Iridium(III) Salts as Homogeneous Metal Catalysts for Hydrogen Isotope Exchange in Organic Compounds: a Comparison with Heterogeneous Iridium for the Deuteriation of Alkylbenzenes

By John L. Garnett, Mervyn A. Long, Ashley B. McLaren, and Kim B. Peterson
(*The University of New South Wales, Kensington, New South Wales, Australia*)

Summary Hydrogen exchange between organic compounds and heavy water is homogeneously catalysed by sodium chloroiridite; results for alkylbenzenes are compared with those from heterogeneous catalysis by iridium metal and are interpreted in terms of the role of π-complex intermediates.

We report hydrogen isotope exchange in organic compounds with iridium(III) salts as homogeneous catalysts. Alkylbenzenes, both short and long-chain, have been deuteriated in an aqueous homogeneous medium containing sodium chloroiridite (Table).

The only system where direct comparisons between homogeneous and heterogeneous catalysis have been possible, has been hydrogen exchange with both aromatic and aliphatic compounds with platinum compounds as catalysts.[1–4] The mechanistic concepts originally proposed for the platinum system[5] appear to be of general application in the catalysis of hydrogen exchange by metal.

The data (Table) show that all alkylbenzenes studied exchange at 130°. In homogeneous systems, exchange in the methyl groups of substituted benzenes such as toluene and the xylenes is almost completely suppressed relative to exchange in the ring. This may reflect either the instability or the excessive stability of the π-allylic intermediate through which the methyl group may exchange.[5] We favour the latter since in ethylbenzene and higher homologues exchange of the α-methylene is less suppressed. With heterogeneous catalysis an analogous deactivation is observed (*o*-xylene). However, with heterogeneous iridium as the total deuterium incorporation in the molecule increases exchange of less active sites becomes significant (toluene, *m*-xylene) so that ultimately toluene deuteriated in all positions can be obtained. In the longer chain alkylbenzenes (n-propyl, n-butyl) homogeneous catalysed exchange occurs in the methyl group of the side-chain in preference to the other positions. This suggests initial π-complex formation *via* the aromatic ring followed by hydrogen abstraction from

TABLE

Exchange of alkylbenzenes with homogeneous (I) and heterogeneous (II) iridium catalysts

				Deuterium orientation (% of H + D)				
System[a]	Compound	D found (%)	D theor. (%)	Aromatic (%)	α-CH_2 (%)	Other CH_2	Terminal CH_3	Methine
(I)	C_6H_6	63	66	63				
	PhMe[b]	20	60	34			0	
	PhEt	18	62	31	5·0		2·8	
	PhPr	14	62	16	14	10	11	
	PhBu	5	41	21	8	8	14	
	$PhPr^i$	10	62	24			0	0
	$PhBu^t$	7	62	17			1·4	
	o-MeC_6H_4Me	13	62	33			0·3	
	m ,,	14	62	37			0	
	p- ,,	3·6	62	12			0	
(II)	C_6H_6	50	52	50				
	PhMe[b]	27	50	32			17	
	PhEt	14	53	21	8·2		4·3	
	PhPr	11	52	13	6·2	1·0	3·3	
	o-MeC_6H_4Me	9	53	20			1	
	m- ,,	20	53	23			19	

[a] System (I): Na_3IrCl_6 (0·02M) in 25 mol % $MeCO_2D/D_2O$ for 160 h at 130°, except for benzene (138 h) and n-butylbenzene where 50 mol % $MeCO_2D/D_2O$ for 144 h at 130° was used. Blanks without iridium salt gave no exchange. Deuterium analysis was by m.s. and n.m.r.[2] System (II): $IrO_2,2H_2O$ reduced with aqueous $NaBH_4$.[5] Reacted for 24 h at 130°. [b] Orientation in ring determined by oxidation to benzoic acid (n.m.r.). In system (I), 7% of D in *o* and 48% *m* + *p*; in system (II), 16·5% *o* and 42·6% *m*+*p*.

the terminal carbon[6] as already proposed for platinum.[6,7] Exchange in the aromatic ring is predominantly to the *meta* and *para* positions of the alkylbenzenes, a similar but less specific orientation being also observed in heterogeneous systems with iridium catalysts. The iridium systems are substantially slower than the platinum at a given temperature, but they have higher thermal stability and exchange temperatures of 130 °C for long periods are possible with the iridium system without metal precipitation occurring. Thus the higher temperature of exchange attainable with homogeneous iridium systems compensates for their slower rate.

Preliminary kinetic measurements indicate that analogous π-complex mechanisms,[1,8] to those proposed for the platinum system operate for both homogeneous and heterogeneous iridium systems. Detailed kinetic studies of these reactions are continuing.

We thank the Australian Research Grants Committee, the Australian Institute of Nuclear Science and Engineering and the Australian Atomic Energy Commission for the support of this research.

(*Received*, 16*th July* 1973; *Com.* 1009.)

---

[1] K. Davis, J. L. Garnett, K. Hoa, R. S. Kenyon, and M. A. Long, Proc. Vth Internat. Cong. Catalysis, Palm Beach, Florida, 1972, in the press.
[2] J. L. Garnett and R. J. Hodges, *J. Amer. Chem. Soc.*, 1967, **87**, 4546.
[3] N. F. Gol'dshleger, M. B. Tyabin, A. E. Shilov, and A. A. Shteinman, *Zhur. fiz. Khim.*, 1969, **43**, 2174.
[4] R. J. Hodges, D. E. Webster, and P. B. Wells, *J. Chem. Soc.* (*A*), 1971, 3230.
[5] J. L. Garnett, *Catalysis Rev.*, 1971, **5**, 229.
[6] J. L. Garnett and R. S. Kenyon, *Chem. Comm.*, 1970, 698.
[7] C. Masters, *J.C.S. Chem. Comm.*, 1972, 1258.
[8] E. Crawford and C. Kemball, *Trans. Faraday Soc.*, 1962, **58**, 2452.