JOURNAL OF CATALYSIS 52, 206–217 (1978)

Orientation in Metal-Catalyzed Hydrogen Exchange between Alkanes, Naphthalene, or Biphenyl and Deuterium or Deuterium Oxide

MERVYN A. LONG,*,[1] RICHARD B. MOYES,* PETER B. WELLS,*
AND JOHN L. GARNETT†

* *Department of Chemistry, The University, Hull, HU6 7RX, England, and* † *School of Chemistry, University of New South Wales, Kensington, New South Wales, Australia*

Received May 13, 1977

Hydrogen isotope exchange between deuterium gas and protium in hexane, pentane, 2-methylbutane, 2-methylpentane, 3-methylpentane, 2,3-dimethylbutane, and 2,4-dimethylpentane has been catalyzed by clean platinum films (70–100°C). A selection of these reactions has been catalyzed by films of rhodium and iridium (typically −13 to −35°C). In all cases, multiple exchange occurred. Product analysis by mass and proton NMR spectroscopy showed that exchange in methylene and methine groups was more rapid than that in methyl groups. A similar orientation effect was observed in reactions over platinum powder but not over platinum–alumina. For exchange between deuterium oxide and hexane catalyzed by platinum films at 200°C, the rate of exchange in methyl groups exceeded that in methylene groups. It is proposed that preferential exchange in methylene and methine groups is normal behavior during alkane exchange with molecular deuterium over these platinum metals when their surfaces (i) are initially clean or (ii) contain several adjacent sites which are unperturbed by the presence of any electronegative adsorbed species. In these cases, multiple exchange may occur via the interconversion of C_nH_{2n+x}(ads) and C_nH_{2n+x-1}(ads), where x is probably 1, but may be zero or negative. Preferential exchange in the methyl groups of hexane results from contamination of the surface by adsorbed D_2O, OD, or O; this may be a geometric effect or an electronic effect, depending on the magnitude of the surface coverage of water, which is unknown. It is proposed that, under these circumstances, alkane is adsorbed as a charge-transfer state, and multiple exchange occurs via the interconversion of C_nH_{2n+2}(ads) and C_nH_{2n+1}(ads) in a manner analogous to that proposed earlier for catalysis by chloroplatinate ion in deuterated solvent. Orientation in the exchange between deuterium gas and naphthalene or biphenyl catalyzed by films of platinum and iridium does *not* differ from that observed in exchanges where the isotope source is deuterium oxide or deuterated solvent, but the M value calculated for exchange in naphthalene is higher than that previously reported.

INTRODUCTION

Certain classes of hydrocarbon reactions, including hydrogen isotope exchange, hydrogenation, and double-bond migration, can be catalyzed both heterogeneously by Group VIII metal surfaces and homogeneously by complexes of these metals in solution. In such cases, it is important to establish whether common mechanisms operate in the heterogeneous and homogeneous systems, and hence the extent to which a common chemistry prevails. From such comparisons it may also be possible to assess whether or not an adsorption site in a metal surface has the properties exhibited by a single metal atom in the environment of a defined complex.

Reactions involving hydrogen isotope

---

[1] On leave from the University of New South Wales.

0021-9517/78/0522-0206$02.00/0

exchange are valuable for such comparisons, particularly when the exchange is faster than any other competing process such as hydrogenation. Exchange of protium for deuterium in aromatic hydrocarbons has been much studied from this point of view and similarities between the mechanisms of these reactions, as performed with heterogeneous and with homogeneous catalysts, have been emphasized (*1*, *2*).

Exchange of protium for deuterium in alkanes is another reaction which offers the opportunity for such a comparison. A large number of transition metals are active for the *heterogeneous* catalysis of hydrogen isotope exchange in alkanes (*3*); in these studies it has been customary to use molecular deuterium as the isotope source. *Homogeneous* catalysts for this reaction are presently restricted to complex ions of platinum (*4–7*), iridium (*8*), and rhodium (*9*), and since these ions are susceptible to reduction by deuterium gas the source of the isotope in these reactions has usually been the solvent. In both the heterogeneous and the homogeneous systems all protium atoms in simple alkanes undergo exchange for deuterium. Analysis of the products of homogeneous reactions by mass and proton NMR spectrometry has shown that protium atoms in a methyl group exchange more rapidly than those in a methylene group, and that the exchange rate is slowest in a methine group (*2*, *6*). A mechanism which interprets this pattern of behavior has been proposed (*2*, *6*, *7*).

Most investigations with heterogeneous catalysts were carried out before NMR spectroscopy was widely available, and hence a systematic study as to whether such preferential exchange occurs in these systems has not been reported. Two isolated reports of preferential exchange in alkanes have been made. First, Kauder and Taylor concluded, from an examination of the fragment ions in the mass spectra, that preferential exchange of protium atoms of the methylene group occurred during exchange in propane over platinum gauze (*10*); second, Kemball presented kinetic evidence for the preferential exchange of the secondary hydrogen atoms in propane and of the tertiary hydrogen atom in isobutane in exchange reactions over nickel film (*11*). However, the first of these methods is not reliable and the second is not sensitive as a general method for the detection of preferential exchange in alkanes. Consequently, in the present work, we have used a combination of mass and NMR spectroscopies, which provides the necessary sensitivity to investigative preferential exchange in alkanes catalyzed by evaporated metal films. Orientation effects are reported, and specific conditions for the reversal of the direction of the orientation when the isotope source is changed from D_2 to D_2O are described. The metals used are Pt, Ir, and Rh (those employed in the homogeneous reactions), with the emphasis once again on platinum-catalyzed reactions.

Exchange of protium in alkane for deuterium from D_2O has been little studied. Reaction of propane with D_2O over nickel film at 300°C has been observed to give carbon dioxide and methane as products, but no isotopic exchange in the alkane occurred (*12*).

In view of (i) the comparisons already made in the literature of homogeneous and heterogeneous exchange in aromatic hydrocarbons where the solvent or D_2O is the isotope source (*1*, *2*) and (ii) the unexpected orientation in exchange between alkanes and gaseous deuterium over clean films (this work), it was felt necessary to determine whether or not exchange between two typical aromatics (naphthalene and biphenyl) and gaseous deuterium over clean platinum and iridium films conformed to that previously reported. Confirmation of most of the previously reported characteristics for these reactions (*13*) was obtained.

EXPERIMENTAL

Materials. Platinum, iridium, and rhodium wires (Johnson Matthey) were Specpure grade. Deuterium gas was purified by passage through a heated palladium–silver alloy thimble. Deuterium oxide, 99% (Norsk Hydro), hexachloroplatinic acid, and the various hydrocarbons (Koch–Light) were used as received. The only impurities detected in the hydrocarbons were isomers; no impurity concentration exceeded 1%.

Apparatus. Two ultrahigh vacuum systems were used, one fitted with an ion pump and the other with a polyphenyl ether oil diffusion pump. In each, the Pyrex reaction vessel (485 ml) was attached to a stainless steel flange which, in turn, was sealed to the stainless steel vacuum system by a gold ring. In one system, products from the vessel were leaked to a Vacuum Generators MM6 magnetic deflection mass spectrometer; in the other system the vessel was connected to a Vacuum Generators Q7 quadrupole mass spectrometer. Proton magnetic resonance analysis of products was achieved using a JEOL 100-MHz spectrometer.

Catalyst preparation. Evaporated metal films were prepared by a standard method (*14*), all metal and glass surfaces having previously been outgassed carefully at 10^{-8} Torr. Pressures during film deposition did not rise above 10^{-7} Torr. Typical film weights were Rh, 35 mg; Ir, 35 mg; and Pt, 15 mg.

A platinum powder was prepared by the reduction of an aqueous solution of H_2PtCl_6 with $NaBH_4$; the powder was thoroughly washed and dried *in vacuo* at 150°C.

Platinum supported on sulfate-free α-alumina (10% w/w) was prepared by impregnation of the support with hexachloroplatinic acid and subsequent reduction in hydrogen at 600°C for 15 hr.

Reaction procedure. In a typical procedure, carefully degassed hydrocarbon vapor (2.64×10^{-4} mole) was distilled into the reaction vessel, and deuterium was admitted to a pressure of 30 Torr, the glass section of the vessel being maintained at 77 K. This provided a deuterium:hydrocarbon ratio of ca. 9.4:1. The vessel was then warmed rapidly to the reaction temperature.

When the isotope source was deuterium oxide, the desired quantity was measured volumetrically, degassed, and distilled into the vessel after the hydrocarbon.

The progress of exchange was followed by mass spectrometry until the extent of deuterium incorporation was sufficient for orientation effects to be discernible in the proton NMR spectrum; the hydrocarbon vapor was then condensed into a suitable sample tube containing the solvent (CCl_4). Proton resonance intensities were determined by repeated instrumental integration following careful tuning of the spectrometer, and the ratio (methyl:methylene:methine) was compared to that obtained for hydrocarbon having only the natural abundance of deuterium. Analyses with the natural materials were performed regularly to standardize the integration method, and so to maximize the accuracy of the determination.

The deuterium contents of methyl, methylene, and methine groups recorded in the tables were calculated by combining a knowledge of the total deuterium content per molecule for a sample, $10^{-2}\phi$ [see Eq. (2)], as calculated from the mass spectrum, with a knowledge of the integrated proton resonances (methyl:methylene:methine) determined from the proton NMR spectrum.

In a limited number of cases, values of the multiple exchange parameter, *M*, were determined graphically by the method of Kemball (*15*). The relevant plots were linear. In all other cases, *M* values were calculated by use of Eq. (1):

$$M = \frac{\phi_\infty}{100} \cdot \frac{\log \phi_\infty - \log (\phi_\infty - \phi_t)}{\log (100) - \log (d_o)_t}, \quad (1)$$

where

$$\phi = \sum_{i=0}^{i=n} i(d_i). \qquad (2)$$

Quantities ϕ_t and ϕ_∞ are the values of ϕ at time t and at equilibrium, respectively, and (d_i) is the percentage in the sample of the isotopic species containing i deuterium atoms.

RESULTS

Exchange between Hexane and Deuterium

Results for exchange between hexane and deuterium gas catalyzed by films of rhodium, iridium, and platinum, powdered platinum, and platinum–alumina are shown in Table 1. Exchange was permitted to proceed to a substantial extent, so that the most favorable conditions for detecting intensity changes in the NMR spectrum might pertain. All possible deuterium-labeled hexanes were formed. Figures 1a and b show in histographic form typical distributions of products from rhodium- and platinum-catalyzed reactions.

The activities of the metals, as reflected by the temperature required to effect a given rate of exchange, diminished in the order Rh > Ir > Pt. Exchange in each case was highly multiple in character, initially yielding a high proportion of fully deuterated species, and a further process yielding hexane of low deuterium number also occurred (see Fig. 1). Rhodium and, to a lesser extent, iridium exhibited a tendency for the preferential formation of hexane-d_2 (see Fig. 1a). The three metals gave M values which diminished in the sequence Pt > Ir > Rh; M values for reactions catalyzed by platinum increased with increasing temperature from 8.3 at 50°C to 12.3 at 200°C. These results and trends follow those previously reported for alkane exchange over these metals (*16, 17*).

Values of the ratio of the integrated proton resonances, methylene:methyl, for each reaction of hexane are given in Table 1,

TABLE 1

Exchange between Hexane and Gaseous Deuterium

Catalyst	Temperature (°C)	Reaction time (hr)	%D in hexane		M	Ratio of integrated proton resonance (methylene: methyl)	%D in methylene groups	%D in methyl groups
			Obs.	Equil.				
Pt film	70	1.2	44	60	8.6	1.04	50	36
Rh film	−35	0.6	23	58	4.5	1.05	31	12
Ir film	−25	5.5	24	60	3.2	1.11	30	16
Pt powder[a]	50	0.8	41	60	8.3	1.06	47	34
Pt–Al_2O_3[b]	180	18	31	58	5.0	1.31	32	31
Pt film[c]	80	1.7	37	58	8.7	1.18	41	33
Pt film[d]								
Run 1	200	0.33	53	58	12.3	1.26	54	51
Run 2[e]	200	0.22	47	68	10.1	1.26	49	46
Run 3[f]	150	1.7	42	58	9.4	1.10	47	35

[a] Thirty milligrams of powder, pumped at 150°C for 9.5 hr before use.

[b] Activated at 200°C in 1 atm of H_2 for 1 hr before use.

[c] Film heated at 200°C for 1 hr before standard reaction at 80°C.

[d] Film used for three successive experiments; film pumped at 200°C for 2 hr between runs.

[e] Premixed reactants admitted at 200°C.

[f] Reactant addition by standard procedure.

together with the calculated percentage deuteration in each type of group. Random exchange would result in the ratio having the value 1.33. The substantially lower values observed indicate that there was preferential exchange of hydrogen atoms in the methylene groups for reactions over platinum, rhodium, and iridium films and over platinum powder, i.e., there was an orientation effect. However, exchange over platinum–alumina was random within experimental error (±0.03 in the ratio).

The extent of preferential methylene exchange was similar over each of the three metals studied. However, the degree of multiple exchange over platinum film was higher than that over the other metals and this, together with the high conversions employed, somewhat reduced the magnitude of the measured orientation effect. Over platinum at 200°C, where the multiplicity of the exchange is particularly high, there was a significantly lower specificity in the exchange, whereas, at lower temperatures, where M values were lower, the orientation effect was more marked.

Exchange at 150°C on a platinum film previously used at 200°C gave results similar to those obtained using a clean film at 70°C. The results show that temperature changes within this range and pretreatment of films at 200°C serve only to modify the degree of preferential exchange at the *methylene* groups; such changes in experimental variables do not provide conditions for preferential exchange at the *methyl* groups.

In view of the highly multiple nature of the exchange, it is important to assess the significance of the ratios of integrated proton resonances (see Table 1) in terms of the degree of orientation, remembering that there can be no orientation in C_6H_{14} and C_6D_{14}. A calculation was performed, using the mass spectrum of a typical hexane sample, in which it was assumed that exchange occurred in methylene groups wherever possible, e.g., $C_6H_5D_9$ was assumed to be $CH_3(CD_2)_4CH_2D$. On this basis, the distribution shown in Fig. 1a for the rhodium-catalyzed reaction at −35°C gave a calculated value for the ratio (protium in methylene groups):(protium in methyl groups) of 1.01, compared to the experimentally observed ratio of integrated proton resonances of 1.05. A further calculation, based on an assumption that a protium atom in a methylene group is twice as likely to undergo exchange as a protium atom in a methyl group, gave a value for the ratio of about 1.23. Clearly,

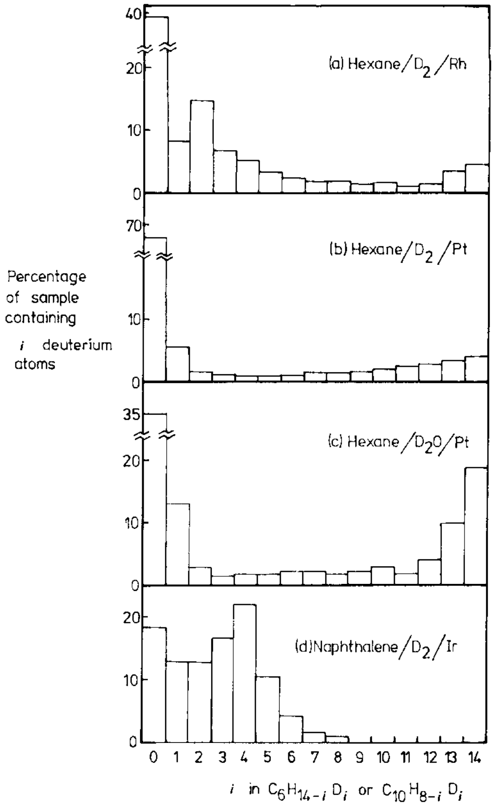


FIG. 1. Distributions of deuterium in hexane and in naphthalene (a) from reaction of hexane with D_2 over rhodium film at −35°C, 24% D in hexane; (b) from reaction of hexane with D_2 over platinum film at 70°C, 18% D in hexane; (c) from reaction of hexane with D_2O over platinum film at 200°C, 42% D in hexane; (d) from reaction of naphthalene with D_2 over iridium film at 80°C, 34% D in naphthalene.

TABLE 2

Exchange between Other Alkanes and Gaseous Deuterium

Alkane	Catalyst (film)	Temperature (°C)	Reaction time (hr)	%D in alkane		M	Ratio of integrated proton resonances				%D in methine groups	%D in methylene groups	%D in methyl groups
				Obs.	Equil.		Methine methylene	Methine + methylene methyl	Methylene: methyl	Methine: methyl			
Pentane	Pt	70	2.5	42	60	8.1			0.77			50	35
	Rh	−25	0.8	27	61	4.5			0.76			37	17
	Ir	−23	6.0	32	61	4.2			0.77			41	23
2-Methylbutane	Pt	100	1.0	35	61	6.0	0.41	0.29			48	37	33
	Pt[a]	78	0.5	31	60	5.5	0.51	0.20			59	59	31
	Rh	−34	1.8	38	61	3.8		0.28			39[b]		28
2-Methylpentane	Pt	85	2.0	27	58	6.2		0.53			29[b]		26
3-Methylpentane	Ir	−34	5.0	22	60	3.3		0.42			35[b]		15
2,3-Dimethylbutane	Pt	80	0.8	39	58	5.9				0.14	47		38
	Rh	−35	3.8	30	58	4.0				0.12	47		27
2,4-Dimethylpentane	Pt	85	0.5	40	58	7.1	0.97	0.26			51	49	36
	Pt	70	1.1	29	58	5.5	1.13	0.19			51	57	20
	Rh	−13	1.0	26	58	4.1	0.96	0.20			51	49	17
	IR	30	1.0	22	58	3.1	1.12	0.22			41	47	15

[a] Thirty milligrams of powder, pumped at 150°C for 0.5 hr before use.

[b] Percentage D in methine and methylene groups together.

therefore, the orientation of the exchange in hexane molecules which have not undergone a high degree of multiple exchange is *heavily* in favor of the methylene groups, much more so than the ratio of integrated proton resonances might suggest at first sight.

Despite the preferential exchange in methylene groups, the usual function plots (*15*) for uniform exchange, the slopes of which represent the initial rate of entry of deuterium into hexane, and the initial rate of disappearance of C_6H_{14} were linear (Pt film, 70°C; Rh film, −35°C; conversion = 20 to 30%). However, this is not unexpected in view of the latest assessment of the sensitivity of this kinetic method for detecting differential rates of exchange in molecules having nonequivalent hydrogen atoms (*18*).

Finally, it should be noted that (a) a number of blank runs in which protium gas was substituted for deuterium and (b) runs in which exchange was allowed to proceed to equilibrium each gave ratios of integrated proton resonances, methylene : methyl, of 1.33 (±0.02) : 1. Gas–liquid chromatographic analysis confirmed that hexane was not converted to other hydrocarbons during exchange.

Exchange between Other Alkanes and Deuterium

Results for the exchange of other alkanes with gaseous deuterium catalyzed by films of rhodium, iridium, and platinum are shown in Table 2. Exchange in pentane resembled that in hexane, protium in methylene groups exchanging more rapidly than that in methyl groups. For exchange in branched-chain alkanes, exchange of protium in methyl groups was again slower than that in methylene or methine groups. Attempts to determine the relative rates of exchange at methylene and methine positions by proton NMR were hindered because of the inaccuracy in the measurement of the methine proton resonance. However, the difference in the rate of exchange at these two positions was not substantial.

Exchange between Aromatic Hydrocarbons and Deuterium

Exchange of protium for deuterium in naphthalene and in biphenyl was catalyzed by iridium and platinum films (Table 3). The temperatures used were those required to provide an adequate vapor pressure of the aromatic hydrocarbon. The NMR spectra revealed that naphthalene underwent preferential exchange at the β positions, and this was supported by a marked cutoff in the mass spectra after $C_{10}H_4D_4$ (Fig. 1d). A trace of tetralin was formed.

Table 3 shows that exchange between biphenyl and deuterium was most rapid at the *meta* and *para* positions taken together, and a cutoff in the distribution at $C_{12}H_4D_6$

TABLE 3

Exchange between Typical Aromatic Hydrocarbons and Gaseous Deuterium

Aromatic hydrocarbon	Catalyst (film)	Temperature (°C)	Reaction time (hr)	%D in aromatic		*M*	Ratio of integrated proton resonances		%D in various positions			
				Obs.	Equil.		α/β	*ortho*/(*meta* + *para*)	α	β	*ortho*	(*meta* + *para*)
Naphthalene	Pt	190	2.0	20	70	2.1	1.17		14	26		
	Ir	80	0.6	34	70	2.2	1.36		24	44		
Biphenyl	Pt	100	0.3	46	66	3.0		1.40			21	62
	Ir	80	0.1	47	66	2.6		1.36			23	62

TABLE 4

Exchange between Hexane and Gaseous D_2O or D_2 + Water Mixtures over Platinum Film

Film pretreatment	Deuterium source	Temperature (°C)	Reaction time (hr)	%D in hexane		M	Ratio of integrated proton resonances (methylene: methyl)	%D in methylene groups	%D in methyl groups
				Obs.	Equil.				
—	D_2O	200	120	48	90	7.7	1.57	45	53
—	D_2O	200	160	42	94	7.6	1.45	40	45
0.1 Torr of H_2O[a]	D_2	65	65	40	60	9.4	1.08	46	33
1.0 Torr of H_2O[a]	D_2	85	85	40	58	8.9	1.19	43	36
15 Torr of D_2O[a]	D_2	170	170	30	58	6.9	1.29	31	29

[a] Platinum film exposed to water vapor at stated pressure for 10 sec before admission of hexane and deuterium.

indicated that the reactivities at the *meta* and *para* positions were comparable.

Exchange between Hexane and Deuterium Oxide

Results for the platinum-catalyzed exchange between hexane and deuterium oxide and between hexane and water/D_2 mixtures are shown in Table 4. Exchange with deuterium oxide required a temperature of 200°C, and processes yielding $C_6H_{13}D$ and C_6D_{14} were evident (Fig. 1c). The amounts of the other deuterated species were considerably lower than those observed in exchange with deuterium gas (compare Figs. 1b and c), a property not reflected in the M values. The proton NMR spectra showed clearly that the rate of exchange of protium atoms in the methyl groups was faster than that of protium in the methylene groups, i.e., the reverse of the situation observed using gaseous deuterium as the isotope source. Platinum films exposed to 0.1 or 1.0 Torr of water vapor before admission of hexane and deuterium catalyzed preferential exchange of protium in methylene groups, but the degree of preferential exchange diminished as the partial pressure of water was increased (Table 4). When 15 Torr of water vapor was admitted, a temperature of 170°C was required for the achievement of a comparable rate of exchange, and the extent of preferential exchange of the methylene groups was marginal. The mass spectrum of hexane from this reaction was intermediate between that typical of exchange with gaseous deuterium and that typical of exchange with pure deuterium oxide.

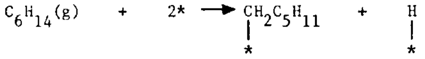
DISCUSSION

General Mechanisms of Exchange in Alkanes

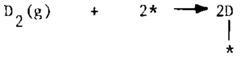
Results of recent studies of metal-catalyzed exchange of hydrogen in alkanes reveal that such exchange is seldom a random process. In some homogeneously catalyzed reactions, protium in methyl groups exchanges more rapidly than that in methylene groups (*2*, *6*, *8*), whereas in this work, under appropriate conditions, the reverse is observed. In this discussion we attempt to rationalize these observations.

Tables 1 and 2 show that exchange of H for D in methylene and in methine groups of alkanes is more rapid than that in methyl groups when the catalyst is an evaporated film of Rh, Ir, or Pt, and the isotope source is molecular deuterium.

These catalyst surfaces, having been prepared in ultrahigh vacuum, are considered to have been clean except for carbonaceous residues formed by dissociative chemisorption of the alkane. Hence preferential exchange of methylene and of methine groups appears to be the normal behavior at these clean surfaces. Furthermore, the typical adsorption site is one in which a metal atom has other surface metal atoms as neighbors, these neighbors also being available to play a role in the process by functioning as additional adsorption sites. Stepwise exchange in an alkane via Eqs. (1), (2), and (3) requires the participation of a group of at least three neighboring sites, and multiple exchange [the first step of which is shown in Eq. (4)] might require more.

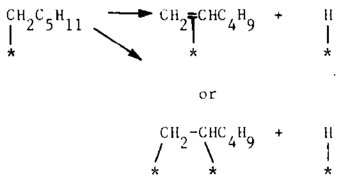


$$C_6H_{14}(g) + 2* \longrightarrow \underset{*}{\underset{|}{CH_2}}C_5H_{11} + \underset{*}{\underset{|}{H}} \quad (1)$$



$$D_2(g) + 2* \longrightarrow 2\underset{*}{\underset{|}{D}} \quad (2)$$

$$\underset{*}{\underset{|}{CH_2}}C_5H_{11} + \underset{*}{\underset{|}{D}} \longrightarrow C_6H_{13}D(g) + 2* \quad (3)$$



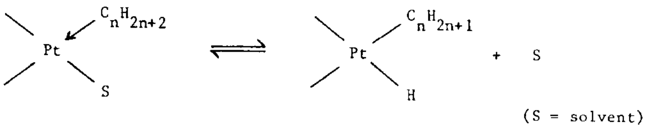
$$\underset{*}{\underset{|}{CH_2}}C_5H_{11} \longrightarrow \underset{*}{\underset{|}{CH_2{=}CHC_4H_9}} + \underset{*}{\underset{|}{H}} \quad \text{or} \quad \underset{* \qquad\; *}{CH_2\text{-}CHC_4H_9} + \underset{*}{\underset{|}{H}} \quad (4)$$

(An alternative mechanism of the Rideal–Eley type would likewise require a number of adjacent sites to effect multiple exchange.) It seems reasonable to suppose that, where (as on the surface of the clean film) the number of available adsorption sites is not artificially limited, the unit of surface responsible for the complete process of stepwise or multiple exchange is a group of several metal atoms, and each asterisk in Eqs. (1)–(4) may represent an individual surface metal atom. Under such conditions, where alkane chemisorption requires carbon–hydrogen bond rupture, the relative concentrations of primary, secondary, and tertiary alkyl intermediates initially formed will depend on the strengths of the carbon–hydrogen bonds to be broken. Since the strengths of these carbon–hydrogen bonds vary in the sequence

$$>CH- \; < \; -CH_2- \; < \; -CH_3,$$

the formation of primary alkyl groups will be disfavored, and thus the rate of exchange of protium for deuterium in methyl groups will be slower than that in methylene and methine groups. Such a situation interprets the results presented in Table 1. On this model, it is expected also that protium in methine groups should undergo exchange more rapidly than that in methylene groups, but the uncertainties in the ratios reported in Table 2 prevent a firm conclusion. However, such an expectation ignores steric effects; the situation of methine groups in branched alkanes is such that the approach of these groups to the catalyst surface may be particularly hindered.

The opposite orientation, in which the exchange of protium for deuterium was fastest in methyl groups and slowest in methine groups was first reported for reactions of alkanes catalyzed by tetrachloroplatinate ion in homogeneous aqueous solution (*2*, *6*). Here, the situation is very different from that prevailing at a clean metal surface in that the whole reaction is achieved at a single metal atom. The initial association of alkane with platinum was the rate-determining step and it was proposed that this occurred by electron donation from a filled molecular orbital of the alkane to the metal. Furthermore, the relative rates of exchange at methyl, methylene, and methine groups were related to the extent to which the relevant molecular orbital was associated with the various C–H bonds in the alkane. Thus, multiple exchange could be achieved by interconversion of the initial charge-transfer complex with an alkyl intermediate [Eq. (5)] and it was not necessary to propose the participation of coordinated alkene. The mechanism is, in most respects, analogous to that proposed earlier by Garnett and Hodges (*19, 20*) for the exchange of protium for deuterium in benzene catalyzed by tetrachloroplatinate ion.



(5)

The present work shows (Table 4) that the exchange of hexane over platinum film using deuterium oxide as the isotope source provides the same preferential exchange of protium in the methyl groups as the reaction catalyzed by tetrachloroplatinate ion. Moreover, this behavior is quite general; Table 5 shows results selected from a current study by Garnett *et al.* (*21*) of reactions catalyzed by carbon-supported rhodium, iridium, and platinum. Reactions catalyzed by ruthenium and palladium behave similarly. Thus the sequence of decreasing exchange rate, methyl > methylene > methine, appears to be general for alkane exchange catalyzed by polycrystalline metal when deuterium oxide is the isotope source. This may be interpreted either as a geometric effect or as an electronic effect.

Alternative A (geometric effect). If the fraction of the surface covered by D_2O and the products of its dissociative adsorption is high, then metal atom sites may exist singly, or in groups insufficient in size to catalyze reaction typical of the clean metal surface. In this case, single metal atom

TABLE 5

Exchange between Alkanes and Deuterium Oxide at 150°C[a]

Alkane	Catalyst[b]	Reaction time (hr)	%D in sample[c]	%D in methine groups	%D in methylene groups	%D in methyl groups
Hexane	Pt–carbon	26	37	—	32	43
	Pt powder	144	28[d]	—	22	35
	Rh–carbon	48	28[e]	—	27	30
Heptane	Ir–carbon	216	6.6	—	6.0	74
2,4-Dimethylpentane	Pt–carbon	12	21	11	18	24
	Rh–carbon	48	20	12	19	22

[a] Conditions: alkane and deuterium oxide degassed and sealed in glass vials.

[b] Carbon-supported catalysts contained 10% by weight of metal and were activated with $NaBH_4$ immediately before use; platinum–carbon supplied by Matthey Garrett; others prepared from chloride salts adsorbed on carbon; platinum powder prepared by reduction of $PtO_2 \cdot 2H_2O$ with $NaBH_4$.

[c] Percentage at equilibrium = 50%.

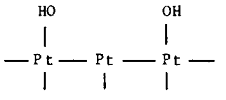
[d] $M = 6.9$.

[e] $M = 4.7$.

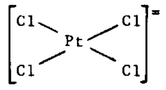
sites may exhibit a behavior similar to that of the single metal atom in tetrachloroplatinate ion, the mechanism of exchange being similar.

Alternative B (*electronic effect*). A given exposed platinum site might be polarized positively by the chemisorption of D_2O, OD, or O at a neighboring site, and this positive polarization would then facilitate the stabilization of the charge-transfer intermediate shown in Eq. (5). [Such a charge-transfer species is assumed to have no more than a transient existence when adsorption occurs at a clean metal surface to give the dissociated species shown in Eq. (1).] The surface coverage of platinum by water and the products of its dissociation under our experimental conditions is unknown. Studies of water adsorption on Fe (*22*), Co (*23*), and Ni (*24*) show that the extent of adsorption is small at low pressures (10^{-5} Torr). We must therefore consider the possibility that the coverage on the more noble metal platinum is small, even at the much higher pressures used in this work. If indeed the coverage is sufficiently small to permit numerous groupings of four, five, or six adjacent platinum atoms to exist, then behavior different from that observed over clean platinum must be attributed to a fairly long-range electronic effect of oxygen adsorption on the behavior of unoccupied sites. A somewhat comparable long-range effect has been observed for nickel and cobalt surfaces, the selectivity of which has been modified by the action of chemisorbed H_2S (*25*).

The electronic effect of chemisorbed oxygen may indeed be of critical importance even when platinum sites occur singly. If this were so, there would be formal similarities between (I) and (II), and we note that platinum complex ions having some of the chlorine ligands in (II) replaced by OH are even more active than (II) for exchange of protium for deuterium in alkanes, the orientation effect in the exchange being retained (*7*).



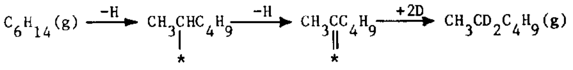
(I)



(II)

Formation of Alkane-d₂

Exchange in hexane catalyzed by films of iridium and rhodium (see Fig. 1a) gave considerable yields of $C_6H_{12}D_2$ (Fig. 1). This, coupled with the observation that exchange occurs preferentially in methylene groups, supports the suggestion (*17, 26*) that $\alpha\alpha$-diadsorbed species were formed and that exchange occurred by processes typified by Eq. (6). Whether the site for adsorption of the $\alpha\alpha$ species is a single metal atom or a pair of adjacent metal atoms is unknown.



$$\mathrm{C_6H_{14}(g)} \xrightarrow{-\mathrm{H}} \mathrm{CH_3}\underset{\underset{*}{|}}{\mathrm{C}}\mathrm{HC_4H_9} \xrightarrow{-\mathrm{H}} \mathrm{CH_3}\underset{\underset{*}{\|}}{\mathrm{C}}\mathrm{C_4H_9} \xrightarrow{+2\mathrm{D}} \mathrm{CH_3CD_2C_4H_9(g)} \tag{6}$$

Exchange in Naphthalene and Biphenyl

Exchange in naphthalene and in biphenyl (Table 3) closely resembles exchange of these compounds in aqueous solution with homogeneous and heterogeneous metal catalysts (*13, 27*). Preferential exchange at the β positions of naphthalene, observed over platinum and iridium films with molecular deuterium as the isotope source, is the same as that recorded for exchange catalyzed by tetrachloroplatinate ion (*28, 29*), various forms of bulk platinum (*13*), and other metals (*21, 30*), in which the isotope source was deuterium oxide. Likewise, deactivation at the *ortho* positions in biphenyl observed in the present work concurs with that reported for platinum-catalyzed reactions in aqueous media (*13,* *28*). The M value of 2.2 observed for naphthalene is significantly higher than the value of unity previously reported (*13*) and may result from the higher temperature used in the present study.

Thus, the similarities discussed in detail previously (*1*, *2*, *31*) for exchange of aromatics in various catalyst systems is now extended to include exchange with gaseous deuterium over clean platinum and iridium films. For exchange in aromatics (unlike that in alkanes) the mechanism is the same whether the isotope source is deuterium gas or deuterium oxide, and hence the presence of water at the surface is not a determining factor. The mechanism proposed for this exchange reaction involves the initial formation of a π complex between an aromatic molecule and a metal atom. Thus, the mechanism under all conditions analogous to that more recently proposed for exchange in alkanes *catalyzed* by chloroplatinate ion and, in this paper, for catalysis by platinum film in the presence of water.

ACKNOWLEDGMENTS

The authors thank Dr. D. F. Ewing for obtaining the proton NMR spectra, the Science Research Council for grants toward the purchase of the magnetic deflection mass spectrometer and the NMR spectrometer, and Imperial Chemical Industries for a grant for the purchase of the quadrupole mass spectrometer. M.A.L. thanks the University of New South Wales for study leave.

REFERENCES

1. Garnett, J. L., *Catal. Rev.* **5**, 229 (1972).

2. Davis, K., Garnett, J. L., Hoa, K., Kenyon, R. S., and Long, M. A., *in* "Proceedings, 5th International Congress on Catalysis." (J. W. Hightower, Ed.), Vol. 1, p. 491. North-Holland, Amsterdam, 1973.

3. Bond, G. C., "Catalysis by Metals," p. 183. (Academic Press, New York, 1962).

4. Gol'dshleger, N. F., Tyabin, M. B., Shilov, A. E., and Shteinman, A. A., *Zh. Khim.* **43**, 2174 (1969).

5. Tyabin, M. B., Shilov, A. E., and Shteinman, *Dokl. Akad. Nauk SSSR* **198**, 380 (1971).

6. Hodges, R. J., Webster, D. E., and Wells, P. B., *J. Chem. Soc. A*, 3230 (1971).

7. Hodges, R. J., Webster, D. W., and Wells, P. B., *J. Chem. Soc. Dalton Trans.*, 2571, 2577 (1972).

8. Garnett, J. L., Long, M. A., and Peterson, K. B., *Aust. J. Chem.* **27**, 1823 (1974).

9. Blake, M. R., Garnett, J. L., Gregor, I. K., Hannan, W., Hoa, K., and Long, M. A., *J. Chem. Soc. Chem. Commun.*, 930 (1975).

10. Kauder, L. N., and Taylor, T. I., *Science* **113**, 238 (1951).

11. Kemball, C., *Proc. Roy. Soc. A* **223**, 377 (1954).

12. McNaught, W. G., Kemball, C., and Leach, H. F., *J. Catal.* **34**, 98 (1974).

13. Davis, K. P., and Garnett, J. L., *J. Phys. Chem.* **75**, 1175 (1971); *Aust. J. Chem.* **28**, 1699 (1975).

14. Moyes, R. B., Baron, K., and Squire, R. C., *J. Catal.* **22**, 333 (1971).

15. Kemball, C., *Advan. Catal.* **11**, 223 (1959).

16. Addy, J., and Bond, G. C., *Trans. Faraday Soc.* **53**, 383, 388 (1957).

17. Gault, F. G., and Kemball, C., *Trans. Faraday Soc.* **57**, 1781 (1961).

18. Dowie, R. S., Robertson, P. J., and Kemball, C., *J. Catal.* **35**, 189 (1974).

19. Garnett, J. L., and Hodges, R. J., *J. Amer. Chem. Soc.* **89**, 4546 (1967).

20. Hodges, R. J., and Garnett, J. L., *J. Phys. Chem.* **72**, 1673 (1968).

21. Garnett, J. L., Long, M. A., and Hoa, K., unpublished work.

22. Grimzewski, J. K., Padalia, B. D., Affrossman, S., Watson, L. M., and Fabian, D. J., *Surface Sci.* **62**, 386 (1977).

23. Moyes, R. B., and Roberts, M. W., *J. Catal.* **49**, 216 (1977).

24. Page, P. J., Trimm, D. L., and Williams, P. M., *J. Chem. Soc. Faraday Trans. 1* **70**, 1769 (1974).

25. George, M., Moyes, R. B., Ramanarao, D., and Wells, P. B., *J. Cat* (in press).

26. Kemball, C., *Catal. Rev.* **5**, 33 (1972).

27. Davis, K. P., and Garnett, J. L., *Aust. J. Chem.* **28**, 1713 (1975).

28. Garnett, J. L., and Hodges, R. J., *J. Chem. Soc. Chem. Commun.*, 1220 (1967).

29. Garnett, J. L., Hodges, R. J., and Soelich-Baumgartner, W. A., *in* "Proceedings, 4th International Congress on Catalysis." (F. F. Vol'keshtein Ed) Akademiai Kaido, Budapest, 1971.

30. Garnett, J. L., Long, W. A., McLaren, A. B., and Peterson, K. B., *J. Chem. Soc. Chem. Commun.*, 749 (1973).

31. Garnett, J. L., and Kenyon, R. S., *J. Chem. Soc. Chem. Commun.*, 698 (1970); *Aust. J. Chem.* **27**, 1023 (1974).