The Activation of Saturated Hydrocarbons by Transition-metal Complexes in Solution. Part II.[1] Hydrogen–Deuterium Exchange in Saturated and Unsaturated Hydrocarbons catalysed by Solvated Platinum(II) Chloro-complexes

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Exchange of hydrogen for deuterium in alkanes and in aromatic hydrocarbons is catalysed by platinum(II) chloro-complexes in acetic [$^2H_1$]acid–deuterium oxide mixtures at *ca.* 100 °C. Solutions of chloro-complexes having Cl : Pt ratios in the range 4·0—2·3 have been used. The effects on the exchange process of hydrocarbon concentration, solvent composition, and catalyst composition are reported. The rate constant for exchange varies exponentially with the adiabatic ionisation potential of the hydrocarbon. This correlation breaks down for certain aromatic hydrocarbons when Cl : Pt < 4 owing to extensive complex formation between reactant and catalyst; values for the formation constants of such complexes are reported.

ALKANES are activated in the presence of tetrachloroplatinate(II) ions in aqueous acetic acid and will undergo hydrogen–deuterium exchange.[1,2] Tetrachloroplatinate(II) ions apparently dissociate losing two chloride ligands to produce the active catalyst.[1,2] The order of reactivity of the hydrogen atoms in the alkanes was

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[1] Part I, R. J. Hodges, D. E. Webster, and P. B. Wells, *J. Chem. Soc.* (*A*), 1971, 3230.

[2] M. B. Tyabin, A. E. Shilov, and A. A. Shteinman, *Doklady Akad Nauk S.S.S.R.*, 1971, **198**, 380.

found to be primary > secondary > tertiary, *i.e.*, the reverse of the order of their carbon–hydrogen bond dissociation energies. Platinum disproportionation is inhibited by the addition of aromatic compounds, *e.g.*, benzene and pyrene, to the reaction mixture.[1]

A mechanism involving an intermediate alkane–platinum complex to interpret multiple exchange in the initial stages of the reaction was suggested.[1] The nature of this intermediate was not established, but it may have a formal similarity to a platinum–alkene complex.[3-5]

It is necessary here to treat alkanes and aromatic compounds as members of a single set, since rate constants for hydrogen–deuterium exchange in a series of alkanes [1] and in a series of aromatic compounds [6] are of the same order of magnitude. There is a need for a parameter that is applicable to both saturated and unsaturated hydrocarbons. For platinum-catalysed hydrogen–deuterium exchange in a series of aromatic compounds, C–C bond order is the parameter that has been used.[6] This concept cannot be applied successfully to alkanes since they all have a nominal carbon–carbon bond order of unity. We have demonstrated that the reactivities of normal alkanes in this hydrogen–deuterium exchange reaction correlate with the ionisation potentials of the alkanes,[1] and this may indicate transfer of electrons from the hydrocarbon to the platinum during the rate-determining step. Ionisation energies of specific orbitals in both alkanes and aromatic compounds can be obtained by photoelectron spectroscopy,[7,8] and this information is important for a consideration of hydrogen–deuterium exchange in substituted alkanes and aromatic compounds (following paper).

Alkenes form strong complexes with platinum(II), but exchange reactions have shown that aromatic compounds and alkanes complex with platinum(II) only when ligands bonded to platinum are of low *trans*-effect.[1,2,9] When bromoplatinate(II) complexes are used, there is almost complete inhibition of exchange in alkanes (following paper) and substantial reduction of exchange in aromatic compounds.[9] Bromide ligands have only a slightly higher *trans*-effect than chloride ligands, and all ligands with a higher *trans*-effect than bromide almost completely inhibit exchange in benzene.[9] As alkanes do not interact with platinum(II) as strongly as aromatic compounds or alkenes, ligands of even lower *trans*-effect than chloride would be advantageous for the achievement of alkane catalysis. Elding has studied the hydrolysis of $PtCl_4^{2-}$ and has concluded that the *trans*-effect of chloride ligands was 100—200 times that of water.[10] Previous studies with alkanes indicated that the added potassium tetrachloroplatinate(II) undergoes solvolysis to produce small concentrations of the active catalyst, mainly $PtCl_2Q_2$ (where $Q =$ water or acetic acid)(1).[1,2] This initial solvolysis emphasises the importance of ligands of exceptionally low *trans*-effect for reactions involving alkanes. Significantly higher concentrations of species (1) can be obtained from sodium tetrachloroplatinate(II) and are used in this study.

This paper reports first that both alkanes and aromatic hydrocarbons, in the presence of platinum(II), can be considered as one group of compounds for hydrogen–deuterium exchange reactions, and secondly, that $PtCl_2Q_2$ (1) in solution has considerable potential as a catalyst for alkane reactions. In the following paper, exchange results for substituted hydrocarbons are reported.

EXPERIMENTAL

Preparation of Catalyst Solutions.—Three procedures were used for the preparation of catalyst solutions. (A) 0·02M-$PtCl_4^{2-}$ in 50 mol % AcOD–D_2O solvent mixture was prepared from K_2PtCl_4 as described previously.[1] (B) An aqueous solution of $Na_2PtCl_4,4H_2O$ (0·5 g in 5 ml) as supplied by Johnson-Matthey and Co. was hydrolysed to an equilibrium mixture of solvated species by heating at 100 °C for 6 days in a sealed tube.[10] After cooling, the solution was freeze-dried and redissolved in 10 ml of acetic [$^2H_1$]acid containing 0·5 ml of acetic anhydride. All soluble salts were dissolved and 53 mg of a white solid were filtered off. The solution was then diluted to 25·0 ml with AcOD. Platinum was determined gravimetrically by reduction of the platinum(II) in a 2·5 ml aliquot portion to metallic platinum with $NaBH_4$, followed by filtration and subsequent heating of the filter paper to 800 °C in a tared crucible. The chloride-ion concentration in the filtrate was estimated by the Volhard procedure. The platinum concentration was found to be 0·036M and the Cl^- : Pt ratio was 3·3. Suitable aliquot portions of this glacial acetic acid solution of platinum were taken to give catalytic solutions which contained 0·0035M-$PtCl_{3\cdot3}^{1\cdot3-}$ in 50 mol % AcOD–D_2O.

A solution of the white solid (previous paragraph) in water (50 ml) was analysed for sodium content by atomic absorption spectroscopy and for chloride content by both the Mohr and the Volhard procedures. Analyses showed that the solid contained 50·3 mg of sodium chloride. This weight corresponded to the removal of 1·0 chloride ligand for each platinum atom in the starting material.

(C) The procedure for preparation (B) was modified. To decrease the solubility of sodium chloride in the acetic acid solution additional sodium ions (200 mg $NaOAc,3H_2O$) were added immediately before the freeze-drying stage; 145 mg of sodium chloride were collected. The filtrate was diluted to 25·0 ml with acetic [$^2H_1$]acid containing 0·1M-$DClO_4$. The platinum concentration in this solution was found to be 0·048M and the Cl^- : Pt ratio was 2·3. The weight of sodium chloride collected indicated that 2·0 chloride ligands had been removed for each platinum atom present. Suitable aliquot portions were taken to give solutions used for the catalytic reactions containing 0·005M-$PtCl_{2\cdot3}^{0\cdot3-}$ in the AcOD–D_2O mixtures.

The chloride analyses for preparations (B) and (C) and for

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[3] J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 1953, 2939.

[4] F. R. Hartley, *Chem. Rev.*, 1969, **69**, 799.

[5] A. Streitwieser, 'Molecular Orbital Theory for Organic Chemists,' John Wiley and Sons, New York, 1961, p. 198.

[6] R. J. Hodges and J. L. Garnett, *J. Phys. Chem.*, 1969, **73**, 1525.

[7] D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, 'Molecular Photoelectron Spectroscopy,' Wiley–Interscience, New York, 1970.

[8] D. W. Turner, *Chem. in Britain*, 1968, **4**, 435.

[9] R. J. Hodges, Ph.D. Thesis, University of New South Wales, 1968.

[10] L. I. Elding, *Acta Chem. Scand.*, 1970, **24**, 1527.

the starting material indicated that an excess of chloride ions equivalent to 0·3 mol of sodium chloride was present in the Na_2PtCl_4 solutions used. There appears to be considerable variation in the sodium chloride content of batches of Na_2PtCl_4 solution as supplied.

Exchange Procedure and Analyses.—The above solutions (A), (B), and (C) were used as described previously.[1] All reactions were carried out in ampoules that were sealed without evacuation and a little pyrene was added to inhibit disproportionation of the catalyst. Distributions of deuterium in products were obtained by mass spectrometry. The spectra were corrected for ^{13}C isotope and ion fragmentation.[1] The results presented for each of the catalyst solutions (A), (B), and (C) are reproducible when the same batch of solution is used.

TABLE 1

Platinum(II)-catalysed hydrogen–deuterium exchange in a series of hydrocarbons in 50 mol % AcOD–D_2O

Compound	Concn./M	t/°C	Reaction time/h	% D	M	k_b (%-[$^2H_0$]alkane removed h^{-1})
Series I [a]						
Methane	0·3	100	25·50	7·80	1·48	0·86
Ethane	0·3	100	5·08	5·56	1·70	3·99
Propane	0·3	100	5·08	7·16	1·63	7·18
Butane	0·3	100	2·00	3·33	1·62	10·46
Pentane	0·3	100	4·00	6·39	1·65	12·00
Hexane	0·3	100	5·08	6·65	1·50	13·8
Cyclopentane	0·3	100	2·00	6·45	1·68	20·0
Cyclohexane	0·3	100	2·00	6·31	1·42	27·5
Pentane	0·2	80	15·83	4·86	1·87	2·02
Cyclohexane	0·2	80	4·33	2·81	1·61	4·92
Benzene	0·2	80	4·00	21·18	3·50	10·7
Naphthalene	0·2	80	2·00	10·92	1·00	46·6
	0·3	80	1·92	10·16	1·02	43·9
Phenanthrene	0·3	80	2·45	13·3	0·95	66·2
Series II [b]						
Ethane	0·3	100	24·25	3·67	1·95	0·55
Propane	0·3	100	24·25	7·38	1·86	1·36
Pentane	0·3	100	7·22	3·21	1·77	3·07
Cyclohexane	0·3	100	7·22	7·09	1·59	7·74
Benzene	0·2	100	0·75	7·82	3·59	27·3
	0·3	100	2·47	31·6	3·49	25·9
Naphthalene	0·2	100	0·75	4·35	1·06	66·8
	0·3	100	1·00	5·61	1·03	45·1
Pyrene	0·035	100	0·75	4·85	0·98	102·1

[a] Catalyst solution (A): $[Pt^{II}] = 0·02M$; $Cl^- : Pt = 4:1$; [pyrene] = 0·05M; $[DClO_4] = 0·2M$. [b] Catalyst solution (B): $[Pt^{II}] = 0·0035M$; $Cl^- : Pt = 3·3$; [pyrene] = 0·012M; $[DClO_4] = 0·2M$.

RESULTS

In previous studies, $PtCl_4^{2-}$ was used to catalyse hydrogen–deuterium exchange in alkanes, in an acetic [$^2H_1$]acid–deuterium oxide solvent.[1] Chloride ions reduced the reaction rate and it was found that dissociation of two chloride ligands preceded the formation of the active catalyst.[1] In the present study, platinum catalysts have been used to compare rates of reaction for alkanes and aromatic compounds. Table 1 lists percentage exchange (%D), values of the multiple exchange parameter (M), and the rate constants for the disappearance of [$^2H_0$]hydrocarbon (k_b) for a series of compounds at 80 °C and 100 °C by use of catalyst solution (A), namely $PtCl_4^{2-}$ (Series I). The quantities %D, M, and k_b have been defined in Part I.[1] Results for a typical series at 100 °C obtained by use of catalyst solution (B) which contains a $Cl^- : Pt$ ratio of 3·3 are included (Series II).

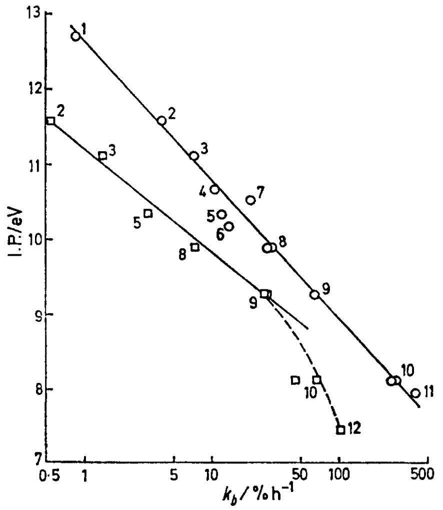
The rates of exchange in naphthalene, phenanthrene, and pyrene were higher than those of the other compounds and their solutions changed colour from orange-red to yellow as reaction occurred. This colour change was more pronounced for catalyst preparation (B) than for (A). It is apparent (Table 1) that naphthalene concentration has a pronounced effect upon the rate constant (k_b) in series II, *i.e.*, increasing the naphthalene concentration from 0·2 to 0·3M reduces the rate by 32% for series II, but by only 6% for series I. Significant amounts of a platinum–naphthalene complex may be formed in solution when the chloride ion concentration is low.

The multiple exchange parameter (M) varies considerably from compound to compound. For alkanes M is in the range 1·4—2·0, for benzene M is *ca.* 3·5, and for naphthalene, phenanthrene, and pyrene M is almost unity (stepwise exchange). As variations in M influence the observed rate of deuteriation (%D h^{-1}), the rate constant for disappearance of [$^2H_0$]hydrocarbon (k_b) is a better measure of the reactivity. For a molecule with all exchangeable positions equivalent, the calculated M-value cannot be less than unity. However where exchange occurs in molecules containing non-equivalent hydrogen atoms, *e.g.*, naphthalene and pyrene, the calculated M-value is low and this may limit the accuracy of k_b. The problem is not considered to be serious here, where initial rates are used.

Values for k_b from Table 1 are plotted on a logarithmic scale against adiabatic ionisation potentials in the Figure; the plot is linear. Results for 0·02M-$PtCl_4^{2-}$ at 80 °C have been adjusted, with n-pentane as the standard, to correspond with those at 100 °C. This adjustment is valid since activation energies for hydrogen–deuterium exchange all lie in a narrow range (22—25 kcal mol^{-1}) for the compounds studied. When 0·0035M-Pt^{II} [where $Cl^- : Pt = 3·3$, solution (B)] is used the values lie on a curve.

Platinum solution (C), containing a $Cl^- : Pt$ ratio of 2·3, was used to estimate the effect of hydrocarbon concentration upon %D, M, and k_b. The effect of changing the concentration of acetic acid and of hydrocarbon is shown in Table 2. The hydrocarbons studied were ethane, pentane, cyclohexane, benzene, biphenyl, naphthalene, and pyrene. This series also indicates the effect of dielectric constant[11] and, in the case of ethane, the effect of pressure upon rate.

The effect of changes in acetic acid or hydrocarbon concentration is not the same for all of the compounds sudied (Table 2). Increase in the acetic acid concentration, and thus decrease in the dielectric constant of the solution, has only a minor effect on k_b for aromatic compounds, but reduces this rate constant substantially for the three alkanes studied. M is affected only slightly by changing the acid concentration, except for benzene and biphenyl where M is reduced as the acetic acid concentration is increased. For the alkanes and benzene the reaction is of the first order, as shown by the independence of k_b on hydrocarbon concentration. Except for benzene, the constant k_b is dependent upon hydrocarbon concentration for each of the aromatic compounds studied and the dependence is most pronounced for naphthalene and pyrene. The significance of the effect of hydrocarbon concentration on the mechanism of exchange will be considered in the Discussion section.



Rate constants (k_b) in 50 mol % AcOD–D_2O at 100 °C for a series of typical alkanes and aromatic compounds plotted on a logarithmic scale against their adiabatic ionisation potentials (I.P.). 1 = Methane (I.P. = 12·70 eV,[a] using photoelectron spectroscopy (p.e.)]; 2 = ethane (11·56 eV,[a] p.e.); 3 = propane [11·08 eV,[b] photoionisation potential (P.I.)]; 4 = n-butane (10·65 eV,[b] P.I.); 5 = n-pentane (10·33 eV,[b] P.I.); 6 = n-hexane (10·17 eV,[b] P.I.); 7 = cyclopentane (10·51 eV,[b] P.I.); 8 = cyclohexane (9·88 eV,[b] P.I.); 9 = benzene (9·25 eV,[c] p.e.); 10 = naphthalene (8·12 eV,[c,d] p.e.); 11 = phenanthrene (7·95 eV, p.e., this work); 12 = pyrene (7·46 eV, p.e., this work).

Circles = solution (A); $[PtCl_4^{2-}]$ = 0·02M, results at 80 °C adjusted to correspond with those at 100 °C by use of n-pentane as the standard.

Squares = solution (B); $[PtCl_{3\cdot3}^{1\cdot3-}]$ = 0·0035M

[a] A. D. Baker, C. Baker, C. R. Brundle, and D. W. Turner, *J. Mass Spectrometry and Ion Phys.*, 1968, **1**, 285. [b] D. W. Turner, *Adv. Phys. Org. Chem.*, 1966, **4**, 31. [c] Ref. 7. [d] Ref. 8.

DISCUSSION

The results for the series of hydrocarbons presented in the Figure show that the rate constants for platinum-catalysed hydrogen–deuterium exchange (k_b) correlate with the first ionisation potentials. Results for simple alkanes and aromatic compounds lie on the same curve, suggesting a common mechanism. The rate constant for phenanthrene is *ca.* 400 times that of methane. This difference in rate is quite small, particularly when compared with the difference in ionisation potential. It is apparent that in reaction with Pt^{II} these compounds are similarly activated.

Solution (B) was of comparable activity with solution (A) (Table 1); at the extremes it catalysed ethane exchange more slowly (factor = 0·7) and benzene exchange more rapidly (factor = 2·5). Solution (C) was the most active (Table 2); at the extremes, it catalysed exchange in ethane and in benzene more rapidly than solution (A) by factors of 1·5 and 3·5 respectively.

Several important physical differences in the exchange reaction were also observed for naphthalene and pyrene. With preparations (B) and (C), these two compounds produced a pronounced colour change from orange-red to yellow during the reaction, whereas when benzene and the alkanes were used the orange-red colour of the platinum catalyst was retained. This suggests the presence of platinum–naphthalene and platinum–pyrene complexes. Formation of such complexes may influence the exchange reaction and will limit the value of k_b if the equilibrium constant for complex formation is large. Strong complex formation will be accompanied by a change in the order of reaction with respect to hydrocarbon; such a change is observed (Table 2).

Values for k_b in Table 2, for acetic acid concentrations of 55, 70, and 85 mol % AcOD in D_2O, show that this constant does not vary greatly with change in alkane concentration, although for pyrene and naphthalene it is inversely related to the hydrocarbon concentration. Table 2 also shows that in 40 mol % AcOD the values for k_b are less reliable; this may be because the solubilities of the hydrocarbons are low. In 100 mol % AcOD, some unidentified red precipitate was produced in several of the reaction tubes, and values for k_b appear to be low. The amount of red precipitate depended upon the concentration of pyrene that was added. The variation in k_b with concentration of pentane and of ethane was assumed to be an artifact due to the volatility of these compounds.

Quantitative information has been obtained concerning the interaction of the aromatic hydrocarbons with Pt^{II} with solution (C). Consider a situation in which equilibria are rapidly established between the catalytic quantity of platinum(II) chloro-complex, solvent, hydrocarbon, and a new complex, (2) [equation (1)], and in which subsequent slow reaction of (2) by a number of elementary steps yields deuteriated hydrocarbon. The total concentration of platinum complexes, $[Pt]_{total}$, and

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[11] S. Kilpi and E. Lindell, *Ann. Acad. Sci. Fennicae*, 1967, *A, II*, 135.

TABLE 2

Effect of hydrocarbon and solvent composition upon the rate constant for platinum(II)-catalysed hydrogen–deuterium exchange in a series of hydrocarbons at 100 °C; $[\mathrm{Pt^{II}}] = 0{\cdot}005$M; Ratio $\mathrm{Cl^-} : \mathrm{Pt} = 2{\cdot}3$

Compound (X)	Reaction time/h	Mol % AcOD [a]	x	% D			M			k-/(%-[$^2H_0$]alkane removed h^{-1})		
				$[X] = x$M	$[X] = \frac{2x}{3}$M	$[X] = \frac{x}{3}$M	$[X] = x$M	$[X] = \frac{2x}{3}$M	$[X] = \frac{x}{3}$M	$[X] = x$M	$[X] = \frac{2x}{3}$M	$[X] = \frac{x}{3}$M
Ethane	74·67	40	0·30	26·9	28·1	32·6	1·89	1·89	1·84	1·35	1·42	1·75
		55	0·30	24·0	26·0	28·4	1·57	1·56	1·54	1·41	1·57	1·75
		70	0·30	16·4	—	22·6	1·35	—	1·37	1·08	—	1·52
		85	0·30	12·2	—	—	1·36	—	—	0·78	—	—
		100	0·30	5·4	5·4	6·5	2·05	1·90	1·86	0·22	0·23	0·39
Pentane	12·00	40	0·20	8·6	11·1	11·5	2·05	1·99	1·98	4·42	5·94	6·21
		55	0·24	9·25	9·37	10·61	1·57	1·60	1·70	6·21	6·18	6·62
		70	0·26	5·13	5·63	5·48	1·35	1·38	1·37	3·91	4·21	4·12
		85	0·28	2·83	2·89	3·64	1·39	1·39	1·56	2·07	2·12	2·38
		100	0·30	1·43	1·54	1·84	2·09	2·10	2·26	0·69	0·74	0·83
Cyclohexane	6·00	40	0·20	10·1	13·2	12·2	1·87	1·77	1·76	11·4	16·0	14·8
		55	0·24	10·2	10·4	10·4	1·52	1·53	1·52	14·28	14·48	14·50
		70	0·26	5·6	5·7	5·7	1·37	1·38	1·38	8·43	8·45	8·43
		85	0·28	3·63	3·64	3·66	1·46	1·42	1·42	5·09	5·20	5·24
		100	0·30	1·89	1·99	2·01	1·76	1·73	1·72	2·17	2·32	2·36
Benzene	2·50	40	0·20	49·2	50·0	49·8	3·66	3·63	3·69	45·5	46·0	45·8
		55	0·24	48·9	49·5	50·6	3·27	3·29	3·36	50·5	51·1	51·6
		70	0·26	43·4	43·8	44·0	2·83	2·83	2·74	48·6	49·1	49·4
		85	0·28	38·5	40·0	40·1	2·50	2·53	2·59	48·8	49·1	49·4
		100	0·30	33·2	33·6	35·1	2·35	2·38	2·41	41·7	41·8	41·9
Biphenyl	1·50	40	0·20	19·7	19·0	—	2·39	2·41	—	61·6	58·5	—
		55	0·24	19·7	21·2	22·4	2·19	2·25	2·27	67·1	71·2	75·2
		70	0·26	19·7	20·2	21·1	2·04	2·02	2·07	72·9	75·2	76·7
		85	0·28	18·2	18·8	19·9	1·87	1·91	1·91	72·1	73·5	75·2
		100	0·30	17·8	18·8	18·1	1·53	1·57	1·59	86·0	88·5	84·5
Naphthalene	1·25	40	0·20	11·6	15·4	—	1·06	1·07	—	75·4	100·3	—
		55	0·24	13·8	17·4	22·5	1·07	1·04	1·02	94·3	118·2	159·5
		70	0·26	16·4	18·1	21·3	1·00	0·99	1·01	116·2	130·1	152·8
		85	0·28	14·0	15·0	19·4	0·98	0·98	0·96	98·7	106·4	143·8
		100	0·30	10·4	13·4	18·1	0·97	0·98	0·95	72·5	94·2	135·3
Pyrene [b]	0·667	40	0·060	5·7	8·3	10·6	1·18	1·11	0·97	74·3	117·3	174·1
		55	0·070	9·5	10·6	11·2	0·99	0·96	0·91	150·6	170·1	196·4
		70	0·078	10·0	10·3	11·1	1·01	1·00	0·92	156·9	163·8	190·3
		85	0·094	9·8	10·2	10·8	1·02	0·95	0·95	151·9	169·7	180·2
		100	0·100	5·8	8·9	10·3	1·12	0·98	0·98	79·6	143·3	168·0

[a] $\mathrm{DClO_4}$ and pyrene are also included in the reaction mixture. $[\mathrm{DClO_4}]$ is 0·3, 0·2, 0·11, 0·05, and 0M and [pyrene] is 0·0068, 0·0079, 0·0088, 0·0094, and 0·010M, in 40, 55, 70, 85, and 100 mol % AcOD respectively. [b] [Pyrene] in any given experiment is that given in the Table plus that given in footnote *a*.

the concentration not present as (2) $[\mathrm{Pt}]_{\mathrm{free}}$, are related

$$\underset{(1)}{\mathrm{PtCl_2Q_2}} + \text{hydrocarbon} \underset{k_{-1}\ +\mathrm{Q}}{\overset{k_1\ -\mathrm{Q}}{\rightleftharpoons}} \underset{(2)}{\mathrm{PtCl_2Q,\ hydrocarbon}} \overset{k_2\ +\mathrm{Q}}{\rightleftharpoons} \mathrm{PtCl_2Q_2} + \text{deuteriated hydrocarbon} \quad (1)$$

$$(\mathrm{Q} = \text{solvent})$$

by the equation $[\mathrm{Pt}]_{\mathrm{total}} = [\mathrm{Pt}]_{\mathrm{free}}\,(1 + K[\text{hydrocarbon}])$ where $K = k_{-1}/k_1$. Now, the rate of removal of reactant is given by $-d[\text{hydrocarbon}]/dt = k_2[(2)]$ whence we obtain equation (2). The differential term in equation

$$-\mathrm{d}(\ln[\text{hydrocarbon}])/\mathrm{d}t = k_2K[\mathrm{Pt}]_{\mathrm{total}}/(1 + K[\text{hydrocarbon}]) \quad (2)$$

(2) is proportional to k_b. This arises because the quantity of deuterium available for exchange is very high, and hence the proportion of $[^2H_0]$hydrocarbon present when isotope equilibrium is attained is negligible. For this situation, the equation [1] which defines k_b may be rearranged to give $-\mathrm{d}(\ln[\text{hydrocarbon}])/\mathrm{d}t = 0{\cdot}01k_b$, and therefore (3). Thus a plot of $[\mathrm{Pt}]_{\mathrm{total}}/k_b$ against [hydrocarbon] should be linear, the formation constant K being

$$[\mathrm{Pt}]_{\mathrm{total}}/k_b = 100[\text{hydrocarbon}]/k_2 + 100/k_2K \quad (3)$$

given by the gradient divided by the intercept. Values of K in Table 3 have been determined by this graphical method. A full set of results is given for the calculation of K when the acetic acid concentration is 55 mol %, for 70 and 85 mol % acetic acid the value of K is simply quoted. Values of K increase on passing from benzene to biphenyl, to naphthalene, to pyrene, and diminish as the acetic acid concentration is raised. For the cases of naphthalene and of pyrene, most of the platinum is present as the complex (2).

With platinum solutions (B) and (C) there is a substantial deviation of k_b from the logarithmic relationship with ionisation potential (Figure and Table 2). The interaction of naphthalene or pyrene with the more solvated platinum complexes present in solutions (B) and (C) is greater than with the complex in solution (A). Thus the exchange rate in naphthalene is least dependent upon naphthalene concentration for solution (A) (Table 1), and the logarithmic relationship between k_b and ionisation potential holds for this case (Figure).

For reactions in solution C, where $\mathrm{Cl^-} : \mathrm{Pt} = 2{\cdot}3 : 1$, the rate constants for exchange in the alkanes are reduced approximately five-fold as the acetic acid concentration of the solvent is increased from 40 to 100 mol % (Table 2). A similar trend occurs in the calculated equilibrium constants for the aromatic compounds (Table 3); there is no such effect for the observed rate constants. The dielectric constant of 40 mol % acetic acid is 37·5 and that of 100 mol % acetic acid is 6·21.[11] It appears that dielectric constant has only a minor influence on the exchange rate.

The high multiple exchange parameters for benzene, biphenyl, and the alkanes indicate that the activated complex producing exchange is a relatively stable complex since it permits an exchange step to occur more than once before it dissociates. The above treatment is only valid where it is considered to involve a preliminary reversible complex formation that precedes and is different from the activated complex producing exchange. Conversely the three compounds, naphthalene, phenanthrene, and pyrene, which complex most strongly and give yellow colours during the course of the reaction, do exchange predominantly by a stepwise process, thus a further activated intermediate need not be postulated. The formation of the intermediate that leads to H–D exchange is considered to be the rate-determining step of the exchange reaction. It involves the π-orbitals of aromatic compounds and, presumably, delocalised σ-orbitals of an alkane.

The calculated equilibrium constants, K_1, for the platinum–aromatic complexes [equation (1)] are approximate since the platinum catalyst is a mixture of species (predominantly $PtCl_2Q_2$). The trend in these values of K_1 is in the sense predicted by both bond order and ionisation potential (Table 3). Molecules with higher π-bond orders, *e.g.*, alkenes, are known to complex more strongly, typical formation constants for platinum–alkene complexes being greater than 1000.[4] However the ionisation potentials for alkenes are similar to those of the alkanes, and the correlations developed above cannot be extended to alkenes. Knowledge of ionisation potential is of empirical value in understanding the behaviour of compounds which form weak complexes with the platinum catalyst, and has considerable predictive power for explaining trends in hydrogen–deuterium exchange reactivity of several classes of compounds (following paper).

TABLE 3

Part A: Comparison for various compounds of bond order, ionisation potential, and equilibrium constant (K)
Part B: Typical derivation for AcOD = 55 mol % [see equation (2)]

	A					B	
			K/l mol^{-1}				
			Mol % AcOD				
Compound (X)	Bond order [a]	I.P.[b]/eV	55	70	85	$\frac{[X]_{total}}{M}$	$\frac{10^5[Pt]_{total}/k_b}{l\ mol^{-1}\ h^{-1}}$
Cyclohexane	1·0	9·88 [c]	<0·01			0·24	35·0
						0·16	34·5
						0·08	34·5
Benzene	1·667	9·25 [d]	0·14	0·09	0·07	0·24	9·90
						0·16	9·79
						0·08	9·69
Biphenyl	1·667	8·30 [e]	0·80	0·30	0·23	0·24	7·45
						0·16	7·02
						0·08	6·65
Naphthalene	1·725	8·14 [d]	6·6	2·1	1·7	0·24	5·30
						0·16	4·23
						0·08	3·14
Pyrene	1·777	7·46 [f]	9·6	4·1	3·3	0·080	3·32
						0·057	2·94
						0·036	2·54

[a] Hückel M.O. calculations (C. A. Coulson and A. Streitwieser, 'Dictionary of π-Electron Calculations,' Pergamon, London, 1965. [b] By photoelectron spectroscopy. [c] D. W. Turner, *Adv. Phys. Org. Chem.*, 1966, **4**, 31. [d] Ref. 7. [e] J. H. D. Eland and C. J. Danby, *Z. Naturforsch.*, 1967, **23a**, 355; S. Pignataro, V. Mancini, J. N. A. Ridyard, and H. J. Lenipka, *Chem. Comm.*, 1971, 142. [f] This work.

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