Differences Between Homogeneous and Heterogeneous Metal Catalysis. Isotope Orientation in the Platinum-catalysed Exchange of the Polyphenyls, Particularly *o*-Terphenyl

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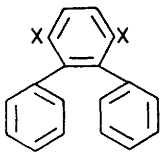
Summary *o*-Terphenyl is a good marker compound for distinguishing between homogeneous and heterogeneous metal-catalysed reactions, particularly isotope exchange; differences in deuterium orientation are observed during initial rates of exchange in *o*-terphenyl with each catalytic system, these differences being attributed to a particular conformation of *o*-terphenyl in the adsorbed state.

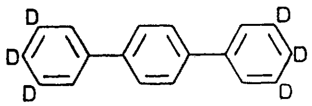
In terms of fundamental catalytic theory, it is of value to be able to correlate homogeneous and heterogeneous metal-catalysed reactions.[1] For isotope exchange, a remarkable similarity between the two systems has been found for a wide range of aliphatic and aromatic compounds, particularly using platinum as catalyst.[2] However, it is often difficult to show unequivocally that a system is truly homogeneous, since metal quite frequently precipitates during such reactions and there could be a heterogeneous contribution. Previously,[3] nitrobenzene, acetophenone, naphthalene, and bromobenzene were cited as exchanging differently in both systems; however, these differences were based on rate phenomena rather than patterns of exchange. Thus isotope orientation in all four compounds during initial rates is the same for both homogeneous and heterogeneous systems, although rates of isotope incorporation vary markedly for the two catalytic processes.

We now report the first example of a compound, *o*-terphenyl (I), where the isotope orientation differs in both systems, especially during initial exchange. *o*-Terphenyl is an elegant compound for the present distinction since n.m.r. spectroscopy can be used rapidly to monitor the effect, *o*-terphenyl giving only two lines separated by 14·6 Hz (at 60 MHz), the upfield line (472·2 Hz from Me$_4$Si) representing the end-ring protons (all equivalent) and the downfield signal, the centre ring protons (all equivalent).

During the platinum-catalysed exchange of the polyphenyls,[2,4] other than *o*-terphenyl, all *ortho* positions are strongly deactivated during initial deuteriation either homogeneously or heterogeneously leading predominantly to *meta* and *para* isotope incorporation [*e.g. p*-terphenyl, species (II)]. This *ortho*-deactivation is a general phenomenon and has also been observed with monosubstituted aromatic compounds.[1] By contrast, *o*-terphenyl shows the expected *ortho* deactivation with homogeneous PtCl$_4^{2-}$ whereas, surprisingly, on heterogeneous platinum, all *ortho* protons of the centre ring [species (I), especially X protons] exchange readily during the initial stages of the reaction. The n.m.r. results are unequivocal since the heterogeneous sample shows virtually zero resonance for all centre ring protons (including *ortho* X) whereas at comparable deuteriation and well removed from equilibrium (*ca.* 50%), there is still a reasonable concentration of residual centre ring protons in the homogeneous sample. From previous work, [1,4] these are *ortho* protons that have not exchanged. The enhanced activity, heterogeneously, of the centre ring X protons may be explained in terms of π-dissociative theory,[1,5] in particular steric effects associated with the adsorption of *o*-terphenyl.[2,6]



(I)



(II)

Preliminary results[7] suggest that an analogous *o*-terphenyl effect may also be found using iridium as catalyst;[8] thus the use of *o*-terphenyl as a marker for differentiating between homogeneous and heterogeneous metal-catalysed isotope exchange reactions may be a general catalytic phenomenon.

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[1] J. L. Garnett, *Catalysis Rev.*, 1971, **5**, 229.

[2] K. Davis, J. L. Garnett, K. Hoa, R. S. Kenyon, and M. A. Long, Proc. Vth Internat. Cong. Catalysis, Palm Beach, Florida, ed., J. W. Hightower, North-Holland, Amsterdam, 1973, p. 491.

[3] J. L. Garnett and R. J. Hodges, *Chem. Comm.*, 1967, 1001.

[4] K. P. Davis and J. L. Garnett, *J. Phys. Chem.*, 1971, **75**, 1175.

[5] E. Crawford and C. Kemball, *Trans. Faraday Soc.*, 1962, **58**, 2452; R. B. Moyes and P. B. Wells, *Adv. Catalysis*, 1973, **23**, 121; R. B. Moyes, K. Baron, and R. C. Squire, Proc. Vth Internat. Cong. Catalysis, Palm Beach, Florida, ed., J. W. Hightower, North-Holland, Amsterdam, 1973, p. 731.

[6] R. A. Hoffman, P. O. Kinell, and G. Bergstrom, *Arkiv. Kemi*, 1960, **15**, 533.

[7] J. L. Garnett, M. A. Long, and K. B. Peterson, unpublished work.

[8] J. L. Garnett, M. A. Long, A. B. McLaren, and K. B. Peterson, *J.C.S. Chem. Comm.*, 1973, 749