Homogeneous and ***Heterogeneous*** Metal-catalysed Isotopic Hydrogen Exchange in Alkylbenzenes. Mechanism of Alkyl Deuteriation in Ethylbenzene

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Summary Homogeneous and heterogeneous metal-catalysed isotopic hydrogen exchange in the alkyl group of [β-^{14}C]ethylbenzene shows that predominant deuteriation does not occur *via* previously suggested mechanisms involving reversible dealkylation or carbonium ion intermediates: instead a π-allylic process is suggested.

IN the recently reported[1,2] homogeneous platinum-catalysed exchange of aromatic compounds with heavy water, isotope incorporation in the alkylbenzenes occurs in both ring and side-chain positions. From preliminary studies[2] with ethylbenzene, the α- and β-positions exchange at almost equal rates. Mechanisms considered[2] to account for this orientation include symmetric intermediates involving (i) reversible dealkylation (Equation 1) and (ii) non-classical carbonium ions such as the π-bonded ethylene phenonium ion (I).

TABLE 1

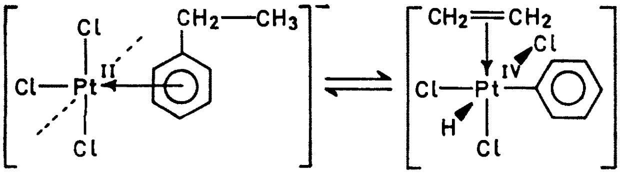
[β-^{14}C]*Ethylbenzene exchange in* D_2O *with homogeneous and heterogeneous catalysts*

		Temp	Reaction time	% D	% D	Mass spectrometric deuterium distribution										
Run	Catalyst	(°)	(h)	(theor.)	(exp.)	$^2H_0$	$^2H_1$	$^2H_2$	$^2H_3$	$^2H_4$	$^2H_5$	$^2H_6$	$^2H_7$	$^2H_8$	$^2H_9$	$^2H_{10}$
1	Homogeneous platinum[a]	80	100	79·0	33·6	1·0	5·7	19·2	32·2	22·8	12·6	4·9	1·4	0·2		
2	Homogeneous platinum[a]	100	22	79·0	28·8	7·6	4·1	25·7	33·4	18·5	7·6	2·6	0·5			
3	Homogeneous platinum[a,c]	120	6·5	79·0	21·8	17·4	16·2	22·6	26·8	10·9	4·6	1·4	0·1			
4	Heterogeneous platinum[b]	150	48	57·2	46·9	0·1	2·2	7·8	15·8	21·0	21·2	16·5	9·8	4·5	1·0	0·1
5	Heterogeneous nickel[b]	150	48	57·2	26·0	3·4	15·9	29·5	28·5	15·7	5·4	1·4	0·2			

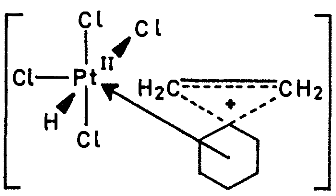
[a] Sample contained ethylbenzene (0·5 ml), 67 mole % $MeCO_2D$ in D_2O (5·0 ml), Na_2PtCl_4 (0·02M), and DCl (0·02M).

[b] Sample contained metal (30 mg), D_2O (0·5 ml), and ethylbenzene (0·5 ml).

[c] A small amount of platinum metal precipitated in this sample; however, under the conditions used for the homogeneous runs, this precipitated platinum metal is not an active heterogeneous catalyst for deuterium exchange.



(1)



(I)

The validity of these mechanisms has now been investigated using ethylbenzene specifically labelled with carbon-14 on the β-carbon atom. If either mechanism is relevant, significant scrambling of isotope to the adjacent α-position should be observed during homogeneous metal-catalysed isotope exchange. This can be readily observed by oxidising the exchanged [β-^{14}C]ethylbenzene to benzoic acid and counting the residual carbon-14 activity in this compound. These homogeneous platinum results have also been compared with analogous exchange data from the corresponding heterogeneous system using platinum and nickel as catalysts, since both metals promote extensive side-chain deuteriation. This comparison is valuable because of the accumulating evidence which indicates that homogeneous and heterogeneous metal catalysis, particularly in isotope exchange, are related, presumably through π-complex formation.[2]

In addition to the implications of the present work in fundamental catalytic theory, the data are important for the general deuterium and tritium labelling of the alkylbenzenes. The occurrence of reversible dealkylation would severely limit the use of the homogeneous technique, particularly for tritiation,[3] since chemical decomposition as a consequence of dealkylation could yield significant quantities of impurities which would seriously prejudice

TABLE 2

Orientation of deuterium[a] *in labelled ethylbenzenes*

Run[b]	% D Total	% D[c] In ring	% D[c] In α-position	% D[c] In β-position
1	33·6	46·5	23·7	18·2
2	28·8	45·2	22·5	18·3
3	21·8	40·0	21·5	16·6
4	46·9	51·7	52·5	27·0
5	26·0	9·5	51·0	39·6

[a] Deuterium expressed as percentage of total hydrogen at each position.

[b] Run number from Table 1.

[c] Orientation of deuterium determined by n.m.r.

ultimate radiochemical purification of the parent compound.

The results (Tables 1—3) showth at no carbon-14 scrambling occurs during the homogeneous metal-catalysed exchange of [β-^{14}C]ethylbenzene, thus eliminating the above mechanisms and leaving the alternative already suggested involving π-allylic species.[2] These conclusions are confirmed by quantitative homogeneous exchange work with n-propyl- and isopropyl-benzenes. In earlier preliminary studies,[2] some dealkylation did occur, with these compounds during homogeneous deuteriation but this was accompanied by precipitation of platinum metal, thus the dealkylation could have been heterogeneously catalysed.[2] In more recent experiments where temperature and acidity of reaction were carefully controlled (Table 1, Runs 1 and 2) conditions for homogeneous metal-catalysed exchange in the propylbenzenes have been obtained where no platinum metal precipitates and there is insignificant dealkylation. Lack of dealkylation is consistent with the above carbon-14 scrambling studies and ensuring mechanistic interpretation.

TABLE 3

Radiometric analysis of [^{14}C]*benzoic acids from deuteriated* [^{14}C]-*ethylbenzenes in Table* 1

Source of benzoic acid	Specific activity[b] (μCi/mmole) $\times$ 10^6
[β-^{14}C]Ethylbenzene[a]	7·6[c]
Run 1	5·7
Run 2	3·5
Run 3	5·9
Run 4	6·3
Run 5	3·9

[a] Specific activity of [β-^{14}C]ethylbenzene was $9{\cdot}3 \times 10^{-3}$ μCi/mmole.

[b] Specific activity required for complete randomisation of carbon-14 is $4{\cdot}65 \times 10^{-3}$ μCi/mmole.

[c] The activity in this sample indicates that the [β-^{14}C]ethylbenzene prepared contained a very small amount of carbon-14 in the α-position. Alternatively the activity may be due to a trace of phenylacetic acid formed during the oxidation step.

In the heterogeneous platinum and nickel catalysed exchange of [β-^{14}C]ethylbenzene, no scrambling of carbon-14 is observed (Table 3) thus dealkylation is also eliminated as a possible mechanism for isotope incorporation in this system and a process involving adsorbed π-allylic intermediates[4,5] appears to occur similar to that suggested above for the homogeneous system. In the heterogeneous runs, ethylbenzene deuteriated more extensively in the α-position of the side-chain than in the corresponding β-position especially when compared with the homogeneous analogue (Table 2). This result would suggest that an additional surface mechanism is operative only in the heterogeneous system and plausibly is the abstraction process suggested by Garnett and Sollich-Baumgartner.[2,6,7]

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