Homogeneous Platinum(II)-catalysed Hydrogen Exchange in the Alkylbenzenes: Relationship to Simple Alkane Exchange

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Summary Deuteriation in the side-chain of the long-chain alkylbenzenes using a homogeneous platinum(II) catalyst occurs predominantly at the α- and terminal carbon positions, isotope incorporation progressively decreasing from n-butyl- to n-nonyl-benzenes; in the side-chain of 1,1-dimethylpropylbenzene exchange is exclusively at the γ-position.

THE deuteriation of methane and ethane has been reported,[1] employing a homogeneous platinum(II) catalyst previously discovered for aromatic compounds.[2] The work has been extended to other alkanes.[3] Independently, we have found that hydrogen will exchange in a unique manner in the side-chain of the alkylbenzenes, particularly the long-chain compounds to nonylbenzene, using the same platinum(II) catalyst. These results are important since there could be similarities between the simple alkane exchange[1,3] (which is usually performed in the presence of an aromatic to stabilize the catalyst) and deuteriation in the long chain of the alkylbenzenes with consequential common implications in the reaction mechanism.

The data (Table 1) show that, in the straight-chain

TABLE 1

Exchange of alkylbenzenes with homogeneous platinum(II) *catalyst*[a]

Compound	D found (%)	No. of D per molecule	Deuterium orientation (% of H + D)				
			Aromatic (%)	α-CH_2 (%)	Other $-CH_2$	Terminal $-CH_3$	Methine
Toluene	43	3·46	42·3	—	—	44·3	—
Ethylbenzene	31	3·13	44·6	22·0	—	15·3	—
n-Propylbenzene	25	3·02	44·6	11·5	7·5	11·7	—
n-Butylbenzene	23	3·22	47·2	15·0	2·2	13·7	—
n-Pentylbenzene	18	2·89	44·8	12·0	1·6	10·7	—
n-Hexylbenzene[b]	15	2·74	44·0	—	—	—	—
n-Heptylbenzene	12	2·43	36·0	5·5	2·3	9·6	—
n-Nonylbenzene	8	1·92	29·9	2·5	2·5	1·0	—
Isopropylbenzene	22	2·61	46·0	—	—	3·9	8·0
s-Butylbenzene	21	2·88	—	—	—	—	—
t-Butylbenzene	16	2·29	40·6	—	—	2·7	—
1,1-Dimethylpropylbenzene ..	15	2·43	—	—	—	—	—
Cyclohexylbenzene	15	2·78	47·7	—	2·5	—	15·0

[a] Sample composition; Alkylbenzene (0·5 ml) with catalyst solution (5 ml) containing CH_3CO_2D (2 mole), D_2O (1 mole), DCl ($2{\cdot}6 \times 10^{-3}$ mole) and Na_2PtCl_4 ($2{\cdot}6 \times 10^{-3}$ mole). Reaction for 5 h at 120° in sealed evacuated ampoules. Analysis by mass spectrometry and n.m.r. as previoulsy.[2]

[b] Some metal precipitation occurred in this sample.

TABLE 2

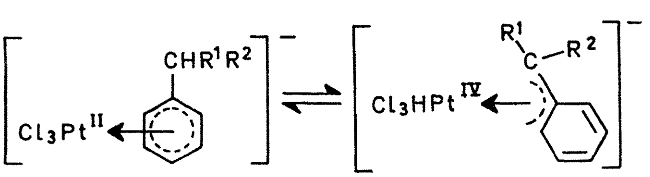
1,1-*Dimethylpropylbenzene.* 4 *exchange cycles, each* 5 *h at* 120°. *Sample composition as in Table* 1

Deuterium Orientation		Ph	— $\overset{CH_3}{\underset{CH_3}{C}}$ —	CH_2 —	CH_3
	No. D	2·539	0·105	0·047	0·726
Deuterium Distribution	%	50·8	1·7	2·3	24·2

Species:	D_0	D_1	D_2	D_3	D_4	D_5	D_6	D_7	D_8	D_9	D_{10}
%	0·3	3·2	16·7	33·9	27·9	10·5	4·0	1·7	1·0	0·7	0·1

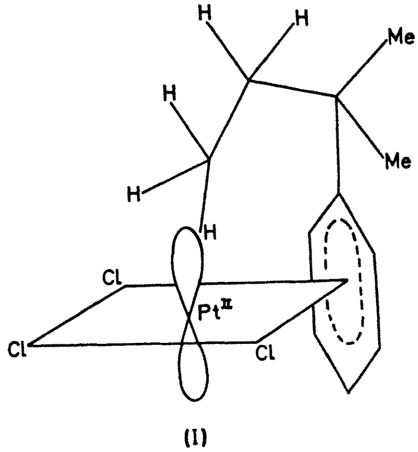
alkylbenzenes, there is a progressive decrease in overall exchange from n-butyl to n-nonyl derivatives. With all compounds, deuteriation in the side-chain occurs predominantly at the α- and terminal carbon atoms. There is also a progressive decrease in isotope incorporation at both α- and terminal positions with increasing chain length. The pronounced activity at the terminal position becomes evident with n-propylbenzene. Exchange in the tertiary butyl group is very slow compared with deuteriation in n-butyl and isopropyl groups. With 1,1-dimethylpropylbenzene (Table 2) exchange in the side-chain occurs almost exclusively at the γ-position even after four equilibrations.

Mechanistically, the alkylbenzene may be complexed to the catalyst through the aromatic ring as previously suggested,[2,4] exchange at the α-position (whether in toluene or nonylbenzene) occurring *via* reversible π-arene to π-allylic rearrangements:



R^1R^2 = Alkyl or H

Accentuated exchange of the terminal positions and low deuteriation in intermediate positions of the side-chain can then be explained by α–β rearrangements to the terminal carbon followed by multiple processes at that position.



(I)

With 1,1-dimethylpropylbenzene the tertiary carbon prevents α–β rearrangements, thus a more plausible mechanism involves formation of intermediate complexes such as species (I) followed by hydrogen abstraction from the terminal carbon. Analogous hydrogen abstractions by transition metals from triarylphosphine ligands are known.[5] Scale models show that hydrogen atoms on γ-carbon atoms are the first in the series which can interact in this way and n-propylbenzene is the first compound where accentuated terminal activity is observed. Further, analogous abstraction of methylene hydrogen atoms is sterically unfavourable. The progressive decrease in the deuteriation of terminal positions out to n-nonylbenzene can then be attributed to an entropy effect.

The fact that exchange occurs in simple alkanes beneficially in the presence of benzene[3] with this same catalyst using perchloric acid suggests that the alkylbenzenes may also be considered as phenyl substituted alkanes such that the ring protons and the terminal positions react independently, possibly by different mechanisms. There is a similarity in isotope orientation between the alkanes and the side-chains of the alkylbenzenes. Also substituent effects have been observed in these exchange reactions.[6] This interpretation would require co-ordination of the alkylbenzenes *via* a molecular orbital localized on the alkyl group. At present, we favour mechanisms involving preferential co-ordination with the more strongly interacting aromatic ring.

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