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Exchange Reactions of Alkanes containing Quaternary Carbon Atoms over Supported Metal Catalysts

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A comparison has been made of the exchange reactions with deuterium of 2,2-dimethylpropane (DMP), 2,2,3,3-tetramethylbutane (TMB) and 2,2,4,4-tetramethylpentane (TMP) over supported catalysts containing iridium, palladium, platinum or rhodium at temperatures in the neighbourhood of 400 K. Reactions were followed mass-spectrometrically and products were also examined by deuterium n.m.r. spectroscopy. Four processes or mechanisms were found to contribute to different extents with the various hydrocarbon–metal systems. These were (I) stepwise exchange, (II) methyl-group exchange, and more general multiple exchange involving (III) $\alpha\gamma$-diadsorbed or (IV) $\alpha\delta$-diadsorbed intermediates. Some isomerisation of TMP was observed to occur simultaneously with exchange with the TMP–rhodium system.

The study[1–3] of exchange reactions of alkanes with deuterium has yielded much evidence about the nature and reactivity of adsorbed intermediates and so supplied information which is fundamental to an understanding of the mechanisms of hydrocarbon reactions on metals. Recently, the use[4–6] of high-field deuterium n.m.r. spectroscopy has provided a means of identifying the groupings of deuterium atoms in the products of exchange reactions and of estimating the distribution of the atoms in the various groupings. Results, so obtained, are more revealing than those from the traditional mass-spectrometric technique and have necessitated a revision of some of the accepted ideas about the mechanisms of exchange reactions.[5,6] With linear or slightly branched hydrocarbons, very extensive multiple exchange is observed on many metal catalysts but with molecules such as 2,2-dimethylpropane (DMP), the quaternary carbon atom restricts the number of possible intermediates that can be formed and limits the types of multiple exchange that can occur.

The purpose of the present work was to compare the behaviour of the hydrocarbons DMP, 2,2,3,3-tetramethylbutane (TMB) and 2,2,4,4-tetramethylpentane (TMP) in reactions with deuterium on supported iridium, palladium, platinum and rhodium catalysts. Studies over a period of years[6–11] with DMP have shown that the exchange of this molecule with deuterium may occur by one or more of three processes. The first of these, process I, involves stepwise exchange through the reversible formation of an adsorbed alkyl radical. Process II gives multiple exchange, but limited to a single methyl group through interconversion between adsorbed alkyl and α,α-diadsorbed (alkylidene) species. Process III, which becomes significant only at higher temperatures, leads to the formation of initial products containing deuterium atoms in two or more methyl groups; it requires the interconversion of adsorbed alkyl radicals and $\alpha\gamma$-diadsorbed species. In contrast to the number of studies with DMP, relatively little work has been carried out with TMB and TMP. The interest in TMB concerns the possibility of multiple exchange through $\alpha\delta$-diadsorbed intermediates. Such species are needed to allow the multiple exchange to propagate beyond the three methyl groups attached to one of the two central carbon atoms. Maier and his colleagues have reported results on the exchange of TMB on platinum[12] and rhodium[13] but in neither case were extensively exchanged initial products detected. On the other hand, preliminary work[14] with a silica-supported rhodium catalyst has shown evidence for an exchange process involving $\alpha\delta$-adsorbed intermediates. With TMP as reactant extensive multiple exchange might occur through the formation of $\alpha\gamma$-adsorbed intermediates if reversible dissociations of C—H bonds both in the methyl groups and the central methylene group were possible. Formation of $\alpha\gamma$-species involving the central group would allow the exchange process to propagate over the whole molecule. Alternatively, if the exchange of the methylene group was unlikely either for steric reasons or from the intervention of isomerisation reactions then the only means of achieving multiple exchange extending beyond three methyl groups with TMP would be through $\alpha\varepsilon$-diadsorbed intermediates. Such species have been shown to play an important part in dehydrocyclisation reactions with TMP and other alkanes on sintered metal films.[15] The sintering of the films had the effect of reducing the rate of the exchange reactions so that processes such as isomerisation and dehydrocyclisation could be studied in the presence of deuterium without complications from exchange. We hoped that a comparative study of the behaviour of DMP, TMB and TMP in exchange reactions would provide clear evidence of the relative importance of $\alpha\gamma$-, $\alpha\delta$- and $\alpha\varepsilon$-intermediates on the four supported metal catalysts.

Experimental

The preparation and pretreatment of the platinum and rhodium catalysts which contained 10^{-4} mol metal g^{-1} silica have been described.[16] The palladium catalyst, donated by I.C.I., contained 2.5×10^{-6} mol Pd g^{-1} calcium aluminate and was pretreated in a similar manner to the previous catalysts. The iridium catalyst, with 2×10^{-5} mol metal g^{-1} γ-alumina, has also been described and characterised.[17] The DMP (99%) and deuterium (99.5%) were supplied by the Matheson Co. and the TMB (99%) was obtained from the Aldrich Chemical Co. Ltd. Prof. J. K. A. Clarke gave us a sample of TMP, an API standard sample as used in the study with sintered films.[15] No further purification of the hydrocarbons was attempted apart from a freeze–thaw cycle prior to each experiment. The deuterium was diffused through a heated palladium–silver alloy thimble.

Two types of apparatus were used (a static system and a recirculation system) and each was connected by a capillary leak to a Vacuum Generators Micromass 601 mass spectrometer. Most of the experiments with DMP and TMB were carried out in the static system[10] which had a volume of 240 cm^3. The usual mixture for runs which were not to be analysed subsequently by n.m.r. spectroscopy was 8:1 of deuterium: hydrocarbon and a pressure of hydrocarbon of 693 Pa, giving 3.5×10^{19} molecules in the reaction vessel. For runs to be examined by deuterium n.m.r. spectroscopy a larger charge of hydrocarbon was needed (4.3 kPa, equivalent to 2.0×10^{20} molecules) and the deuterium hydrocarbon ratio was 5:1. All experiments with TMP were carried out in the recirculation apparatus (1270 cm^3) using an 8:1 ratio of deuterium:hydrocarbon and a hydrocarbon pressure of 733 Pa which gave 2.1×10^{20} molecules in the apparatus. The larger circulation system was necessary for runs with TMP because the vapour pressure was insufficient to give enough material in the static apparatus for subsequent analysis by n.m.r. spectroscopy.

The course of the exchange reactions for all three hydrocarbons were followed using the amounts of the pseudoparent ions formed by loss of a methyl group from the molecules in the mass spectrometer using 35 eV† electrons to bring about ionisation. The usual corrections were made for naturally occurring isotopes and for fragmentation to other ions. In addition, a further small but important correction had to be made with

† 1 eV = 0.1602177 aJ.

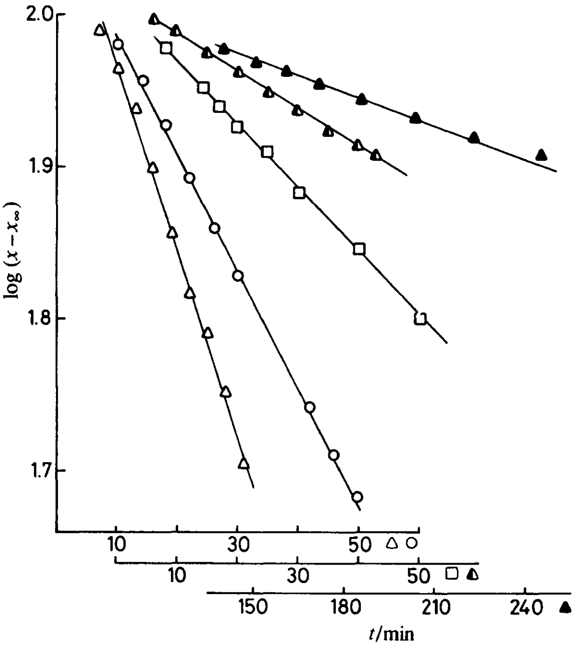

Fig. 1. Rate plots according to eqn (1) for reactions over iridium (◭, ○), palladium (▲) and platinum (△, □): squares, DMP; circles, TMB; triangles, TMP.

TMB and TMP associated with the formation of parent ions. With TMB, the peak at $m/e = 114$ had to be corrected for the parent ion $C_8H_{18}^+$, amounting to 0.28% of the pseudoparent ions, to obtain the contribution from $C_7D_{15}^+$. The corresponding correction with TMP for the presence of $C_9H_{20}^+$ amounted to 1.25% of the pseudoparent ions and was subtracted from the peak at $m/e = 128$ to find the contribution from $C_8H_2D_{15}^+$.

Standard methods[1] were used to obtain the initial rates of exchange and the mean number of deuterium atoms, M, in the pseudoparent ions from the initial products. For each run, the results were plotted according to the reversible first-order equation for the disappearance of the light pseudoparent ions ($C_4H_9^+$, $C_7H_{15}^+$ or $C_8H_{17}^+$, respectively, for DMP, TMB and TMP)

$$-\ln(x-x_\infty) = kt/(100-x_\infty) - \ln(100-x_\infty) \qquad (1)$$

in which x is the percentage of the light ion at time t, x_∞ (≈ 0) is the value at equilibrium and k is the initial rate (in % time^{-1}).

The technique for collecting the hydrocarbon samples and for analysing them subsequently by deuterium n.m.r. spectroscopy has been described.[5]

Results

Kinetic Behaviour

Experiments with the iridium, platinum or rhodium catalysts were carried out at *ca.* 393 and 423 K but temperatures up to 460 K were needed to obtain adequate rates with the palladium catalyst because of its low loading of metal.

Runs with iridium, palladium or platinum conformed to the first-order reversible rate equation (1) as indicated by the representative plots in fig. 1; a slight decrease in rate was apparent for the experiment with TMP on palladium at 456 K but only after 250 min.

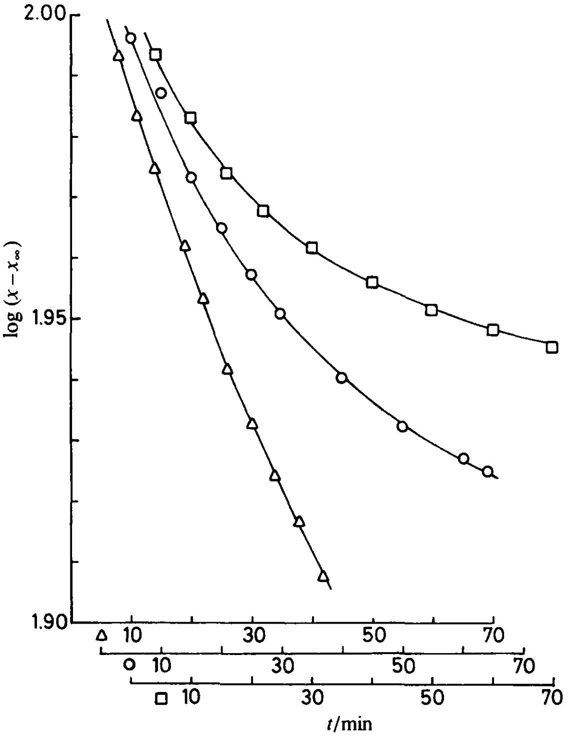

Fig. 2. Rate plots according to eqn (1) for reactions over Rh–SiO_2 at 423 K: (□) DMP, (○) TMB, (△) TMP.

However, the rates of exchange reactions using rhodium decreased with time, see fig. 2, and the effect was most pronounced with DMP and least noticeable with TMP.

Initial rates for all the exchange reactions are given in the Arrhenius diagram for each metal in fig. 3. Similar rates of reaction were found with the three hydrocarbons, particularly over palladium which gave results close to a common Arrhenius line with activation energy 91 ± 4 kJ mol^{-1}. The line given for rhodium is based on previous data[14] for the exchange of TMB and corresponds to an activation energy of 54 kJ mol^{-1}. Likewise for iridium the line is parallel to that found[11] for exchange of DMP over the temperature range 301–452 K with $E = 38$ kJ mol^{-1}. With platinum, the line drawn gives an activation energy of 103 ± 13 kJ mol^{-1} but this value is higher than the activation energy of 56 kJ mol^{-1} reported for an alumina-supported platinum catalyst.[11]

Product Distributions

For each exchange experiment the product distributions in terms of the pseudoparent ions were obtained from the mass-spectrometric analyses at low conversions and the kinetic data were used[1] to calculate M the mean number of D atoms in the ions from the initial products. Results for palladium are given in the upper part of table 1. The values of M at both temperatures for DMP and for TMB at 424 K showed that stepwise exchange was the dominant process with these systems. This conclusion was confirmed by the agreement between the observed product distributions at 10% conversion and the calculated random distributions. With TMP at 456 K, stepwise exchange was again the main type of reaction but there was a contribution from some other process as well.

Results for platinum and iridium are given in table 2 at a slightly greater conversion

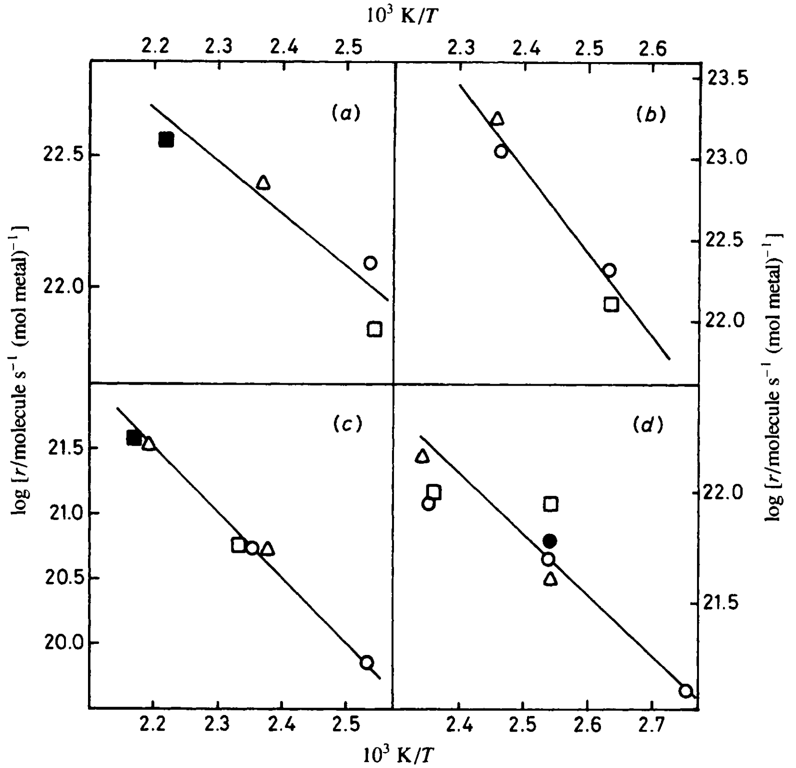

Fig. 3. Rates of exchange plotted on Arrhenius diagrams for (*a*) iridium, (*b*) platinum, (*c*) palladium and (*d*) rhodium: squares, DMP; circles, TMB; triangles, TMP. Filled symbols were rates from experiments on the static line planned for n.m.r. with the higher pressure of hydrocarbon and a 5:1 ratio of D_2:hydrocarbon.

of 15%. This value was chosen in order to show the small amounts of the more highly exchanged products. At 15% conversion there is a significant contribution from molecules that have made two effective visits to the catalyst surface: about 14% of the molecule will have exchanged once and 1% will have reacted twice. With iridium, some multiple exchange limited to methyl groups, *i.e.* process II, occurs with all three reactants but further multiple exchange contributes only to a very small extent. General multiple exchange plays a greater part in the reactions over platinum and increases with temperature as shown by the two sets of results with TMB. Results for reactions over rhodium at 10% conversion are given in table 3 and show significant contributions from multiple exchange processes. The influence of temperature on the values of *M* for exchange over iridium, platinum and rhodium catalysts are shown in fig. 4.

N.M.R. Analyses

DMP

The main features associated with the deuterium n.m.r. spectra of exchanged DMP have been established.[5, 6] The chemical shift for the —CH_2D group occurs at $\delta = 0.918 \pm 0.007$ ppm. The groupings —CHD_2 and —CD_3 are easily recognised because each additional deuterium atom gives rise to an α-shift of -20.7 ppb and the resonances are well separated. For highly exchanged products, such as those formed over rhodium catalysts,

Table 1. Product distributions for exchange on palladium

reactant...	DMP			TMB		TMP
temp./K...	429		460	424		456
MS distribution of ions at 10% conversion		calc. A			calc. B	
D_1	9.54	(9.51)	9.33	9.46	(9.52)	9.05
D_2	0.43	(0.45)	0.64	0.52	(0.47)	0.62
D_3	0.03	(0.01)	0.03	0.02	(0.01)	0.11
$\geqslant D_4$	—	—	—	—	—	0.03
M	1.00	—	1.03	1.03	—	1.16
conversion for n.m.r. analyses...	—	—	20.3	—	—	19.8
%D in groupings		calc. C			calc. D	
$—CH_2D$		(95)	93		(97)	88
$—CHD_2$		(5)	7		(3)	6
$—CD_3$			—			3
$—CD_3 + \gamma$ shifts			—			3

The calculated distributions A and B, for the pseudoparent ions are those expected for stepwise exchange at 10% conversion for 9 and 15 exchangeable H atoms. Distribution C corresponds to a random distribution with a chance $d = 0.0256$ of a D atom in each position based on the mass spectrometrically determined average D-content of the $C_4X_9^+$ ions of 0.231. Distribution D corresponds to a random distribution with a chance $d = 0.0165$ of a D in 15 positions based on the mass spectrometrically determined average D-content of the $C_8H_2X_{15}^+$ ions of 0.248.

Table 2. Product distributions for exchange on platinum and iridium at 15% conversion

catalyst...	platinum				iridium		
reactant...	DMP	TMB		TMP	DMP	TMB	TMP
temp./K...	394	395	423	424	392	394	422
composition of ions							
D_1	10.30	8.69	6.12	4.99	12.78	11.22	12.01
D_2	2.66	3.25	3.03	2.91	1.86	2.74	2.03
D_3	1.30	1.45	1.52	1.79	0.32	0.67	0.42
D_4	0.44	0.73	1.08	1.28	0.04	0.12	0.16
D_5	0.18	0.32	0.78	0.98	—	0.03	0.09
D_6	0.08	0.19	0.60	0.74	—	0.02	0.06
D_7	0.04	0.11	0.43	0.59	—	0.01	0.06
D_8	0.03	0.08	0.35	0.49	—	0.01	0.06
D_9	0.02	0.07	0.30	0.41	—	0.05	0.06
D_{10}	—	0.04	0.26	0.32	—	0.02	0.06
D_{11}	—	0.03	0.19	0.19	—	0.02	—
D_{12}	—	0.03	0.15	0.16	—	0.04	—
D_{13}	—	0.01	0.11	0.11	—	0.02	—
D_{14}	—	0.00	0.07	0.04	—	0.01	—
D_{15}	—	0.00	0.00	—	—	0.02	—
M	1.45	1.75	2.24	2.64	1.11	1.35	1.27

Table 3. Product distributions for exchange on rhodium at 10% conversion

reactant...	DMP		TMB		TMP	
temp./K... composition of ions	393	423	394	424	393[a]	426
D_1	6.80	4.18	6.47	4.82	6.24	4.32
D_2	1.30	1.35	1.22	1.13	1.17	1.13
D_3	0.95	1.29	0.42	0.51	0.49	0.62
D_4	0.36	0.72	0.14	0.17	0.25	0.39
D_5	0.18	0.51	0.05	0.15	0.25	0.43
D_6	0.12	0.44	0.03	0.14	0.21	0.36
D_7	0.10	0.44	0.04	0.18	0.21	0.43
D_8	0.10	0.52	0.09	0.29	0.33	0.61
D_9	0.10	0.55	0.22	0.31	0.25	0.51
D_{10}	—	—	0.12	0.38	0.18	0.45
D_{11}	—	—	0.13	0.40	0.21	0.42
D_{12}	—	—	0.28	0.50	0.13	0.20
D_{13}	—	—	0.16	0.41	0.05	0.10
D_{14}	—	—	0.25	0.42	—	—
D_{15}	—	—	0.35	(0.18)[b]	—	—
M	1.51	(3.2)[b]	3.79	(4.6)[b]	2.50	3.54

[a] The ratio of D_2:hydrocarbon in this experiment was 5:1 compared with 8:1 in the others.
[b] Values which were subject to greater error.

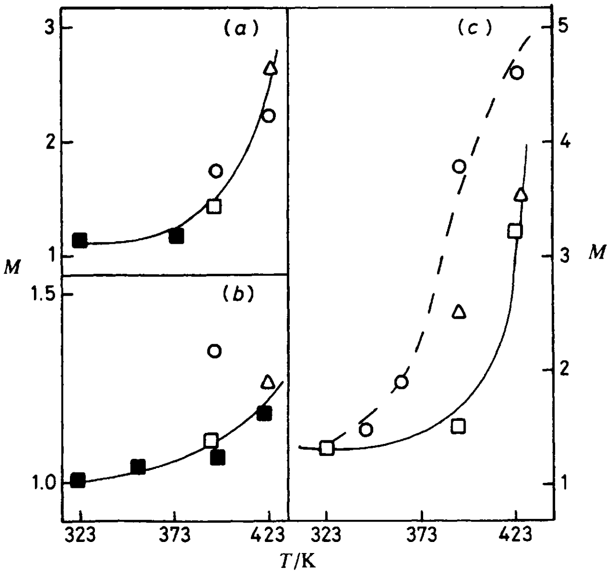

Fig. 4. Influence of temperature on the values of M, measuring the multiplicity of exchange, for reactions on (*a*) platinum, (*b*) iridium and (*c*) rhodium catalysts: squares, DMP; circles, TMB; triangles, TMP. Filled symbols are results obtained previously for DMP on platinum[5,10] or iridium.[18]

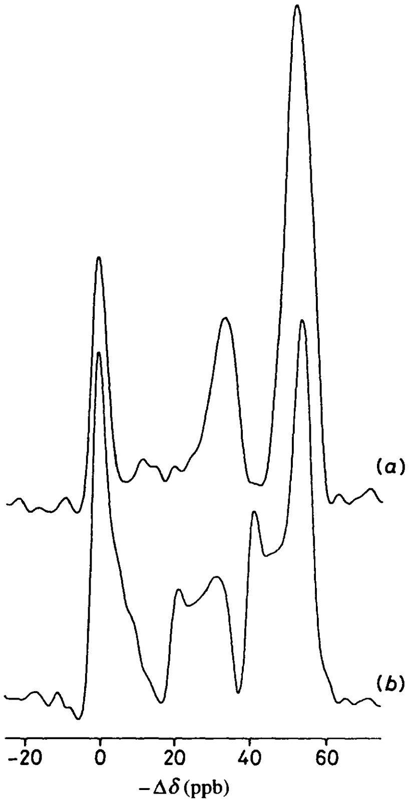

Fig. 5. N.m.r. spectra for DMP and TMB exchanged over rhodium: (*a*), TMB 15.9% reacted at 424 K using 5:1 ratio of D_2:hydrocarbon and highest-frequency peak at $\delta = 0.869$ ppm; (*b*), DMP 12% reacted at 423 K using 8:1 ratio of D_2:hydrocarbon with highest-frequency peak at $\delta = 0.924$ ppm with respect to TMS.

additional peaks are found corresponding to the groupings $—CHD_2$ and $—CD_3$ in molecules which are substantially exchanged in the other methyl groups as well. The position of these resonances are influenced by γ isotopic shifts due to the deuterium atoms in the other methyl groups. Even though the individual γ shifts are small, the combination of a number of them leads to a total shift which is sufficient to enable a separate resonance to be detected. An example of such a spectrum is shown in fig. 5(*b*); the separation between the two peaks for the $—CHD_2$ groupings is -10.2 ppb and that for the two peaks for $—CD_3$ is -12.7 ppb. A comparison of this and other spectra with the relevant mass-spectrometric analyses indicated that the value for each γ-shift was *ca.* -1.7 ppb.

TMB

The chemical shift for the $—CH_2D$ was $\delta = 0.865 \pm 0.007$ ppm, and spectra of the products from three reactions are shown in fig. 5–7. Small peaks from the spectra from the rhodium experiments indicated that the α-shift was *ca.* -20 ppb and the total shifts for the highly exchanged molecules were -53.4 and -55.1 ppb. If the two α shifts accounted for -40 ppb of these displacements the remaining -14 ppb represented the combined effect of up to six γ and nine δ shifts.

The spectrum of the relatively highly exchanged sample from the reaction over platinum at 423 K, fig. 6, shows just three slightly broadened resonances corresponding

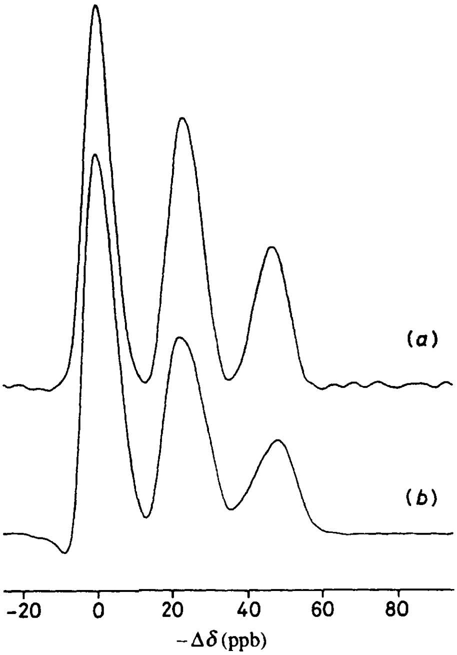

Fig. 6. N.m.r. spectra for TMB and TMP substantially exchanged over platinum: (*a*), TMP 49.3% reacted at 424 K and highest-frequency peak at $\delta = 0.983$; (*b*), TMB 70.3% reacted at 423 K with highest-frequency peak at $\delta = 0.868$ with respect to TMS.

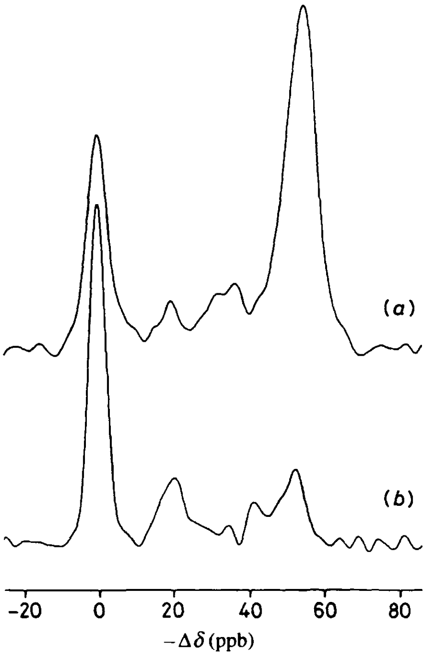

Fig. 7. N.m.r. spectra for TMB and TMP exchanged over rhodium: (*a*), TMB 13.7% reacted at 393 K using a 4:1 ratio of D_2:hydrocarbon and highest-frequency peak at $\delta = 0.858$ ppm; (*b*), TMP 15.9% reacted at 394 K using a 5:1 ratio of D_2:hydrocarbon with the highest-frequency peak at $\delta = 0.983$ with respect to TMS.

Table 4. Distributions of deuterium atoms in the methyl groups in the products from reactions over platinum and iridium

Catalyst	platinum			iridium
reaction...	DMP	TMB	TMP	TMP
temp./K...	431	423	424	422
% conversion...	14.4	70.3	49.3	19.0
M_x[a]	1.86	3.24	3.43	1.58
grouping	percentage of total deuterium			
$—CH_2D$	63	50	44	91
$—CHD_2$	25	34	37	9
$—CD_3$	12	16	19	0

[a] M_x is the mean number of deuterium atoms in the pseudoparent ions from exchanged molecules.

to $—CH_2D$, $—CHD_2$ and $—CD_3$ groups. The isotopic shifts associated with the latter peaks were −22.4 and −48.5 ppb and so they correspond to the usual α shifts together with small contributions from the minor γ and δ shifts.

TMP

The chemical shift for primary deuterium in TMP was 0.979 ± 0.007 ppm. A spectrum using the naturally occurring deuterium in the molecules showed that the chemical shift for deuterium in the methylene group was 1.24 ppm, but no exchange was detected in this position in any of the reactions. Spectra of products from exchange over palladium and iridium showed that the α-shift for the grouping $—CHD_2$ was −20.7 ppb, a value identical to that found for DMP. A spectrum for substantially exchanged TMP over platinum is shown in fig. 6 and gave the usual resonances for $—CH_2D$, $—CHD_2$ and $—CD_3$ with some contributions from minor isotopic shifts as the displacements were −23.2 and −46.7 ppb.

Part of the spectrum for TMP reacted over rhodium is shown in fig. 7, but two small peaks containing 7% of the total deuterium observed by n.m.r. were also present with chemical shifts of 1.445 and 1.484 ppm. In a second experiment using rhodium, 6% of the deuterium was associated with a small peak at 1.438 ppm. These results show unequivocally that exchange over rhodium was accompanied by other reactions such as isomerisation with the peaks in the region of $\delta = 1.45$ ppm representing secondary (or tertiary) deuterium atoms in the products. Since the isomerised products were likely to contain primary deuterium atoms as well they probably contributed to some of the small peaks in the spectrum, shown in fig. 7, which was therefore not attributable solely to primary deuterium in exchanged TMP.

Distributions of Primary Deuterium Atoms in Products

Results for the distributions of the deuterium atoms in different groupings for products from reaction over palladium are given in the lower part of table 1. Corresponding results for reactions over platinum and iridium are shown in table 4 and the more detailed analyses made for rhodium are presented in table 5.

Table 5. Distributions of deuterium atoms in the methyl groups in the products from reactions over rhodium

reactant...	DMP	TMB		TMP
temp./K...	423	394[a]	423	394
% conversion...	12.0	13.7	15.9	15.9
M_x[b]	3.18	2.98	4.63	2.61
grouping	percentage of total deuterium			
$—CH_2D$	22.6	25.8	16.4	53.5
$—CH_2D$+minor shifts	7.2	1.3	4.6	—
$—CHD_2$	8.6	3.6	2.0	16.5
$—CHD_2$+minor shifts	12.8	4.5	23.0	1.4[c]
$—CD_3$	13.3	6.6	0.0	5.8
$—CD_3$+minor shifts	35.5	58.2	54.0	15.7[c]
	100.0	100.0	100.0	92.9[d]

[a] The D_2:hydrocarbon ratio was 4:1 in this experiment. [b] M_x is the mean number of deuterium atoms in the pseudoparent ions from exchanged molecules. [c] These percentages probably include some primary deuterium atoms from isomerised products. [d] Some 7% of the total deuterium was present as secondary or tertiary atoms in isomerised products.

Discussion

Reactions other than Exchange

The work of Finlayson *et al.*[15] has shown that TMP will undergo cyclisation or isomerisation on sintered films of iridium, palladium, platinum or rhodium at temperatures only slightly greater than those used in the present investigation. Sintered films proved useful for their purpose which was to observe the deuterium content of the products from the other reactions without the complications from too much exchange of TMP. The supported catalysts we used appear to have given us the results we wanted, *i.e.* exchange without other reactions, except in the case of rhodium. The presence of some 6–7% of the total deuterium in the products from the TMP–rhodium system in n.m.r. peaks with $\delta = 1.45$ ppm was evidence of isomerisation but did not provide sufficient data to identify the products. Finlayson *et al.*[15] found that 2,2,5-trimethylhexane was the major product over sintered rhodium at 513 K and obtained evidence for a D_{11} ion ($m/e = 124$) in the relevant mass spectrum. Our results for reaction of TMP over rhodium at 393 K show small maxima for the D_8 and D_{11} ions, table 3, which may have resulted from isomerised products. Since the peaks around $\delta = 1.45$ ppm would have represented secondary or tertiary deuterium atoms in the isomerised products it is probable that primary deuterium atoms in these products contributed to the same region of the n.m.r. spectrum as the primary atoms in exchanged TMP, as suggested in table 5.

No evidence for isomerisation of DMP or TMB was found in our work over rhodium or the other three metals and it is of interest to consider why only TMP should react in this way. The results reported by Finlayson *et al.*[15] provide a possible explanation. The main type of isomerisation observed with TMP over rhodium films was the formation of 2,2,5-trimethylhexane and the mechanism was thought to involve a 1,2-neopentyl shift of an adsorbed alkyl species. This type of reaction cannot occur with the smaller molecules DMP and TMB which would have to isomerise by a 1,2-methyl shift: a reaction which occurs less readily on rhodium films than the neopentyl shift.[15]

Palladium

The results in table 1 show that the most important reaction with all three compounds over palladium was stepwise exchange. With DMP, even at 460 K, the agreement between the mass-spectrometric distribution of deutero-ions and the calculated random values is good and the amount of deuterium in $—CHD_2$ groups is close to the expected value. On the other hand, with TMP at 456 K there appears to be a small contribution either from multiple exchange or possibly even from isomerisation, *cf.* results[15] with sintered films at 468 K. Nevertheless, it is clear that the dominant mechanism with all three compounds on palladium is the reversible formation of adsorbed alkyl intermediates and that little dissociation to either $\alpha\alpha$- or $\alpha\gamma$-adsorbed species takes place. The behaviour of palladium with the hydrocarbons containing quaternary carbon atoms is in marked contrast to the very extensive multiple exchange found with other hydrocarbons[1, 2] which can lose hydrogen atoms to adsorbed alkene and so form multiply exchanged products by the $\alpha\beta$-process, *i.e.* the interconversion between adsorbed alkyl and adsorbed alkene intermediates.

The kinetically well behaved exchange reactions observed with palladium, fig. 1, and the identical rates and common activation energy for all three reactants, fig. 3, may be a consequence of the fact that stepwise exchange and little else is occurring over palladium in the temperature range used. The carbon–hydrogen bond strengths in the methyl groups attached to the quaternary carbon atoms are presumably similar for all the reactants and the minor differences in the nature of the rest of the molecules have no influence on the reaction over palladium.

Rhodium

This metal gives the greatest contributions from multiple exchange with all three reactants as shown by the mass spectrometric distributions in table 3, and the n.m.r. analyses in table 5 and fig. 5 and 7. Process II, multiple exchange in a single methyl group, leading to D_2 and D_3 ions and forming the groupings $—CHD_2$ and $—CD_3$ without substantial exchange in the rest of the molecule is an important component of the reactions particularly with DMP but also with TMP and to a lesser extent TMB.

The difference between the reactants in regard to the extent and contribution of more general multiple exchange over rhodium is demonstrated most clearly in the values in fig. 4 of M which are higher for TMB than for DMP or TMP. The interest lies in the extent to which ions with 10 or more deuterium atoms are observed in the early stages of reaction with TMB or TMP. Such ions provide evidence for initial products resulting from a multiple exchange process capable of exchanging both ends of the molecules. A mechanism involving $\alpha\delta$-adsorbed intermediates is necessary to give this kind of exchange with TMB. Two mechanisms might operate with TMP, multiple exchange through $\alpha\varepsilon$-adsorbed species or propagation of the exchange over the whole molecule through $\alpha\gamma$-species involving the central $—CH_2—$ group. The latter can be ruled out since no evidence for deuterium atoms in the methylene group was found in the n.m.r. spectra of the products. Bearing in mind possible contributions from multiply exchanged isomerisation products of TMP, we do not believe that sufficient D_{10} or higher ions are observed to indicate that $\alpha\varepsilon$-diadsorbed species contribute significantly to the exchange of this molecule over rhodium. In other words, TMP and DMP show similar extents of general multiple exchange involving $\alpha\gamma$-intermediates which can lead to complete exchange of DMP and exchange limited to the three methyl groups at one end only of TMP. The situation is different with TMB which gives initially more ions in the range from D_{10} to D_{15} than from D_4 to D_9. Obviously the exchange process can propagate over all six methyl groups and this requires a mechanism involving interconversion between alkyl and $\alpha\delta$-diadsorbed intermediates which we call process IV. The maxima in the distributions of the ions at D_9, D_{12} and D_{15} which can be seen in the results for reaction at 394 K in table 3 provide evidence of another aspect of process IV. There must be some means which helps to complete the exchange of the methyl groups involved in the $\alpha\delta$-bonding to the catalyst surface. A likely explanation of this behaviour is that $\alpha\delta$-intermediates can interconvert with $\alpha\alpha\delta$-adsorbed or more highly dissociated forms. The shape of the distributions of ions suggests that rhodium forms $\alpha\delta$-adsorbed species more readily than $\alpha\gamma$-adsorbed intermediates with TMB. The n.m.r. traces in fig. 5 and 7 show that TMB gives more of the —CD_3 grouping with high exchange in the remainder of the molecule than either DMP or TMP and this is confirmed by the quantitative results in table 5. All these results combine to demonstrate that with TMB over rhodium the main mechanisms of exchange are stepwise exchange together with process IV and a minor contribution from process II. On the other hand with DMP and TMP, stepwise exchange and processes II and III occur together with some isomerisation of TMP.

Self-poisoning of the exchange reactions appears to be a characteristic of rhodium catalysts and as shown in fig. 2 the influence of self-poisoning is greater with DMP and least with TMP. The explanation is probably the formation of more highly dissociated adsorbed species which are more strongly adsorbed and less readily rehydrogenated. Such species may be important for hydrogenolysis which is known[16] to occur with DMP at 463 K, *i.e.* only some 40 K above the highest temperature used in this work with rhodium. It is not surprising that the results for rhodium in fig. 3 show the greatest scatter of any of four metals from a common Arrhenius line for the three reactants because of the variety of mechanisms and possible complications at higher temperatures from self-poisoning of the exchange reactions.

Iridium

Results in tables 2 and 4 show that the dominant process with all three reactants over iridium is stepwise exchange with a minor contribution from process II, methyl-group exchange. General multiple exchange is just detectable and appears to be more extensive with TMB, see table 2 and fig. 4, than with the other reactants. So, as with rhodium, $\alpha\delta$-adsorbed species may be formed more readily than $\alpha\gamma$-species, but neither plays a substantial part in the mechanism of exchange over iridium.

Platinum

Results in table 2 and 4 and fig. 6 show that for all three reactants the mechanisms in order of importance are stepwise exchange, process II and process III. The character of process III is not the same on platinum as on rhodium. The amounts of the ions from D_4 upwards observed in reactions over platinum decrease with increasing deuterium content and the average number of deuterium atoms acquired by any molecule undergoing the $\alpha\gamma$-type of exchange over platinum is not as great as with rhodium. This implies that the number of alkyl to $\alpha\gamma$-adsorbed interconversions before an exchanged molecule desorbs is not as large on platinum as on rhodium. The M values for all three reactants are similar over platinum and the extent of multiple exchange depends mainly on the temperature and not on the nature of the hydrocarbon. The results in fig. 6 show that the n.m.r. traces for fairly extensively reacted TMB and TMP are similar and the resonances for —CHD_2 and —CD_3 groupings are broadened but not resolved into components. Clearly, the average number of γ isotopic shifts is insufficient to give rise to separate resonances as was found with rhodium. At 423 K, TMB and TMP both give *ca.* 0.8% of ions in the range from D_{10} to D_{14} at 15% conversion, see table 2, but this does not amount to significant evidence for a contribution from $\alpha\delta$- of $\alpha\varepsilon$-adsorbed intermediates since 1% of the molecule will have undergone repeated reaction at this conversion.

Relative Rates

The results in fig. 3 permit a comparison of the relative activities of the four metals for exchange of the three hydrocarbons. The ratios of the activities at 400 K ignoring any differences in the degree of dispersion of the catalysts are 260:120:60:1 for Pt:Ir:Rh:Pd. These ratios are in broad agreement with results from earlier studies[10, 11] with DMP and are influenced markedly by choice of temperature because of the different activation energies on the four metals.

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