The Activation of Saturated Hydrocarbons by Transition-metal Complexes in Solution. Part I. Hydrogen–Deuterium Exchange in Alkanes Catalysed by Potassium Tetrachloroplatinate(II) in Acetic Acid

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All isomeric alkanes from methane to the hexanes, cyclopentane, and cyclohexane, undergo hydrogen–deuterium exchange with a deuterium oxide–acetic [$^2H_1$]acid solvent catalysed by potassium tetrachloroplatinate(II). The catalyst is stabilised by the acidity of the solution and the presence of a small concentration of a weak complexing agent such as pyrene. Exchange is preceded by dissociation of chloride ligands from the added tetrachloroplatinate(II) to form an uncharged platinum(II) complex which may be monomeric or dimeric. The relative reactivity for the hydrogen-deuterium exchange is in the order primary > secondary > tertiary which is in the reverse order to the reactivity expected from bond energy data. Exchange rates in the series of n-alkanes have been related to their ionisation potentials. Branched chain alkanes are less reactive than their respective n-isomers, whereas the cycloalkanes are more reactive. The results indicate that the initial interaction between the alkanes and the platinum involves a reversible electron transfer from the delocalised molecular orbitals in the alkanes to the uncharged platinum(II) complex. Subsequent steps in the proposed exchange mechanism involve a reversible oxidative-addition of the alkane to the platinum(II) complex to form a hydrido-platinum(IV) complex which can lose HCl to, and gain DCl from, the solvent.

DURING recent years the reactions of organic compounds catalysed by complexes of transition-elements in solution have been extensively studied, and some of these reactions are of considerable industrial importance and potential.[1] The organic compounds are almost invariably olefins or aromatic compounds; there are few publications of this type of catalysis involving the alkanes. At present, large amounts of the gaseous saturated hydrocarbons are used as fuels; for example, extensive natural deposits of methane under the North Sea are being used solely as an energy source, and the development of chemical uses for this inexpensive raw material is a worthwhile task.

The reports in the literature involving the interaction of a transition-metal complex at a saturated carbon atom are, with one exception, concerned with molecules containing a reactive group adjacent to the saturated carbon atom. For example, Halpern [2] has studied the formation of alkyl-metal complexes by the insertion of a transition-metal compound into the carbon–iodine bond of methyl iodide, and there are many studies on the formation of π-allylic complexes, where the saturated carbon atom is part of an allylic group.[3]

One of us has previously studied the replacement of hydrogen by deuterium in the side-chains of alkylbenzenes,[4] using an aqueous-acetic acid solution of sodium tetrachloroplatinate(II). In this study it was found that the hydrogen atoms of the methyl group in toluene were almost as reactive as the hydrogen atoms of the aromatic ring, and for ethylbenzene the rates of deuteriation of the methylene and methyl groups were similar. A mechanism involving a step where the ethyl group becomes detached from the aromatic ring during the reaction, has been proposed to explain these latter observations, but this has been shown to be incorrect by Garnett and Kenyon [5] by the use of ^{14}C-labelled ethylbenzene, and they concluded that the exchange in

[1] C. L. Thomas, 'Catalytic Processes and Proven Catalysts,' Academic Press, New York and London, 1970.

[2] J. Halpern, *Advances in Chemistry Series No.* 70, 1968, 1.

[3] M. L. H. Green and P. L. I. Nagy, *Adv. Organometallic Chem.*, 1964, **2**, 325.

[4] R. J. Hodges and J. L. Garnett, *J. Catalysis*, 1969, **13**, 83.

[5] J. L. Garnett and R. J. Kenyon, *Chem. Comm.*, 1970, 698.

the alkyl side-chain occurred *via* the formation of π-allylic intermediates. However, the ethyl group need not be attached to the benzene ring for it to become involved in hydrogen-deuterium exchange. Gol'dshleger *et al.*[6] have observed that a little hydrogen–deuterium exchange occurs in ethane and in methane under conditions similar to those used for the study of the alkylbenzenes. This is a significant observation. For the first time activation under homogeneous conditions appears to have occurred in an alkane, and it could represent a significant step in the use of transition-metal complexes as catalysts for reactions of the alkanes. It is also possible that the exchange in the alkyl side-chain of an aromatic compound occurs independently of the exchange in the aromatic ring.

The objects of the present work were to confirm and extend these observations and to achieve an understanding of hydrogen-deuterium exchange in saturated hydrocarbons. A preliminary report of this work has been published.[7]

EXPERIMENTAL

Preparations.—Acetic anhydride was freed from traces of acetic acid by heating it under reflux over magnesium turnings for 1 h, followed by distillation. The acetic anhydride was converted into acetic [$^2H_1$]acid by reaction with deuterium oxide. When cold these two reactants are immiscible and cautious heating was required to initiate the highly exothermic reaction. After the initial reaction had subsided, the mixture was heated under reflux for ½ h.

Deuterioperchloric acid was prepared by heating perchloric acid until dense white fumes were produced, allowing the solution to cool and diluting with deuterium oxide. This procedure was repeated three times, and finally a solution of 5M-$DClO_4$ was prepared.

Two solutions were prepared for each batch of experiments: an aqueous solution containing potassium tetrachloroplatinate(II) and perchloric acid, and an acetic acid solution containing the alkane and either benzene or pyrene. During the preparation of the aqueous solution, potassium perchlorate was precipitated and this was removed by centrifugation.

Part of each of these solutions was transferred to 5-ml reaction tubes and sealed without evacuation. For gaseous hydrocarbons, a vacuum line was used for the transfer of the alkane to reaction tubes constructed with breakseals. For each batch of samples used in kinetic studies, one tube contained a 'standard' alkane, namely pentane, and this enabled comparison of the results from different batches. The 'standard' was included as it was not possible to reproduce exactly the experimental conditions from batch to batch. In particular it was impossible to reproduce the concentrations of the tetrachloroplatinate(II) ion; apparently variable amounts of it are adsorbed on the potassium perchlorate precipitate.

The tetrachloroplatinate of metals that have soluble perchlorates, *e.g.* lithium or sodium, were not used as they are unstable and hygroscopic compounds and again reproducibility from batch to batch would not be possible.

Analyses.—After reaction, the samples were analysed using an A.E.I. MS902 or MS3 mass spectrometer, and with a J.E.O.L. 100 MHz n.m.r. spectrometer. A computer program, using equations (1) to (4),[8] was used to calculate the deuterium content (%D), the rate constant for the disappearance of the [$^2H_0$]alkane (k_b), and the multiple exchange parameter (M) after appropriate corrections for ^{13}C and ion-fragmentation. For a hydrocarbon containing n hydrogen atoms, the percentage replacement by deuterium (%D) is given by ϕ/n where the function ϕ is defined:

$$\phi = \sum_{i=0}^{n} i \,.\, [^2H_i] \qquad (1)$$

and [^2H_i] is the percentage of the hydrocarbon present containing i deuterium atoms. For an exchange reaction, the variation of ϕ with time is given by

$$\frac{d\phi}{dt} = \frac{k\phi}{\phi_\infty}(\phi_\infty - \phi) \qquad (2)$$

where k_ϕ is the initial rate of entry of deuterium atoms into 100 molecules of the [$^2H_0$]hydrocarbon and ϕ_∞ is the calculated equilibrium value. As the entry of deuterium into the hydrocarbon is not altogether stepwise, it is also necessary to define k_b, the rate of disappearance of [$^2H_0$]hydrocarbon in percent per unit time; and M, the multiple exchange parameter.

$$-\frac{db}{dt} = \frac{k_b(b - b_\infty)}{100 - b_\infty} \qquad (3)$$

$$M = \frac{k_\phi}{k_b} \qquad (4)$$

where b is the percentage of the hydrocarbon present as non-deuteriated material at time t and b_∞ is the calculated equilibrium value of b.

RESULTS

In preliminary experiments, n-pentane was used as a representative alkane. Using what appear to be the conditions described by Gol'dshleger *et al.*[6] (namely 30 mol% acetic [$^2H_1$]acid in deuterium oxide containing unspecified amounts of hydrochloric acid and benzene) we observed that a small amount of deuteriation (*ca.* 6%) of the pentane occurred before the platinum complex disproportionated according to equation (5).[9]

$$2PtCl_4^{2-} \rightleftharpoons Pt\downarrow + PtCl_6^{2-} + 2Cl^- \qquad (5)$$

Once some platinum metal had been formed then the disproportionation proceeded rapidly. Throughout the course of this work it was observed that when platinum metal was precipitated in a reaction, the deuterium content of the pentane was lower than expected. The disproportionation products did not catalyse this hydrogen–deuterium exchange reaction in alkanes.

The disproportionation [equation (5)] is substantially reduced by increasing the acidity of the solvent. From previous studies in acetic acid,[10] an acidity equivalent to a

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[6] N. F. Gol'dshleger, M. B. Tyabin, A. E. Shilov, and A. A. Shteinman, *Zhur. fiz. Khim.*, 1969, **43**, 2174.

[7] R. J. Hodges, D. E. Webster, and P. B. Wells, *Chem. Comm.*, 1971, 462.

[8] J. R. Anderson and C. Kemball, *Adv. Catalysis*, 1957, **9**, 51.

[9] O. Ginstrup and I. Leden, *Acta Chem. Scand.*, 1967, **21**, 2689.

[10] R. J. Hodges and J. L. Garnett, *J. Phys. Chem.*, 1968, **72**, 1673; 1969, **73**, 1525.

pH of −1 was found necessary to inhibit this reaction. In aqueous acetic acid, this acidity is attained only when the solvent is almost glacial; however, additions of hydrochloric or perchloric acid may be used to maintain the acidity when water is added. To give an acidity sufficient to suppress the disproportionation for 20 hours at 100° in the solvent used by Gol'dshleger *et al.*[6] *viz.* 30 mol% acetic [$^2H_1$]acid in deuterium oxide, 0·2M-hydrochloric acid had to be used. Previous studies with a 50 mol% acetic [$^2H_1$]acid deuterium oxide mixture, however, have shown that hydrochloric acid concentrations above 0·02M reduce exchange rates inversely with the added chloride ion concentration.[10] For this reason, perchloric acid was used to inhibit disproportionation in the present study.

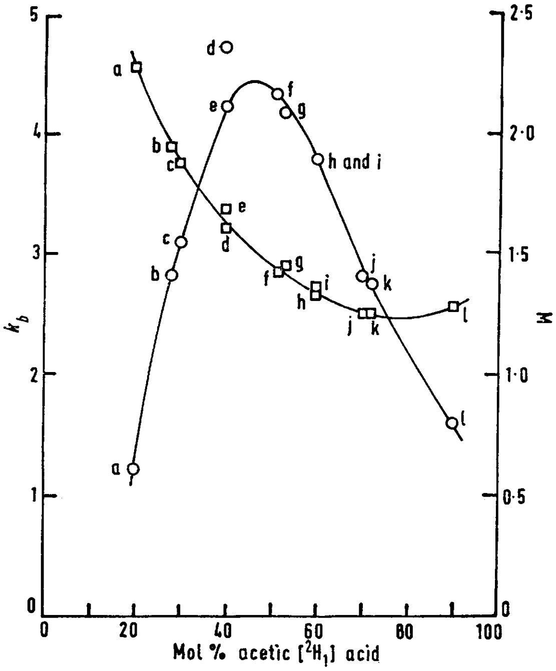


FIGURE 1 The effect of acetic acid upon the rate constant (k_b) (circles), and the M value (squares), for the $PtCl_4^{2-}$ catalysed deuteriation of pentane. Temperature = 100 °C. Time = 21 h. [Pentane] = 0·3M; [C_6D_6] = 0·1M; [$PtCl_4^{2-}$] = 0·01M; [Cl^-] = 0·02M; [$DClO_4$] = 1·70, 0·40, 0·18, 0·20, 0·14, 0·16, 0·10, 0·11, 0·07, 0·05, 0·067, 0·02M (for a to l respectively)

For a comparison of rates at different acetic acid concentrations, the minimum perchloric acid concentration necessary to suppress the platinum disproportionation was used. Once sufficient perchloric acid was present to permit the determination of accurate initial rates of exchange, more acid did not alter the exchange rate. The effect of acetic acid upon the initial exchange rate in pentane, at the corresponding perchloric acid concentration, is shown in Figure 1.

The maximum exchange rate, at 45—50 mol% acetic [$^2H_1$]acid, occurs because alkanes are only sparingly soluble in solvents where the concentration of acetic acid is low, and at high acetic acid concentrations the exchange rate and the M value are reduced, presumably due to the low dielectric constant of the medium. 50 mol% Acetic [$^2H_1$]acid in deuterium oxide containing 0·2M-deuterioperchloric acid was used for most of this work.

Added aromatic compounds also stabilise the catalyst, and for initial studies 0·1M-benzene was used. Exchange reactions in aromatic compounds have been studied previously[10] and all of the alkanes are found to be less reactive than benzene. To obtain a reasonable amount of deuteriation of an alkane (greater than 10%) in a 1 : 1 molar mixture (50 mol%) of acetic [$^2H_1$]acid in deuterium oxide, it was necessary to use higher acidities, longer reaction times, and higher temperatures (100—120°) than had been used for the studies of aromatic compounds.[10] Under these conditions it was considered essential to monitor the concurrent acid-catalysed hydrogen–deuterium exchange in the methyl group of the acetic acid. This could have been done by direct mass analysis of the acetic acid, but it was more convenient to analyse the benzene added to the reaction mixture. As exchange in benzene was much more rapid than in pentane, then mass spectrometric analysis of the benzene measured the loss of deuterium from the hydroxy-groups of acetic acid and water. For experimental convenience, perdeuteriobenzene was substituted for the benzene used by Gol'dshleger.[6] In all the studies at 100°, acid exchange of the hydrogen atoms of the methyl-group of the acetic acid did not seriously affect the kinetic results; the benzene always contained in excess of 95% deuterium (see Table 4, column 4). The perdeuteriobenzene, acetic [$^2H_1$]acid, and the deuterium oxide contained greater than 99·5% deuterium, and the calculated equilibrium values excluding and including the methyl hydrogens are 92% and 47% respectively. At 120°, the exchange of hydrogen for deuterium in the methyl group of the acetic acid was substantial, and extensive deuteriation of the alkanes (in excess of 90%) was only possible when perdeuterioacetic acid was used.

Table 1 presents the results of experiments designed to illustrate the effect of the concentrations of benzene, deuterioperchloric acid, tetrachloroplatinate(II) ion, and alkane on the rate constant for the deuteriation of pentane at 100°. The exchange rate is independent of the concentration of

TABLE 1

Parameters influencing the exchange reaction in pentane; solvent = 50 mol% CH_3CO_2D in D_2O. T = 100 °C

[C_6D_6]/ M	[$DClO_4$]/ M	[$PtCl_4^{2-}$]/ M	[C_5H_{12}]/ M	[DCl]/ M	t/h	% D in pentane
C_6D_6 varied:						
0·0	0·0	0·02	0·3	0·04	18·0	9·97[a]
0·1	0·0	0·02	0·3	0·04	18·0	10·55
0·2	0·0	0·02	0·3	0·04	18·0	10·43
0·3	0·0	0·02	0·3	0·04	18·0	10·41
$DClO_4$ varied:						
0·3	0·00	0·02	0·3	0·04	18·0	10·41
0·3	0·02	0·02	0·3	0·04	18·0	10·81
0·3	0·04	0·02	0·3	0·04	18·0	10·72
0·3	0·06	0·02	0·3	0·04	18·0	11·13
$PtCl_4^{2-}$ varied:						
0·1	0·2	0·002	0·3	0·04	5·2	0·40
0·1	0·2	0·004	0·3	0·04	5·2	0·80
0·1	0·2	0·008	0·3	0·04	5·2	1·47
0·1	0·2	0·016	0·3	0·04	5·2	2·70
0·1	0·2	0·030	0·3	0·04	5·2	4·61
C_5H_{12} and C_6D_6 varied:						
0·033	0·2	0·02	0·1	0·0	17·0	17·61
0·067	0·2	0·02	0·2	0·0	17·0	17·74
0·100	0·2	0·02	0·3	0·0	17·0	16·37
0·167	0·2	0·02	0·5	0·0	17·0	14·63
0·333	0·2	0·02	1·0	0·0	17·0	10·51

[a] Some Pt(O) formed.

both the benzene and the deuterioperchloric acid, it decreases with increase in the alkane concentration when this exceeds 0·3M because a two-phase system is produced and, at the concentration of the complex and chloride ion reported here, it is almost directly proportional to the tetrachloroplatinate(II) ion concentration.

Benzene was used to stabilise the tetrachloroplatinate(II) ion against disproportionation so as to allow exchange in ethane to occur.[6] Earlier studies [10] had indicated that the interaction of benzene with the tetrachloroplatinate(II) ion was weaker than that of other polycyclic aromatic compounds, and with this in mind the possibility of using a more efficient stabiliser was investigated. The rate of hydrogen–deuterium exchange in benzene in the presence of other aromatic compounds (Figure 2) confirms that these will preferentially co-ordinate to the platinum, and that they should, therefore, be more effective than benzene for stabilising the tetrachloroplatinate(II) ion against disproportionation. A comparison of the amount of deuteriation of pentane using a series of aromatic compounds as the stabiliser is given in Table 2. After 67·5 h at 120°, all the complex had disproportionated and the reaction had, consequently, stopped. Thus the amount of deuterium in the pentane is a measure of the effectiveness of the aromatic to prevent disproportionation and thus prolong the exchange reaction. It is apparent that, of the compounds studied, pyrene is the most effective. During the reaction simultaneous acid-catalysed exchange occurred in the methyl group of the acetic acid and the equilibrium value for these results is only 47·5% D. This means that with pyrene as the stabiliser the deuteriation of the pentane attains over 80% of the equilibrium value.

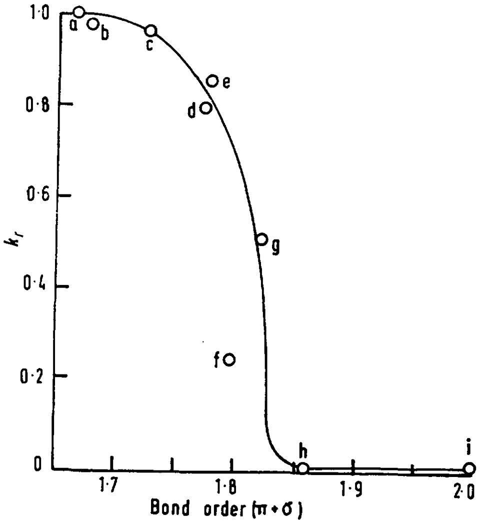


FIGURE 2 The effect of unsaturated hydrocarbons upon the rate of exchange of hydrogen for deuterium in benzene. Bond order ($\pi + \sigma$) = highest bond order of the molecules (a) to (i);[10] k_r = rate constant for exchange in benzene in the presence of the compounds (a) to (i) relative to the value for the same rate constant in benzene alone. Solvent = 67 mol % CH_3CO_2D in D_2O. T = 80 °C. $[C_6H_6]$ = 1·0M; $[PtCl_4^{2-}]$ = 0·016M; [DCl] = 0·04M; [unsaturated hydrocarbon] = 0·1M; a = benzene, b = diphenyl, c = naphthalene, d = phenanthrene, e = pyrene, f = acenaphthylene, g = *trans*-stilbene, h = cinnamyl alcohol, and i = pent-1-ene

Table 3 shows the amount and location of deuterium in eight representative compounds after reaction at 120° for several days, using pyrene as stabiliser and perdeuterioacetic acid–deuterium oxide as solvent. All the samples are extensively deuteriated and n.m.r. analysis shows that the exchange in several positions is almost at equilibrium.

TABLE 2

$PtCl_4^{2-}$ catalysed hydrogen–deuterium exchange in pentane using aromatic compounds as stabilisers. Solvent = 50 mol% CH_3CO_2D in D_2O. T = 120 °C. $[PtCl_4^{2-}]$ = 0·02M; $[DClO_4]$ = 0·2M; [pentane] = 0·3M; [aromatic] = 0·1M. %D at equilibrium = 47·5

Aromatic	t/h	% D in pentane
Benzene [a]	67·5	24·3
Naphthalene	67·5	27·8
Phenanthrene	67·5	22·8
Pyrene	67·5	38·3
Benzene	18·0	14·78
Naphthalene	18·0	16·67
trans-Stilbene	18·0	14·24

[a] Analysis of the acetic acid solvent indicated 46·3% deuterium in the methyl group of the acetic acid. This exchange was found to be dependent upon the acidity of the solvent mixture only.

Exchange proceeds more slowly in the branched-chain alkanes than in n-alkanes and the highest reactivity is in isolated methyl groups. Two alkylbenzenes were included in this study for comparison of reactivity. With the exception of the α-hydrogen atoms in n-pentylbenzene, the highest reactivity in the alkyl side-chain is, again, in isolated methyl groups.

The effect of added chloride ion and added tetrachloroplatinate(II) ion on the exchange rate was studied in solutions that were stabilised against disproportionation [equation (5)] using either benzene or pyrene. Table 4 gives the exchange rates and M-values for various chloride ion and $PtCl_4^{2-}$ ion concentrations. Added chloride ion reduced the rate in a non-linear fashion, and the rate increased non-linearly as the tetrachloroplatinate(II) concentration was increased. The latter result apparently conflicts with the third series of results in Table 1 where the dependence was almost linear with concentration. This occurs because $PtCl_4^{2-}$ undergoes dissociation in solution (see Discussion).

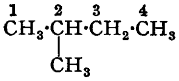
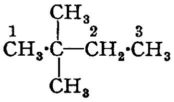
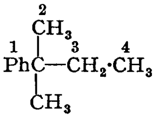
The initial rates of exchange in all isomers of the compounds, C_nH_{2n+2} (n = 1—6), together with cyclopentane and cyclohexane are given in Table 5. For normal alkanes, the methyl hydrogen atoms were found to be more reactive than methylene hydrogen atoms (Table 3). An exchange study of n-pentane at 100° showed that the rate of incorporation of deuterium into the two methyl groups is 4·5 ± 0·8 times as fast as into the three methylene groups. Somewhat surprisingly, cyclohexane, which contains only CH_2 groups, was the most reactive alkane studied. An isotope effect for cyclohexane was determined; the rate of exchange of hydrogen for deuterium in cyclohexane was 1·7 ± 0·1 times the rate of exchange of deuterium for hydrogen in perdeuteriocyclohexane. The significance of these results and the factors influencing the reaction rate are considered below.

DISCUSSION

The results indicate that $PtCl_4^{2-}$ in aqueous acetic acid is a very useful catalyst in the preparation of a

TABLE 3

Deuteriation of alkanes and alkylbenzenes at 120° using $PtCl_4^{2-}$ in CD_3CO_2D. Solvent = 50 mol% CD_3CO_2D in D_2O. [Alkane] or [alkylbenzene] = 0·5M; [pyrene] = 0·05M; $[DClO_4]$ = 0·2M

Compound	$[PtCl_4^{2-}]$/M	t/h	% D (mass spectrum) Obs.	% D (mass spectrum) Calc. (% D_∞)	% D (n.m.r. spectrum) Position	% D (n.m.r. spectrum) % D
$\overset{1}{C}H_4$	0·04	95·0	25·0	97·3	1	25·0
$\overset{1}{C}H_3\cdot CH_3$	0·04	136·6	91·4	96·2	1	91·4
$\overset{1}{C}H_3\cdot\overset{2}{C}H_2\cdot CH_2\cdot CH_2\cdot CH_3$	0·04	136·6	74·6	92·8	1 2	92 ± 2 57 ± 2
 $\overset{1}{C}H_3\cdot\overset{2}{C}H(CH_3)\cdot\overset{3}{C}H_2\cdot\overset{4}{C}H_3$	0·04	136·6	68·8	92·8	1 and 4 2 3	82 ± 2 9 ± 3 37 ± 2
$(\overset{1}{C}H_2)_6$	0·01	110·0	70·1	92·8	1	70·1
 $\overset{1}{C}H_3\cdot C(CH_3)_2-\overset{2}{C}H_2\cdot\overset{3}{C}H_3$	0·02	91·0	18·2	90·2	1 2 3	4·15[a] 2 ± 2 70·3[a]
$\overset{1}{Ph}\overset{2}{C}H_2\cdot\overset{3}{C}H_2\cdot\overset{4}{C}H_2\cdot\overset{5}{C}H_2\cdot\overset{6}{C}H_3$	0·03	92·0	38·1	89·6	1 2 3, 4, and 5 6	70 ± 2 41 ± 2 8 ± 3 39 ± 2
 $\overset{1}{Ph}C(\overset{2}{C}H_3)_2-\overset{3}{C}H_2\cdot\overset{4}{C}H_3$	0·03	92·0	30·0	89·6	1 2 and 3 4	64 ± 2 2 ± 2 53 ± 2

[a] Determined by mass spectrum of ion fragments.

large number of deuteriated alkanes that are not readily prepared by other methods. Active positions in simple alkanes may be deuteriated to approximately 90% D in this single-step procedure. Repeated exchanges may be used to give higher isotopic purity. Experimental conditions suitable for preparative work, are only achieved by careful attention to detail in the preparation of solutions (see below). Problems arise because the catalyst, the tetrachloroplatinate(II) anion, disproportionates readily in solution at 100° and above. Highest

TABLE 4

Effect of Cl^- and $PtCl_4^{2-}$ upon exchange rate in pentane. Solvent = 50 mol% CH_3CO_2D in D_2O. T = 100 °C. $[DClO_4]$ = 0·1M; [pentane] = 0·3M

t/h	$[Cl^-]$/M	$[PtCl_4^{2-}]$/M	% D (C_6D_6)	% D (C_5H_{12})	k_b/h^{-1}	M value
Stabiliser: 0·1M C_6D_6						
3·25	0·005	0·02	97·1	4·98	11·04	1·71
3·25	0·010	0·02	97·4	4·46	10·07	1·67
5·5	0·020	0·02	96·8	5·22	6·995	1·67
10·5	0·040	0·02	95·4	6·48	5·320	1·44
16·83	0·084	0·02	96·0	6·31	3·182	1·46
32·5	0·160	0·02	95·7	5·78	1·533	1·44
49·17	0·325	0·02	96·1	4·36	0·764	1·42
110·5	0·640	0·02	95·2	4·18	0·326	1·42
Stabiliser: 0·05M pyrene						
2·75	0·005	0·02		4·43	12·02	1·65
4·25	0·010	0·02		5·69	10·43	1·59
6·25	0·020	0·02		6·41	8·266	1·54
9·83	0·050	0·02		6·14	5·304	1·46
21·0	0·100	0·02		6·79	2·866	1·41
39·0	0·200	0·02		5·88	1·343	1·39
94·5	0·500	0·02		4·88	0·468	1·36
5·00	0	0·000		0·00	0·00	—
5·00	0	0·005		4·30	5·68	1·86
3·92	0	0·010		5·11	8·94	1·80
2·87	0	0·015		4·82	11·68	1·77
1·75	0	0·030		4·13	17·05	1·70
0·95	0	0·050		2·69	20·45	1·69

TABLE 5

Hydrogen–deuterium exchange in alkanes at 100° using $PtCl_4^{2-}$ in solution. Solvent = 50 mol% CH_3CO_2D in D_2O. T = 100 °C. $[PtCl_4^{2-}]$ = 0·02M; $[DClO_4]$ = 0·2M; [alkane] = 0·3M; [aromatic] = 0·05M

Compound	Aromatic *	t/h	% D in alkane	M value	k_b/h^{-1}
Methane	P	3·40	0·18	—	0·2
Ethane	B	5·08	5·6	1·70	3·99
Propane	B	5·08	7·2	1·63	7·18
Pentane	B	5·08	7·3	1·53	11·75
Hexane	B	5·08	6·7	1·50	12·67
2,2-Dimethylpropane[a]	B	5·08	0·4	1·52	0·37
Pentane	P	2·00	3·41	1·63	12·77
Butane	P	2·00	3·33	1·62	10·46
Cyclopentane[b]	P	2·00	6·45	1·68	20·0
Cyclohexane	P	2·00	6·31	1·42	27·5
Pentane	P	4·83	7·29	1·63	11·60
2-Methylpropane	P	4·83	3·13	1·76	3·76
2-Methylbutane	P	4·83	3·94	1·52	6·57
3-Methylpentane	P	4·83	5·02	1·54	9·74
2-Methylpentane	P	4·83	5·63	1·56	10·80
Pentane	P	4·00	6·39	1·65	12·00
2,2-Dimethylbutane[c]	P	4·00	1·42	1·38	3·75
2,3-Dimethylbutane	P	4·00	1·85	1·45	4·52
Cyclohexane	P	2·50	8·74	Isotope effect = 1·7 ± 0·1	
Perdeuteriocyclohexane[d]	P	2·50	94·10		

[a] Analysis using $C_4H_9^+$ ion fragment. [b] Some decomposition of the $PtCl_4^{2-}$. [c] Analysis using $C_5H_{11}^+$ ion fragment. [d] C_6D_{12} (99·28% D); exchange studied using CH_3CO_2H in H_2O as solvent.

* P = Pyrene, B = benzene.

deuterium contents were obtained when this disproportionation was inhibited by the high acidity of the solution and the presence of pyrene, and when the reaction tubes were sealed without evacuation.

Acidity in aqueous acetic acid has been studied by Schwarzenbach and Stensby [11] and discussed previously in relation to exchange in aromatic compounds.[10] This study with alkanes required longer reaction times, higher temperatures, and higher acidities, than did the earlier work.[10] Perchloric acid was used to increase the acidity, because other acids, such as hydrochloric acid (Table 4) reduced the exchange rate. The use of higher acidities had one disadvantage; the methyl group in acetic [$^2H_1$]acid was extensively deuteriated by the slow acid-catalysed reaction (Table 2; see footnote). Initial rates of $PtCl_4^{2-}$-catalysed exchange of the alkanes (Tables 1, 4, and 5) were obtained using acetic [$^2H_1$]acid prepared from deuterium oxide and acetic anhydride. High deuterium contents (Table 3) could only be obtained using perdeuterioacetic acid. This acid is also required for extensive deuteriation in the alkyl groups of alkylbenzenes (Table 3); however the more reactive aromatic ring could be deuteriated by using a shorter time, $PtCl_4^{2-}$, and 0·02M-DCl in a solvent containing acetic [$^2H_1$]acid.[4]

An aromatic compound present in the reaction solution will inhibit the disproportionation of the catalyst (Table 2). Of the aromatic compounds studied, pyrene was the most suitable as this does not appreciably reduce the exchange rate in the alkane.

Air in the reaction tube when the sample was sealed increased, to a small extent, the stability of the catalyst but did not affect the initial rates. The nature of this stabilising effect is not clear and is being investigated further. Davidson and Triggs [12] have observed that oxygen has a pronounced effect on the acetoxylation and the dimerisation of aromatic compounds in acetic acid using both $Pd(OAc)_2$ and $Pb(OAc)_4$; they found that oxygen inhibited the reduction of the palladium and lead acetates. Platinum metal was produced in our reaction solutions after long reaction times at 120° (Table 2) and at low acidities, but this did not appear to be produced by the reduction of the $PtCl_4^{2-}$ by the acetic acid or by the benzene,[12] as oxidation products of these latter two compounds were not detected. Presumably the platinum was formed by disproportionation [equation (5)], and a combination of perchloric acid with benzene, or preferably pyrene, was used to inhibit this reaction. Nevertheless, the reaction mixtures were more stable when air was present, and it is possible that oxygen also inhibits the reduction of Pt^{II} to Pt^0 in our solutions. The samples were sealed without evacuation and for gaseous hydrocarbons where a vacuum line was used to transfer the gases, air (500 mmHg) was admitted to the tubes before sealing.

The use of deuterioperchloric acid in place of the deuterium chloride used previously [10] distinctly improves the reaction conditions for exchange; it allows slightly higher rates to be obtained and allows the effect of lower chloride ion concentrations to be studied. The low chloride-ion concentration used in the present study has permitted kinetic experiments that indicate that the reaction is preceded by dissociation of chloride ligands from the tetrachloroplatinate(II) anion (see later). It is possible that these steps occur during exchange in aromatic compounds but they were not detected in the presence of the 0·02M-DCl used.[10] In addition, excess of deuterioperchloric acid may be used to remove the unwanted potassium ions in K_2PtCl_4 during the preparation (see Experimental section). K_2PtCl_4 is the most suitable Pt^{II} salt as it is a readily available crystalline solid; however it is only sparingly soluble, especially in solutions containing above 50 mol % acetic [$^2H_1$]acid. The use of excess $DClO_4$ to remove K^+ during preparation eliminates this problem.

The remainder of this discussion will be concerned with the nature of the catalyst, the nature of the interaction between the alkane and the catalyst, and the mechanism of the exchange reaction.

The amount of the complex formed between the platinum(II) species in solution and benzene or pyrene, when 0·04M-chloride ion is present, is small. Figure 2 shows that only molecules with high π-bond order complex strongly with the platinum and inhibit exchange in benzene, and this has also been found for exchange in pentane. Colours formed in solution give an indication of the extent of complex formation. Platinum–olefin complexes in acetic acid are yellow whereas solvated $PtCl_4^{2-}$, $PtCl_3^-$, and $PtCl_2$ are orange-red. For the series presented in Figure 2, where $[Cl^-] = 0·04M$, the yellow colour, *i.e.* a complex, was formed with pent-1-ene (i), cinnamyl alcohol (h), and to a lesser extent with *trans*-stilbene (g). Solutions were orange-red with benzene (a), diphenyl (b), naphthalene (c), phenanthrene (d), and pyrene (e); *i.e.* the amount of complex formation was small but sufficient to be detected by the exchange reactions recorded in Figure 2. The formation of only a low concentration of complex is supported by the fact that perdeuteriobenzene does not greatly alter the rate of exchange in pentane (Table 1). When no chloride ion was added, a slight yellow colouration, *i.e.* partial complex formation, was observed with naphthalene and with pyrene, and these compounds were more effective than benzene in reducing the disproportionation (equation 5; Table 2).

The results of Table 4 indicate that solvolysis of $PtCl_4^{2-}$ occurred. Such solvolyses, using aqueous perchloric acid, have been studied extensively by Elding,[13] who found that two days were required for the equilibrium concentrations of $PtCl_4^{2-}$, $PtCl_3^-$, $PtCl_2$, $PtCl^+$, and Pt^{2+} to be formed at 60°, and he suggested that about 3 h would be required for equilibrium to be attained at 100°. However, there was no appreciable induction period for the exchange reaction and, from

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[11] G. Schwarzenbach and P. Stensby, *Helv. Chim. Acta*, 1959, **42**, 2342.

[12] J. M. Davidson and C. Triggs, *J. Chem. Soc. (A)*, 1968, 1324, 1331.

[13] L. I. Elding, *Acta Chem. Scand.*, 1970, **24**, 1331, 1341, 1527.

our analysis of the results given in Table 4, we infer that displacement of the chloride ligands occurs rapidly in the acetic acid solution, even though the dielectric constant of acetic acid is much lower than that of water.

Displacement of chloride ligands from $PtCl_4^{2-}$ accounts for the pronounced non-linear dependence of rate on added $PtCl_4^{2-}$ or chloride ion concentration (Table 4). As indicated above, solutions containing benzene or pyrene do not form high concentrations of platinum(II)–aromatic complex; apparently the displacement of chloride ligands is due to solvent molecules. The catalytic species, if formed by displacement of one chloride ion, would be $PtCl_3{\cdot}S^-$ [equation (6)], where S is a solvent molecule (D_2O or CH_3CO_2D), but a better linear correlation for a plot of log [catalyst] *vs.* log k_b is obtained if the active species is formed by displacement of a second chloride ion [equation (7)].

$$PtCl_4^{2-} + S \xrightleftharpoons{K_1} PtCl_3{\cdot}S^- + Cl^- \qquad (6)$$

$$PtCl_3{\cdot}S^- + S \xrightleftharpoons{K_2} \underset{(1)}{PtCl_2{\cdot}S_2} + Cl^- \qquad (7)$$

The kinetics could be complicated further by the formation of a dimeric species by either reaction (8) or (9); it is known that $PtBr_4^{2-}$ will dimerise to a small extent in aqueous perchloric acid.[14] If the catalyst

$$2PtCl_3{\cdot}S^- \rightleftharpoons (PtCl_2{\cdot}S)_2 + 2Cl^- \qquad (8)$$

$$\underset{(1)}{2PtCl_2{\cdot}S_2} \rightleftharpoons \underset{(2)}{(PtCl_2{\cdot}S)_2} + 2S \qquad (9)$$

is (*1*) then the gradient of the plot of log [(*1*)] against log k_b would be unity, whereas if the dimeric species (*2*) is the catalyst then the gradient of the same plot would be 2·0. For simplicity, we shall use reactions (6) and (7) only in our analysis to illustrate that extensive dissociation of one chloride ligand from the $PtCl_4^{2-}$ occurs, and that a further dissociation to give small concentrations of (*1*) produces linear correlations for log [(*1*)] *vs* log k_b. The gradient of this plot also gives an indication of the extent of dimerisation.

A computational recursive procedure was used to simulate the above dissociation [reactions (6) and (7)], and values for K_1 and K_2 that gave the best correlation for the log-log plot were calculated. When benzene was used to prevent disproportionation [reaction (5)], best values of K_1 and K_2 were $K_1 = 2{\cdot}40$ mol l^{-1} and $K_2 = 7{\cdot}0 \times 10^{-3}$ mol l^{-1} (correlation coefficient = 0·9993). When pyrene was used in place of benzene, $K_1 \approx \infty$ mol l^{-1} and $K_2 = 16{\cdot}0 \times 10^{-3}$ mol l^{-1} (correlation coefficient = 0·9998). In both cases, the equilibrium (6) lies to the right, and it is apparent that the aromatic compound participates in the dissociation to a small extent as the amount of species (*1*) formed by equilibrium (7) is increased by a factor of *ca.* 2 when benzene is replaced by pyrene.

In the presence of pyrene, where K_1 is very large, the concentration of (*1*) was calculated using equation (10); values are given in Table 6; column 3. The relationship between rate of exchange in pentane and the concentration of (*1*) is represented by equation (11).

TABLE 6

Comparison of calculated and observed exchange rates in pentane when $[PtCl_4^{2-}]$ is varied. (For conditions see Tables 1 and 4)

$[Cl^-]$ (added)/ M	$[PtCl_4^{2-}]$ (added)/ M	$PtCl_2{\cdot}S_2$ (calc.) [x]/ 10^3M	k_b/h^{-1} (obs.)	k_b/h^{-1} (calc.) [y]
Stabiliser: 0·05M pyrene				
0	0·005	3·29	5·68	4·6
0	0·010	5·14	8·94	8·2
0	0·015	6·41	11·7	11·2
0	0·030	8·76	17·0	17·0
0	0·050	10·5	20·4	21·2
Stabiliser: 0·1M C_6D_6				
0·04	0·002	0·278	0·64	0·57
0·04	0·004	0·535	1·27	1·18
0·04	0·008	0·985	2·38	2·33
0·04	0·016	1·705	4·39	4·35
0·04	0·030	2·60	7·71	7·00

[x] Using $K_1 = \infty$ mol l^{-1}, $K_2 = 16 \times 10^{-3}$ mol l^{-1} for the reactions (6) and (7) when pyrene was present and $K_1 = 2{\cdot}40$ mol l^{-1}, $K_2 = 7{\cdot}0 \times 10^{-3}$ mol l^{-1} when C_6D_6 was present. [y] Using the corresponding Cl^- effect series for obtaining proportionality constants in the kinetic equation (11).

For these conditions, the constant of proportionality for equation (11) is calculated using the set of results in Table 4 wherein the $[Cl^-]$ is varied. The validity of this treatment is shown by using this calculated constant in equation (11) with the concentrations of (*1*) calculated for the set of results in Table 4 wherein $[PtCl_4^{2-}]$ is varied, to give calculated values for k_b. These are given in Table 6, agreement with the experimental values is good. The results obtained in the presence of perdeuteriobenzene (Tables 4 and 1) were treated in a similar manner; (the calculation of [(*1*)] was complicated because K_1 was not very large and hence values had to be calculated using an approximation technique). Again the agreement between the observed and calculated values of k_b is good (Table 6).

$$[(1)] = \frac{K_2{\cdot}[PtCl_3{\cdot}S^-]}{[Cl^-]} \qquad (10)$$

$$k_b \propto [(1)]^x \qquad (11)$$

Values of the exponent x used were 1·12 ± 0·02 when benzene was present and 1·34 ± 0·01 when pyrene was present. The values exceed unity, and this may indicate some participation by species (*2*).

The importance of preliminary dissociation to produce the catalytically active species is shown by the above results. It might be possible to produce higher concentrations of the catalyst (*1*) if a starting material was used which contained fewer chloride ligands than $PtCl_4^{2-}$. Recently, we have prepared $PtCl_3,OAc^{2-}$. This species gives characteristic yellow solutions with naphthalene and with pyrene in aqueous acetic acid. The solutions are considerably more reactive than

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[14] L. I. Elding, *Acta Chem. Scand.*, 1970, **24**, 2546, 2557.

PtCl$_4^{2-}$ as catalysts for exchange both in aromatic compounds and in alkanes. Details of the preparation will be given in a subsequent paper.

The n.m.r. results presented in Table 3 show that the reactivity of the different positions in the alkanes decreases primary > secondary > teriary (*cf.* pentane and 2-methylbutane). Both methyl and methylene groups adjacent to a quarternary carbon atom have very low reactivity, *e.g.* in 2,2-dimethylbutane and 1,1-dimethylpropylbenzene. A more complete comparison is given in Table 5; these results have been obtained during the initial stages (first 8%) of the exchange reaction. As explained in the Experimental section, pentane was used as a ' standard ' to enable comparison of samples from different batches. These results (Table 5) show that the rate constant for the disappearance of [$^2H_0$]-alkane (k_b) increases with increase in the carbon-chain length for n-alkanes (methane to hexane) and decreases with increase in branching, *e.g.* pentane, 2-methylbutane, and 2,2-dimethylpropane.

As indicated in our preliminary communication,[7] we have been able to correlate the reactivity of the n-alkanes with their ionisation potentials. In Figure 3, rate constants for the compounds given in Table 5 have been plotted against their respective photoionisation potential (*P.I.*).[15] This correlation has been found not only for alkanes, as reported here, but also for substituted alkanes and for aromatic hydrocarbons and their derivatives, and will be the subject of a future paper in this series. The n-alkanes, with the exception of methane, give an apparently linear correlation of exchange rate with ionisation potential; the overall correlation, when aromatic compounds are included, will be shown as logarithmic. The ionisation potential is a measure of the energy of the highest occupied orbital in the molecule, it is a one-electron property [16] and in an alkane requires a fully delocalised molecular orbital description of its specification. Isomeric molecules have similar ionisation potentials but the exchange rates in the butane, the pentane, and the hexane series of compounds decrease with an increase of the branching in the molecule.

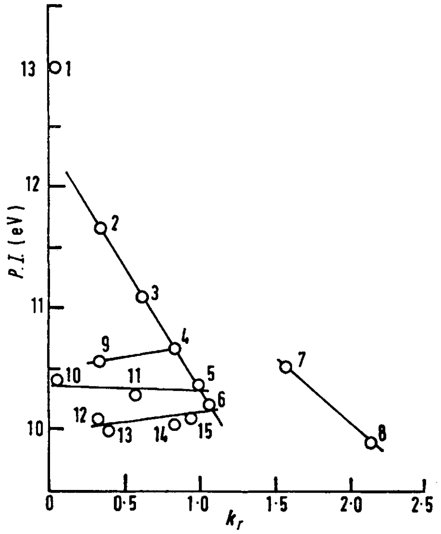
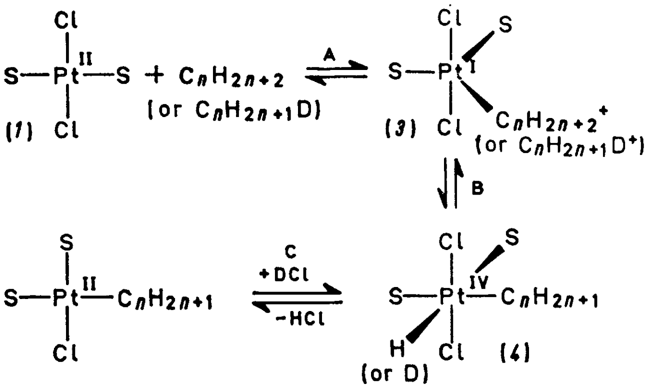


FIGURE 3 Exchange rates in alkanes relative to pentane (k_r), plotted against photoionisation potential (*P.I.*).[15] 1 = Methane, 2 = ethane, 3 = propane, 4 = butane, 5 = pentane, 6 = hexane, 7 = cyclopentane, 8 = cyclohexane, 9 = 2-methylpropane, 10 = 2,2-dimethylpropane, 11 = 2-methylbutane, 12 = 2,2-dimethylbutane, 13 = 2,3-dimethylbutane, 14 = 3-methylpentane, and 15 = 2-methylpentane

We consider that the preliminary interaction of an alkane with the catalyst involves electron transfer from delocalised molecular orbitals in the alkane to the platinum atom in the complex. The details proposed for this interaction, and the subsequent steps to give deuteriated alkane are given in the Scheme. The intermediate (*3*) in which alkane is co-ordinated to platinum, is thought to be analogous to the palladium(I)–benzene complex which is formed when palladium(II) acetate is reduced by benzene in a perchloric–acetic acid medium.[12] Step A in the Scheme involves co-ordination of a electron pair from the alkane to the platinum. This step is considered to be rate-determining. As in the case of previous studies of exchange in aromatic compounds using platinum catalysts,[10] subsequent steps are reversible and involve transfer of a proton to the platinum to give a platinum(IV) intermediate which exchanges rapidly with the deuteriated solvent. Branched-chain alkanes have a lower reactivity and this may be explained in terms of steric hindrance. In addition, the methyl groups of linear alkanes have higher reactivity than methylene groups, presumably because of the preference for the formation of primary rather than secondary alkylplatinum complexes.[17]



SCHEME

One of the important features of this exchange reaction is the fact that the *M*-value exceeds unity; the presence of intermediate complexes which allow reversible rearrangements to occur is necessary to explain this observation. There appears to be two possibilities. Steps B and C (Scheme) may occur several times before dissociation of the complex (*3*) (*i.e.* before step A from

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[15] D. W. Turner, *Adv. Phys. Org. Chem.*, 1966, **4**, 31.

[16] M. J. S. Dewar, ' The Molecular Orbital Theory of Organic Chemistry,' McGraw-Hill, New York, 1969, p. 139.

[17] J. Chatt, R. S. Coffey, A. Gough, and D. T. Thompson, *J. Chem. Soc.* (*A*), 1968, 190.

right to left) thus giving multiple exchange. This mechanism requires that species (*3*) is sufficiently stable for this exchange process to occur. Alternatively, multiple exchange can occur if the hydrocarbon entity interacts with both platinum atoms of the chlorine-bridged dimer (*2*) [equation (8) or (9)]. The reduction in M-value with the increase in chloride ion concentration (Table 4) is expected if the dimer is formed by reaction (8).

The evidence indicates that hydrogen–deuterium exchange in alkanes is essentially the same as exchange in aromatic compounds.[10] Further support for this view is provided by the similarity of the observed isotope effects, for alkanes (cyclohexane) $1{\cdot}7 \pm 0{\cdot}1$ (Table 5) and for benzene $1{\cdot}65 \pm 0{\cdot}05$.[10] Furthermore, rates of reaction are similar, the least reactive aromatic compound, benzene, has an exchange rate only three times that of the most reactive alkane, cyclohexane.

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