

Activation of Saturated Hydrocarbons by Homogeneous Metal Catalysts: Deuterium Exchange in Iridium(III) Solution*

J. L. Garnett, M. A. Long and K. B. Peterson

University of New South Wales, School of Chemistry,
P.O. Box 1, Kensington, N.S.W. 2033.

Abstract

Isotopic hydrogen exchange between simple alkanes and D_2O is homogeneously catalysed by sodium chloroiridate at $160^\circ C$. Initial isotope orientation favours hydrogen on the primary carbon atoms. High M values for the exchange are typical.

The activation of saturated hydrocarbons by homogeneous metal catalysts is difficult because such hydrocarbons do not easily complex with metals in homogeneous solution. However, the concept that such complexes do exist is important in fundamental catalytic theory since it suggests that some aspects of the chemistry of inorganic complexes in solution may be relevant in postulating the manner of bond formation of a species activated on a metal surface. In this respect, platinum is unique, since sodium chloroplatinate(II) is the only homogeneous Group VIII transition metal salt¹⁻³ found to activate alkanes in isotopic hydrogen exchange reactions at temperatures of $100-130^\circ C$.

We now report for the first time the activation and deuteration of the simple alkanes in aqueous solution containing iridium(III) salts as homogeneous metal catalysts. Previously this same iridium catalyst was found to homogeneously catalyse exchange in the alkylbenzenes,⁴ but the optimum deuteration conditions were significantly different to those of the present alkane system. In particular, with compounds such as toluene, isotope incorporation using the present iridium(III) catalyst was confined almost exclusively to the ring, suggesting (i) the absence of direct complexing between the saturated side chain and the iridium(III) and (ii) the likelihood that alkanes may not exchange with this same catalyst.

A wide range of alkanes have now been deuterated by the present homogeneous iridium(III) catalyst; the results in Table 1 demonstrate the type of reactivity found.

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Table 1. Exchange of alkanes with D₂O in presence of homogeneous iridium(III) catalyst

A typical experiment involved causing Na₃IrCl₆ (0.02M) in 25 mole % MeCO₂D/D₂O (2 ml) to react with organic substrate (0.3 ml) and stabilizer (equimolar with catalyst unless otherwise specified). D_t and D_r denote the theoretical and the found concentrations of deuterium expressed as replacement (in %) of total hydrogen by deuterium

Run No.	Alkane substrate	Stabilizer (moles)	Temp (°C)	Time (d)	D _t (%)	D _r (%)	D ₀	D ₁	D ₂	D ₃	D ₄	D ₅	D ₆	D ₇	D ₈	D ₉	D ₁₀	D ₁₁	D ₁₂	D ₁₃	D ₁₄
1	Methane	none	165	5	70	15.1	73.7	4.7	11.5	7.9	2.2										
2	Methane	naphthalene	165	5	70	19.8	67.7	5.1	11.6	11.5	4.1										
3	Methane	pyrene	165	5	70	29.1	56.1	6.3	11.4	17.4	8.8										
4	Propane	naphthalene	165	5	68	14.3	74.6	2.4	1.5	2.6	4.8	5.8	5.1	2.6	0.5						
5	Butane	naphthalene	165	5	67	9.7	80.9	1.8	0.6	1.3	2.9	4.1	3.5	2.4	1.6	0.7	0.1				
6	Pentane	naphthalene	150	5	60.7	15.1	70.7	2.9	1.5	1.6	2.0	2.7	3.5	4.3	4.2	3.4	2.0	0.7	0.5		
7	Hexane	naphthalene	150	5	60.4	7.1	85.9	1.9	0.7	0.4	0.5	0.6	0.9	1.5	1.7	2.0	1.8	1.3	0.6	0.2	
8	Heptane	naphthalene	150	5	60.3	6.6	86.8	1.8	0.5	0.4	0.4	0.4	0.5	0.7	1.1	1.4	1.7	1.7	1.4	0.8	0.4
9	Hexane	benzene	160	3	63.6	8.9	82.8	2.1	0.8	0.6	0.7	0.9	1.1	1.5	1.8	2.3	2.2	1.8	0.9		
10	Hexane	naphthalene	160	3	63.6	9.9	80.4	2.9	0.8	0.6	0.8	0.9	1.2	1.5	2.4	2.7	2.3	1.8	1.1	0.6	
11	Hexane	azulene	160	3	63.6	0															
12	c-Pentane	naphthalene																			
		(6 × 10 ⁻⁵)	170	4	60.5	14.8	71.9	3.0	1.5	1.8	2.7	4.5	5.3	5.1	3.0	1.1	0.2				
13	c-Hexane	none	170	4	60.1	15.2	62.8	8.0	3.3	3.0	3.1	3.5	3.8	4.0	3.6	2.8	1.6	0.7	0.1		
14	c-Hexane	naphthalene																			
		(9 × 10 ⁻⁵)	170	4	60.1	21.3	53.9	6.6	3.2	3.1	3.7	4.5	5.5	6.1	5.7	4.3	2.5	0.9	0.2		
15	c-Hexane	naphthalene																			
		(3 × 10 ⁻⁴)	170	4	60.1	11.0	76.3	3.4	1.9	1.6	1.8	2.2	2.8	3.2	3.0	2.3	1.2	0.5			
16 ^a	c-Hexane	naphthalene	170	7	74.6	54.0	22.6	2.2	0.9	1.0	1.4	2.3	4.3	8.4	13.4	16.7	15.2	9.0	2.6		
17 ^b	c-Hexane	naphthalene	170	7	66.4	42.2	26.4	4.7	2.4	2.5	3.6	5.7	8.4	11.6	13.1	11.3	7.0	2.9	0.5		
18 ^c	c-Hexane	naphthalene	170	7	56.5	14.1	66.5	6.1	2.1	2.4	3.2	3.5	4.3	4.7	3.9	2.3	1.1				
19 ^d	c-Hexane	naphthalene	170	7	49.0	0															

^a Acid concentration 9.8 mole % MeCO₂D/D₂O.

^b Acid concentration 17.5 mole % MeCO₂D/D₂O.

^c Acid concentration 28.5 mole % MeCO₂D/D₂O.

^d Acid concentration 38.5 mole % MeCO₂D/D₂O.

Exchange is favoured by lower acetic acid activities (runs 16–19) and the presence of small concentrations of aromatic compounds as stabilizers to minimize metal precipitation. The presence of such stabilizers was also found to be beneficial for the exchange of the alkanes with platinum.³ Of the aromatic stabilizers studied, pyrene (runs 1–3) is the most effective and azulene the least effective (runs 9–11); this presumably reflects the degree of π -olefin type poisoning. Orientation of isotope during initial exchange appears to favour the hydrogens on the terminal primary carbon atoms of the alkane. This conclusion is suggested by the D_5/D_6 cut-off in the low voltage mass spectrum of deuterated propane (Table 1, run 4). With prolonged reaction, appreciable deuteration of the methylene positions also occurs, this result being confirmed by n.m.r. for a number of alkanes in Table 1. Deuteration involves a high M value⁵ (5.4 for cyclohexane) and depends upon the concentration of the stabilizer (runs 14, 15). Cyclohexane exhibits the fastest exchange rate of the alkanes studied to date.

Iridium is now the second Group VIII transition metal capable of activating saturated hydrocarbons under homogeneous conditions. Solvent concentrations required to show alkane exchange with iridium are different to those required for platinum, to the extent that, if the optimum conditions found for platinum are used for iridium, no exchange is observed. Iridium is slower than platinum but is thermally stable in solution to higher temperatures, the higher temperature of exchange (160° as against 100°) compensating for the slower iridium rate. There is also no necessity to use mineral acid to stabilize the catalyst as required with platinum.

Mechanistically the present alkane results are consistent with the formation of a charge-transfer complex intermediate between iridium(III) and the substrate, as recently proposed for the alkylbenzene exchange with this catalyst.⁴ From these preliminary experiments we favour a delocalized rather than a localized complex intermediate between alkane and iridium(III).⁴

Experimental

In a typical exchange experiment, the liquid alkane (0.3 ml) was treated with a solution (2 ml) of 25 mole % CH_3COOD in D_2O containing Na_3IrCl_6 (0.02M). Where required catalyst stabilizer was also added in equimolar amounts with the catalyst, unless otherwise specified in Table 1. The mixture was vacuum sealed at $<10^{-3}$ Torr and heated to the required temperature for the necessary time. After reaction, the organic component was recovered from the mixture by dilution with water in a similar procedure to that adopted previously with homogeneous platinum.¹ Deuterium analysis of the product was by low voltage mass spectrometry (Hitachi-Perkin Elmer RMU-6L instrument) and n.m.r. (Varian A-60). Where the alkanes were gases at room temperature, the required volume of alkane was condensed into the reaction vessel by means of a refrigerant technique.

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