Application of ^{3}H N.M.R. Spectroscopy to Metal Catalysis. Orientation of Incorporated Isotope in Halogenated Benzenes and Alkylbenzenes Tritiated by Heterogeneous Platinum Exchange

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Summary ^{3}H N.m.r. spectroscopy is shown to be a powerful tool for the mechanistic study of metal catalysed reactions; using the technique, data obtained from a re-investigation of platinum catalysed isotopic hydrogen exchange correct previously reported anomalous *ortho* effects in the halogenated benzenes and also, with the alkylbenzenes, provide additional orientation information which supports the predominant participation of a π-dissociative process for the heterogeneous system; steric and not electronic effects appear to determine the pattern for degree of exchange.

THE relationship between homogeneous and heterogeneous metal catalysis is mechanistically important since recent work has shown that the manner of bond formation involving adsorbed molecules at a metal surface and the chemistry of inorganic co-ordination complexes are closely related.[1,2] In one of the simplest catalytic processes, *viz.* isotope exchange, evidence to support this relationship comes in part from a comparison of the orientation of isotope in the labelled molecule.

Deuterium has been the preferred isotope for these reactions since instrumental techniques such as n.m.r., e.s.r., and mass spectrometry can be used to estimate directly the isotope incorporation.[3] However, for many labelled compounds, particularly aromatics, quantitative estimation of deuteriation at particular positions by these earlier methods is severely limited since relatively high (*ca.* 20%) isotope incorporation is generally required for satisfactory analysis. Furthermore, *ortho*, *meta*, and *para* peaks in the ^{1}H n.m.r. spectra of molecules such as toluene cannot be easily resolved.

The additional difficulty, unique to heterogeneous catalytic systems, is the presence of a scrambling reaction[4] which can be appreciable at the deuteriation level needed for isotope orientation analysis by ^{1}H n.m.r. spectroscopy. This scrambling process leads to enhanced *ortho* isotope incorporation and can result in apparent anomalies when comparing data for the exchange of certain monosubstituted benzenes under homogeneous and heterogeneous conditions. For this purpose it is necessary to be able to observe orientation of exchange in the heterogeneous system at low levels of isotope incorporation, *i.e.* before the onset of the scrambling reaction.

We now report the unique value of ^{3}H n.m.r. spectroscopy[5,6] for this purpose. The results (Table) demonstrate that in the heterogeneous platinum catalysed exchange of both halogenated benzenes and alkylbenzenes, tritiation at the *ortho* positions is severely hindered. In addition, the halogenated benzene data show that as the size of the halogen increases, the *ortho* : *meta* ratio for isotope incorporation decreases. These results contrast with earlier heterogeneous data where the reverse was observed.[7] At that time, i.r. spectroscopy was the only method available for these analyses. However, it is now known that the i.r. procedure is unreliable because of the problems associated with the presence of multiple deuteriated species and the difficulty of assigning one single band in the spectrum to represent quantitatively the isotope at a particular position. ^{3}H N.m.r. spectroscopy does not suffer from these limitations and can analyse accurately total isotope incorporated at each position at low isotopic levels. In the earlier halogenated benzene results,[7] the observed *ortho* : *meta* ratio was attributed to electronic effects[7,8] and was related to the electronegativity of the halogen substituent, whereas the overall *ortho* deactivation was explained by steric considerations. The current ^{3}H n.m.r. data show that the conclusion based on electronic effects was incorrect and both the *ortho* : *meta* ratios and overall *ortho* deactivation are predominantly due to steric effects. The present results of ^{3}H n.m.r. spectroscopy of halogenated benzenes are also consistent with previous[9] and current heterogeneous alkylbenzene data where the *ortho* : *meta* ratio for deuteriation decreases with increasing size of alkyl substituent.

Table. Orientation of tritium in halogenated and alkyl benzenes using heterogeneous platinum exchange[a]

Compound	% of tritium in compound per site[b] *ortho*	*meta*	*para*	Alkyl
Fluorobenzene	8·3	29	25	
Chlorobenzene	4·0	30	32	
Bromobenzene	<2	33	33	
Toluene	9·8	15	18	CH_3, 11
Isopropylbenzene	5·5	13	13	CH_3, 7; CH, 11
Cyclohexylbenzene	4·1	19	21	CH_2, 1; CH, 25
Triphenylmethane	2·3	9·5	9·7	CH, <1

[a] Reaction conditions: unsupported platinum (0·1 g) obtained by sodium borohydride reduction (ref. 4) of PtO_2, organic compound (0·1 ml), and tritiated water (0·1 ml, 5 Ci ml^{-1}), heated to 100—130 °C for appropriate time in sealed ampoule (5 ml). [b] Total activities of products typically 30—100 Ci mol^{-1}. Assignment of n.m.r. peaks confirmed by comparison with compounds specifically labelled by other techniques (M. A. Long, J. L. Garnett, and R. F. W. Vining, *J.C.S. Perkin II*, 1975, 1298).

Data for the alkylbenzenes (Table) provide important information about the magnitude of the steric effect for exchange in the side chain. Thus the methylene groups in cyclohexylbenzene show little isotope incorporation indicating that the molecule is preferentially adsorbed through the ring, and must be strongly tilted during this π-complex interaction such that aromatic and allylic positions can exchange preferentially. In triphenylmethane, even the allylic position is strongly hindered in adsorption by the three aromatic rings and tritiation by a π-allylic mechanism is precluded.

The final significant feature of the data in the Table is that for the first time it is unequivocally shown that the rate of isotope incorporation is approximately the same in the *meta* as in the *para* positions for all seven monosubstituted benzenes exchanged over heterogeneous platinum. This conclusion had previously been inferred qualitatively from indirect mass spectral evidence[1] and the results thus support the proposal that the participation of a π-dissociative process in the heterogeneous exchange mechanism is predominant.

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