Evidence for the Formation of an αδ-Adsorbed Hydrocarbon Intermediate on a Rhodium Catalyst†

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Exchange of 2,2,3,3-tetramethylbutane with deuterium over rhodium provides evidence for a mechanism involving αδ-adsorbed intermediates.
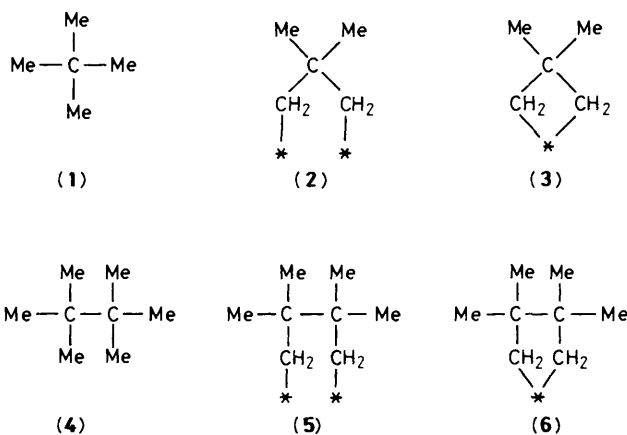
The role of αγ-absorbed intermediates in the exchange of hydrocarbons with deuterium on metal catalysts was demon-

† The terms αδ- and αγ-adsorbed conform to the usual nomenclature in publications on catalysis and are equivalent to 1,4- and 1,3-adsorbed, respectively.

strated many years ago through studies[1] with 2,2-dimethyl-propane (1). The main process for the exchange of this compound is stepwise exchange (I), involving reversible formation of adsorbed alkyl intermediates, but two other processes also contribute; these are multiple exchange limited to a single methyl group (II) and multiple exchange ranging

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         Me                    Me   Me                 Me    Me
         |                      \  /                     \  /
Me — C — Me                      C                        C
         |                     /    \                    /   \
         Me                  CH2    CH2               CH2   CH2
                              |      |                  \    /
                              *      *                    *

        (1)                     (2)                      (3)
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    Me  Me               Me   Me              Me  Me
    |   |                 |    |               |   |
Me— C — C —Me        Me— C  —  C — Me      Me— C — C — Me
    |   |                 |    |               |   |
    Me  Me               CH2  CH2            CH2 CH2
                          |    |               \  /
                          *    *                 *

    (4)                   (5)                   (6)
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over the whole molecule (**III**). The contribution from process **III** is greater on rhodium than on other metals[1–3] and becomes more important as the temperature is increased. The mechanism of this reaction, which permits the exchange of all four methyl groups in (**1**), must involve interconversion between adsorbed alkyl and $\alpha\gamma$-adsorbed intermediates; these may require two surface sites (**2**) or can be represented[4–6] as a metallocyclobutane (**3**) on a single site.

The purpose of the present work is to determine whether $\alpha\delta$-adsorbed intermediates can be formed with appropriate hydrocarbons. The compound 2,2,3,3-tetramethylbutane (**4**) is a good test reactant to settle this question and also to establish the relative importance of mechanisms involving $\alpha\gamma$- or $\alpha\delta$-adsorbed intermediates. The latter, which again may involve two sites (**5**) or a metallocyclopentane (**6**) on one site, would permit the multiple exchange to range over the whole molecule. In contrast, if $\alpha\gamma$-adsorbed intermediates are formed but $\alpha\delta$-species are not, the exchange process could not propagate beyond the three methyl groups attached to one of the two central carbon atoms in (**4**). Exchange of (**4**) with deuterium has been reported recently on platinum[7] and rhodium[8] catalysts but in neither case were extensively exchanged molecules observed.

The present reactions were carried out in a static system[9] connected by a capillary leak to a Vacuum Generators Micromass 601 spectrometer. The charge of hydrocarbon (693 Pa) in the reaction vessel was 3.5×10^{19} molecules with an 8:1 ratio of D_2:hydrocarbon. The silica-supported rhodium catalyst,[10] containing 10^{-4} mol metal g^{-1} silica, was reduced in flowing hydrogen for 1 h at 673 K and evacuated for 30 min at the same temperature. The reaction was followed from the composition of the fragment ions $C_7X_{15}^+$ (X representing H or D) formed by loss of a methyl group from the parent molecule ionised by 35 eV electrons. The usual corrections for naturally occurring isotopes and fragmentation to other ions were made and also the peak corresponding to $C_7D_{15}^+$ was corrected for a small amount of the parent ion, $C_8H_{18}^+$, equivalent to 0.28% of the $C_7H_{15}^+$ peak. Product distributions at similar conversions at three temperatures are given in Table 1 together with a comparable result for (**1**) at the highest temperature in terms of the composition of the $C_4X_9^+$ ions. Rates and the contributions from the various exchange processes are shown in Table 2.

Several points emerge from the results, in Table 1 and at other conversions, and these are discussed in terms of four processes.

Process **I**. In every case stepwise exchange is the most important component of the overall reaction and gives the D_1-species as the main product. The rates of reaction of (**1**) and (**4**) are similar at 393K.

Table 1. Isotopic composition of the $C_7X_{15}^+$ ions from (**4**) and the $C_4X_9^+$ ions from (**1**) after 15% reaction with deuterium on rhodium.

Reactant	(4)	(4)	(4)	(1)
T/K	344	363	394	393
D_1	11.83	11.54	9.57	10.06
D_2	1.76	1.59	1.86	2.13
D_3	0.65	0.52	0.68	1.40
D_4	0.14	0.12	0.24	0.51
D_5	0.06	0.06	0.10	0.26
D_6	0.03	0.04	0.05	0.19
D_7	0.03	0.04	0.05	0.15
D_8	0.04	0.06	0.14	0.15
D_9	0.11	0.20	0.32	0.15
D_{10}	0.04	0.09	0.19	—
D_{11}	0.05	0.09	0.22	—
D_{12}	0.12	0.22	0.40	—
D_{13}	0.05	0.09	0.26	—
D_{14}	0.06	0.13	0.39	—
D_{15}	0.05	0.22	0.52	—

Table 2. Rates of reaction and contributions from the various processes for the exchange of (**4**) and (**1**).

Reactant	T/K	Initial rate r/molecule s^{-1} (mol Rh)$^{-1}$	Process contribution (%)			
			I	II	III	IV[a]
(4)	344	5.3×10^{20}	85	11	—	4
(4)	363	1.22×10^{21}	82	9	—	9
(4)	394	5.1×10^{21}	69	14	—	17
(1)	393	8.6×10^{21}	73	21	6	—

[a] Process **IV** is the multiple exchange ranging beyond one methyl group with (**4**).

Process **II**. Methyl group exchange occurs to an appreciable extent as shown by the formation of the D_2- and D_3-ions. The values in Table 2 for the contribution of process **II** were estimated after allowing for the fraction of the D_2-ion formed by successive stepwise exchange. Process **II** occurs to a greater extent at 393K with (**1**) than with (**4**).

Process **IV**. The significant amounts of products beyond the D_9-ion with (**4**) provide clear evidence for a multiple exchange process ranging over the whole molecule with a mechanism involving $\alpha\delta$-adsorbed intermediates. A special feature of the product distributions is the existence of maxima at the D_9-, D_{12}-, and D_{15}-ions indicating that the completion of methyl group exchange occurs more readily in association with process **IV** than in process **II**. This observation suggests that while the reacting molecules are held on the surface as $\alpha\delta$-intermediates interconversion can occur with species such as $\alpha\alpha\delta$-adsorbed or other more highly dissociated forms related to (**5**) or (**6**).

Process **III**. The more highly exchanged products from (**1**) are evidence for a mechanism involving $\alpha\gamma$-adsorbed intermediates. We cannot exclude a possible contribution from process **III** to the formation of the multiply-exchanged products from (**4**) but the shape of the distributions indicates that it is small compared with that of process **IV**. The conclusion is that rhodium forms $\alpha\delta$-adsorbed intermediates in preference to $\alpha\gamma$-adsorbed species. This conclusion is confirmed by the small contribution of process **III** with (**1**) at 393K compared with the part played by process (**IV**) with (**4**). In estimating the percentages in Table 2 attributed to processes **III** and **IV**, the amounts of the D_4-ion from (**1**), and both the D_4- and D_5-ions from (**4**) were ignored as these products were likely to have originated through successive reactions by processes **I** and **II**.

The results with (4) give some indication of activation energies for the various processes. The value for the overall exchange reaction is 54 kJ mol^{-1}. The effects of temperature on the relative contributions of II to I and of IV to I show that the additional activation energies of processes II and IV compared with I are 10 and 38 kJ mol^{-1}, respectively.

The evidence that $\alpha\delta$-adsorbed intermediates are formed to a significant extent with (4) provides some support for the suggestion[6] of a role for metallocyclopentane intermediates in the reactions of hydrocarbons on some metals.

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References

1 C. Kemball, *Trans. Faraday Soc.*, 1954, **50**, 1344.
2 I. H. B. Haining, C. Kemball, and G. L. Haller, *J. Chem. Soc., Faraday Trans. 1*, 1981, **77**, 2519.
3 R. Brown, C. Kemball, J. A. Oliver, and I. H. Sadler, *J. Chem. Res.*, 1985, (S) 274; (M) 3201.
4 J. K. A. Clarke and J. J. Rooney, *Adv. Catal.*, 1976, **25**, 125.
5 O. E. Finlayson, J. K. A. Clarke, and J. J. Rooney, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 191.
6 J. J. Rooney, *J. Mol. Catal.*, 1985, **31**, 147.
7 C. B. Lebrilla and W. F. Maier, *J. Am. Chem. Soc.*, 1986, **108**, 1606.
8 J. M. Cogen and W. F. Maier, *J. Am. Chem. Soc.*, 1986, **108**, 7752.
9 J. A. Oliver, C. Kemball, R. Brown, and E. W. Jamieson, *J. Chem. Soc., Faraday Trans 1*, 1985, **81**, 1871.
10 T. C. Wong, C-T. Chang, G. L. Haller, J. A. Oliver, N. R. Scaife, and C. Kemball, *J. Catal.*, 1984, **87**, 389.