 1, 2), the introduction of deuterium into the methyl group of toluene leads to a small inverse KIE, apparently due to the higher rate constant of the electrophilic attack on toluene-α-D_3 compared with undeuterated toluene. This is stipulated by the higher reactivity of toluene-α-D_3 due to its increased basicity /7/. The results indicate /8, 9/ that the trans-alkyla-

Table 1
Trans-alkylation of toluene and benezene-1-6^{14}C with ethylbenzene
in hexane in the presence of $AlBr_3$ at 313 K
(mole ratio ethylbenzene : toluene : benzene-1-6^{14}C : $AlBr_3$: hexane = 20 : 40 : 40 : 1 : 60)*

No.	Deuterated initial compound	$k_T^{**} \times 10^2$	$k_B^{**} \times 10^2$	k_T/k_B	k_H/k_D	
					toluene	benzene
1	–	1.05	0.98	1.07	–	–
2	$CD_3C_6H_5$	1.20	0.99	1.22	0.88	–
3	$C_2D_5C_6H_5$	0.86	0.73	1.18	1.20	1.30

Notes:

*Reaction was studied up to 20–30% conversion of ethylbenzene. By-products were not formed. Experimental, analysis and calculation procedures were described elsewhere /5, 6/. Absence of H–D exchange was established by NMR spectroscopy.

**k_T/k_B are given in l/mol h.

tion proceeds through a π-complex transition state and hence does not agree with mechanism (a). Our conclusion is also confirmed by the very low values of substrate selectivity (k_T/k_B) in this reaction (Table 1) characteristic for the π-complex transition state /8/.

The comparison of the data obtained in experiments 1 and 3 (Table 1) indicates that the deuterium in the ethylbenzene alkyl group does not exert any significant influence on the trans-alkylation rate constants of either toluene (k_T) and benzene (k_B). The absence of a direct primary KIE ($k_H/k_D > 2$) indicates that the rate-determining step is not associated with the hydride ion abstaction as would be predicted by mechanism (d). According to the first order of the reaction with respect to reagent and substrates, we suppose that the rate-determining step is the interaction between the α-phenylethyl cation and benzene (toluene). It has been shown previously /10/ for diphenylethane-1,1 benzene-1-6^{14}C that $k_H/k_D = 0.55$–0.2, which can be attributed to changes in the configuration of the reaction center from sp^2 to sp^3 in the transition state /11, 12/. The case is similar for the reaction proceeding through the alkyl cation detachment. However, there is no inverse KIE (Table 1) and hence, either the trans-alkylation does not follow mechanisms (b) or (d), or their contribution to the reaction is very small.

The existence of direct KIE (exp. 3, which due to its low (~ 20–30%) value must be secondary, can be attributed to the increased basicity of ethylbenzene after deuterium incorporation into the alkyl group and hence, the decreased electrophilic reactivity substantiated by a higher k_T/k_B (Table 1).

Thus, the results indicate that the reaction follows mechanism (c).

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