The Mechanism of Exchange between Deuterium and Alkanes in the Liquid Phase[1]

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THE mechanism of the metal-catalysed gas-phase reaction between alkanes and deuterium has been much investigated[2] but that for the liquid-phase reaction has been largely ignored. Recently we prepared[3] a series of fully deuteriated high molecular weight hydrocarbons, and now we can report on certain mechanistic aspects of liquid-phase exchange. By using n-dodecane and cyclododecane as model compounds, low conversion exchange between liquid alkane and deuterium gas gave mainly monodeuteriated species[4] with sharply decreasing proportions of polydeuteriated molecules. These results are strikingly different from the perdeuteriation tendency found in gas-phase work particularly over palladium.[2b] For example, liquid-phase exchange of n-dodecane over Pd–C at 195° gave an M value (average number of deuterium atoms incorporated per residence of alkane on catalyst) of 3·17 whereas gas-phase n-hexane exchange over palladium film at 135° gave an *M* value of 13·6.[5]

Exclusive mono-exchange would yield an isotope distribution corresponding to a random-distribution pattern,[6] as Schrage and Burwell found for adamantane.[7] However, as the data in the Table for cyclododecane indicate, there is also an appreciable amount of multiple exchange per adsorption step, although mono-exchange predominates for both palladium and platinum catalysts. The distribution from a rhodium catalyst (not shown) was similar to that from palladium, and the distribution patterns for n-dodecane over the three catalysts, although differing in detail

$^2H_2$ *Exchange of cyclododecane at* 195°

	Pd–C		Pt–C	
Species	Found (%)	Random (%)[6]	Found (%)	Random (%)[6]
$[^2H_0]$	87·52	80·33	85·93	80·54
$[^2H_1]$	7·55	17·67	10·62	17·55
$[^2H_2]$	2·72	1·87	1·86	1·79
$[^2H_3]$	0·91	0·13	0·61	0·12
$[^2H_4]$	0·70		0·43	
$[^2H_5]$	0·30		0·21	
$[^2H_6]$	0·20		0·19	
$[^2H_7]$	0·10		0·12	
$[^2H_8]$			0·03	
$[^2H_9]$–$[^2H_{24}]$				
Atom % D	0·91		0·88	
M Value	1·69		1·42	

from those of cyclododecane, were very similar, with a strong preference for $[^2H_1]$species.

The distribution of deuterium between the methylene and methyl positions was also investigated on a low conversion sample of n-dodecane. This was determined directly by ^{2}H n.m.r. and gave a ratio of 4·20 : 1, which, on a statistical basis indicates only a slight preference for exchange of a methylene position over a methyl group (1·26 : 1).†

The conditions used[3] to generate the results reported were such as to provide a high ratio of hydrocarbon to deuterium adsorbed on the catalyst, a condition expected to give low M values even with metals known to promote multiple exchange. However, contact of a 15 : 1 mixture of perdeuterion-dodecane and n-tetracosane with Pd/C at 195° gave partially deuteriated n-tetracosane with an average of 12·80 deuterium atoms per molecule, an M value lower than expected by analogy with gas phase, n-alkane exchange but much higher than the values reported above.

These results suggest that gas-phase and liquid-phase alkane–deuterium exchange do not proceed by different mechanisms although this possibility cannot be completely discounted. It is clear, however, that preparative liquid-phase exchange conditions give initial products containing few deuterium atoms and that perdeuteriation arises only by repetition of adsorption-desorption sequences.

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† We have used deuterium n.m.r. in several other such systems and found it to be a very powerful tool to determine deuterium location in low incorporation experiments. (*Cf.* L. K. Montgomery, A. O. Gaus, A. M. Crelier, and L. E. Applegate, *J. Amer. Chem. Soc.*, 1967, **89**, 3453.

[1] Part of the series on 'Aspects of Stable Isotope Chemistry,' for previous Part see J. G. Atkinson, D. W. Cillis, and R. S. Stuart, *Canad. J. Chem.*, 1969, **47**, 477.

[2] For pertinent references to the extensive literature on gas-phase exchange see (a) J. Addy and G. C. Bond, *Trans. Faraday Soc.*, 1957, **53**, 368; (b) C. Kemball, *Adv. Catalysis*, 1959, **11**, 223; (c) K. Schrage and R. L. Burwell, jun., *J. Amer. Chem. Soc.*, 1966, **88**, 4549.

[3] J. G. Atkinson, M. O. Luke, and R. S. Stuart, *Chem. Comm.*, 1967, 474; *Canad. J. Chem.*, 1967, **45**, 1511.

[4] Presented in part at the 156th A.C.S. Meeting, Atlantic City, September, 1968. Abstracts, ORGN 158.

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[6] For the method of calculation see: J. N. Wilson, J. W. Otvos, D. P. Stevenson, and C. D. Wagner, *Ind. Eng. Chem.*, 1955, **45**, 1480.

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[8] *Cf.* L. K. Montgomery, A. O. Clouse, A. M. Crelier, and L. E. Applegate, *J. Amer. Chem. Soc.*, 1967, **89**, 3453.