The Activation of Saturated Hydrocarbons by Transition-metal Complexes in Solution. Part IV.[1] Oxidation of Benzene and of Alkanes by Hexachloroplatinate(IV)

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Benzene is oxidised to chlorobenzene by H_2PtCl_6 in aqueous trifluoroacetic acid at 120 °C. The initial formation of a water-soluble complex of platinum(IV) and benzene is accelerated by an increase in the H_2PtCl_6 concentration and by addition of $K_2[PtCl_4]$, and is reduced by the addition of chloride ion. Subsequent reactions give chlorobenzene; some of it complexes with platinum. An analogous study has been made of the oxidation of alkanes, particularly hexane, using the same system. Evidence for the formation of chlorohexanes from hexane and of platinum complexes with hydrocarbon ligands has been obtained. 2- And 3-chlorohexanes are further oxidised and, from determinations of the amount of Pt^{IV} reduced during the reaction, it appears likely that polychlorinated carboxylic acids are formed. The mechanisms of aromatic and alkane oxidation in this system are initially very similar. The reaction of cyclohexane with H_2PtCl_6 is more complex. In addition to chlorination, dehydrogenation occurs to give benzene and chlorobenzene.

STUDIES in this laboratory,[1-3] and elsewhere,[4,5] have shown that, in the presence of platinum(II) salts, alkanes undergo hydrogen–deuterium exchange with the aqueous acetic acid solvent, and that the mechanism of this reaction is very similar to platinum(II)-catalysed hydrogen–deuterium exchange in aromatic hydrocarbons.[6,7] We wished to investigate the possibility of carrying out substitution reactions, other than isotope replacement, in an alkane attached to platinum or some other transition metal. It is known that platinum(IV) complexes are inactive as catalysts for hydrogen–deuterium exchange in alkanes[8] and aromatic hydrocarbons,[6] but it was shown some time ago that a stoicheiometric reaction took place between an aromatic hydrocarbon and $[PtCl_6]^{2-}$ ion to give $[PtCl_4]^{2-}$ that then catalysed hydrogen–deuterium exchange.[6]

In this paper we report investigations into the reactions of benzene, cyclohexane, hexane, and other alkanes with $[PtCl_6]^{2-}$. Very recently a similar study for benzene has been published.[9] This work differs from ours in that aqueous acetic acid was used as the solvent, and the only concentrations measured were those of organic products. We report reasons why acetic acid is not an ideal solvent, and we have analysed for organic reactant and products and for Pt^{II}, thus providing more positive information concerning the mechanism of the reaction. Garnett and West[9] also investigated the competition between chlorination and hydrogen–deuterium exchange; no deuterium-tracer work is reported here. In a brief note[10] Shilov and his co-workers reported that alkanes are chlorinated by hexachloroplatinic(IV) acid in aqueous trifluoroacetic acid at 120 °C over a period of hours to give mainly *n*-chloroalkanes, and that this reaction is coupled with the reduction of Pt^{II} to Pt^{IV}. The reactions reported are summarised by equation (1) where R is an aryl or alkyl

$$RH + [PtCl_6]^{2-} \xrightarrow[\text{catalyst}]{Pt^{II}} RCl + [PtCl_4]^{2-} + HCl \quad (1)$$

group. These reactions are stoicheiometric in the aromatic hydrocarbon or the alkane and in Pt^{IV}, although Pt^{II} is a necessary catalyst for the reaction.

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[1] Part III, R. J. Hodges, D. E. Webster, and P. B. Wells, *J.C.S. Dalton*, 1972, 2577.

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

[3] R. J. Hodges, D. E. Webster, and P. B. Wells, *J.C.S. Dalton*, 1972, 2571.

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

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

[6] R. J. Hodges and J. L. Garnett, *J. Phys. Chem.*, 1968, **72**, 1673.

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

[8] R. J. Hodges, D. E. Webster, and P. B. Wells, unpublished work.

[9] J. L. Garnett and J. C. West, *Austral. J. Chem.*, 1974, **27**, 129.

[10] N. F. Gol'dshleger, V. V. Eskova, A. E. Shilov, and A. A. Shteinman, *Zhur. fiz. Khim.*, 1972, **46**, 1353.

EXPERIMENTAL

Samples (0·8 cm^3) of standard aqueous solutions of H_2PtCl_6 (sometimes containing also $K_2[PtCl_4]$ or NaCl) were placed in glass tubes of 3 cm^3 capacity. Acetic or trifluoroacetic acid (1·2 cm^3) and the appropriate quantity of benzene, hexane, or cyclohexane were added and the tubes sealed at −180 °C without evacuation. Reaction took place in the tubes as they were mechanically tumbled in an oil-bath. As reaction proceeded the solutions became darker in colour but remained clear and homogeneous.

Analysis of Reactions of Benzene.—Tubes were cooled and broken open, and the contents were added to a mixture of water and diethyl ether containing known quantities of toluene and *m*-chlorotoluene (see below). The ether layer was separated and analysed using a Pye series 104 gas chromatograph with flame-ionisation detector with a 3 ft column of 10% poly(propylene glycol) on Chromosorb W-AB at 100 °C. The benzene and chlorobenzene present were estimated using toluene and *m*-chlorotoluene respectively as internal standards. The analysis was continued in one of two ways.

Procedure (A). A second sample of diethyl ether containing toluene and *m*-chlorotoluene was added to the aqueous layer, followed by hydrazine hydrate (10 cm^3) whereupon a black precipitate of platinum metal was rapidly produced. The mixture was boiled under reflux for 1 h and this ether layer was analysed for benzene and chlorobenzene. Either of these two compounds detected here had originally been in the aqueous layer as a water-soluble benzene or chlorobenzene complex.

Procedure (B). The aqueous and ether layers were recombined and an excess of 0·1M-cerium(IV) sulphate in 10% sulphuric acid was added.* This mixture was titrated potentiometrically, using gold and calomel electrodes, with a standard solution of ammonium iron(II) sulphate in 10% sulphuric acid using a Radiometer TTT2 automatic titrator with an ABU13 autoburette and SBR3 titrigraph. After titration the ether layer of the solution was sometimes analysed again for benzene and chlorobenzene, to see if either of these compounds had been released from their complexes when the Pt^{II} in the system was oxidised to Pt^{IV}. In all such analyses the amounts of benzene and chlorobenzene did not increase.

Analysis of Reactions of Hexane.—The method of analysis was the same as that for benzene except that the g.l.c. standards used were methylcyclopentane (for hexane), 1-chloropentane (for 1-chlorohexane), and *iso*-valeric acid (for fatty acids). The ether layers were analysed using the poly(propylene glycol) column at 40 °C for hexane and at 100 °C for 1-chlorohexane. Carboxylic acids in the ether layers were analysed using a column containing either 8% tri-2,4-xylyl phosphate and 2% phosphoric acid on 40/60 Chromosorb B at 100 °C or Carbowax 20M on Chromosorb W extensively extracted at 280 °C [11] and coated with Carbowax 20M terminated with terephthalic acid (FFAP). The aqueous layer produced during the work-up of a reaction mixture was analysed by procedure (A) given above, or the extent of reduction of Pt^{IV} to Pt^{II} was determined using (B).

A further procedure, (C), for determining the composition of involatile components in the ether layer involved the removal *in vacuo* of all volatile material from the ether layer. A red oil remained that could not be crystallised. The ^1H n.m.r. spectrum of this oil was examined in chloroform or in perdeuterioacetone using a JEOL 100 MHz spectrometer. The red oil was then redissolved in diethyl ether containing the standards given above and hydrogen was passed through the solution whereupon a black precipitate slowly formed. The remaining solution was again analysed by g.l.c.

RESULTS AND DISCUSSION

Reaction of Benzene.—When aqueous acetic acid was used as the solvent for the reaction between benzene and H_2PtCl_6 the amount of benzene found in the reaction mixture at first decreased with time but then increased again to *ca.* 90% of the initial value and remained constant (Table 1). At the same time the amount of chlorobenzene increased to a constant value of *ca.* 8·5%. These results are readily understood. In addition to the oxidation of benzene to chlorobenzene, acetic acid solvent was oxidised by the platinum(IV) [10] and some Pt^{IV} that had formed a platinum–benzene complex released its benzene as it was reduced to platinum(II). Garnett and West [9] used acetic acid as the solvent in their study and the possibility that this oxidation of acetic acid occurred in their work cannot be discounted, although it is thought not to be serious.[12] It was not possible for these authors to compare their yield of product with their loss of reactant as only the yield of product chlorobenzene was determined. Throughout the present study the concentrations of both reactant benzene and product chlorobenzene were measured. Acetic acid, therefore, is not a suitable solvent for this oxidation of benzene and is certainly an unsatisfactory solvent for the oxidation of the less reactive alkanes.

TABLE 1

Percentages of free benzene and chlorobenzene in reaction mixtures using aqueous acetic or aqueous trifluoroacetic acid as solvent

	Benzene		Chlorobenzene	
t/min	(A)	(B)	(A)	(B)
1	96	93		
30	64	78	2·2	1·5
60	75	65	5·6	5·4
150	88	54	8·7	17
360	90	43	8·4	36
500	88		8·6	
920	88		8·7	

Reaction conditions: C_6H_6 (538 μmol); H_2PtCl_6 (543 μmol); $K_2[PtCl_4]$ (34 μmol); CH_3CO_2H (1·2 cm^3) (A) or CF_3CO_2H (1·2 cm^3) (B); H_2O (0·8 cm^3); and 120 °C.

It was necessary to use a solvent in which both platinum salts and organic compounds are soluble and which is not itself oxidised by Pt^{IV}. Aqueous trifluoroacetic acid meets these requirements and was used for the remaining work. In Table 1 are listed the amounts of benzene and of chlorobenzene found in reaction mixtures using either acetic or trifluoroacetic acid as solvent. The amount of chlorobenzene formed steadily increased when trifluoroacetic acid was the solvent,

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* 1M = 1 mol dm^{-3}.

[11] W. A. Aue, C. R. Hastings, and S. Kapila, *J. Chromatog.*, 1973, **77**, 299.

[12] J. L. Garnett, personal communication.

in contrast to the reaction in acetic acid which behaved as described above. During the analysis of reaction products the trifluoroacetic acid concentrated in the aqueous layer and did not seriously interfere with the g.l.c. analysis.

Detailed results of the amount of benzene and chlorobenzene in the reaction mixture as the reaction proceeded are given in Figure 1. The induction period reported by Garnett and West [9] for the formation of chlorobenzene can be seen. Biphenyl was the only other oxidation product of benzene found, but the amount, after 2 h, was $<1\%$ of the benzene added and it is not considered further. Although no significant quantities of other oxidation products could be found, not all the benzene lost was accounted for as chlorobenzene or biphenyl. This loss has not been reported previously. It appeared likely that some of the benzene had formed a complex with platinum that, during the analysis, was either not soluble in diethyl ether or, if ether-soluble, did not release its benzene during g.l.c. analysis. It was found that both a platinum–benzene and a platinum–chlorobenzene complex were formed and that these concentrated in the aqueous layer during work-up of the reaction mixture. The benzene and chlorobenzene were released on reduction of the platinum complex to platinum metal. Tin(II) chloride, sodium tetrahydroborate, hydrogen gas, and hydrazine hydrate were all effective reducing agents. Highest yields of benzene and chlorobenzene were obtained when hydrazine hydrate was used with prolonged boiling, and this treatment was subsequently used for all quantitative studies. The concentrations of these two platinum–aromatic complexes are also given in Figure 1, and the 'total' line in the Figure shows that all the aromatic reactant and products are now accounted for.

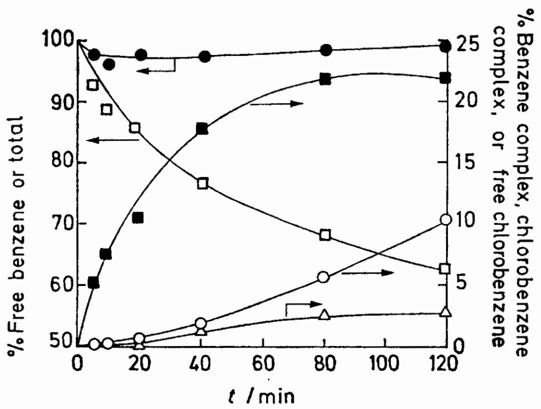


FIGURE 1 Molar percentages of aromatic compounds in a typical reaction mixture at 120 °C with reactants H_2PtCl_6 (672 μmol) and C_6H_6 (672 μmol) in H_2O (0·8 cm^3) and CF_3CO_2H (1·2 cm^3): (□), C_6H_6; (■), C_6H_6 complex; (△), C_6H_5Cl complex; (○), C_6H_5Cl; (●), total organic reactants + products

To check that benzene is not formed from chlorobenzene when a chlorobenzene–platinum complex is reduced by hydrazine hydrate, a solution of chlorobenzene (200 μmol) and H_2PtCl_6 (760 μmol) in aqueous CF_3CO_2H was allowed to react at 120 °C for 2 h. The reaction mixture was then separated into aqueous and ether layers and the former was analysed by procedure (A) (Experimental section). Only a trace of benzene was found, demonstrating that, under these conditions, no significant amount of chlorobenzene is reduced to benzene. There was no induction period for the formation of the benzene complex, whereas there was for the chlorobenzene complex (Figure 1). This suggests that the reaction proceeds, as might be expected, in three steps; benzene is converted into a platinum–benzene complex in the first step, then to a platinum–chlorobenzene complex, and finally to free chlorobenzene.

If the overall reaction of benzene with hexachloroplatinic(IV) acid is as in (1) ($R = C_6H_5$), 1 mol of Pt^{II} is produced for every mol of chlorobenzene formed. The concentration of Pt^{II} formed in the system can be found by reoxidation to Pt^{IV} with cerium(IV) sulphate. Table 2 shows the amounts of Pt^{II} and chlorobenzene found at various times during a typical reaction. The amount of chlorobenzene after oxidation of all the Pt^{II} to Pt^{IV} had not increased; this indicates that any chlorobenzene–platinum complexes present do not release chlorobenzene on oxidation of the Pt^{II} to Pt^{IV}. More Pt^{II} than chlorobenzene was produced throughout the reaction (Table 2); the Pt^{II} concentration was approximately equal to that of chlorobenzene plus chlorobenzene–platinum complex, as can be seen by comparing values, at comparable times, for Pt^{II} in Table 2 and chlorobenzene plus chlorobenzene–platinum complex in Figure 1. Furthermore, the concentration of the benzene–platinum complex at any time was considerably greater than that of Pt^{II} (Figure 1 and Table 2). This means that the benzene complex is a complex of Pt^{IV}. [A much less likely alternative is that it is a complex of Pt^{II} that is not oxidised by Ce^{IV} under our conditions.] When complexed benzene has been converted to complexed chlorobenzene, reduction of Pt^{IV} to Pt^{II} has taken place. Hence the amount of Pt^{II} in the reaction mixture at any time equals the amount of chlorobenzene, both free and complexed. This was found to be so. No information about the form of the stable chlorobenzene–platinum complex can be obtained from the measurement of the Pt^{II} concentration.

TABLE 2

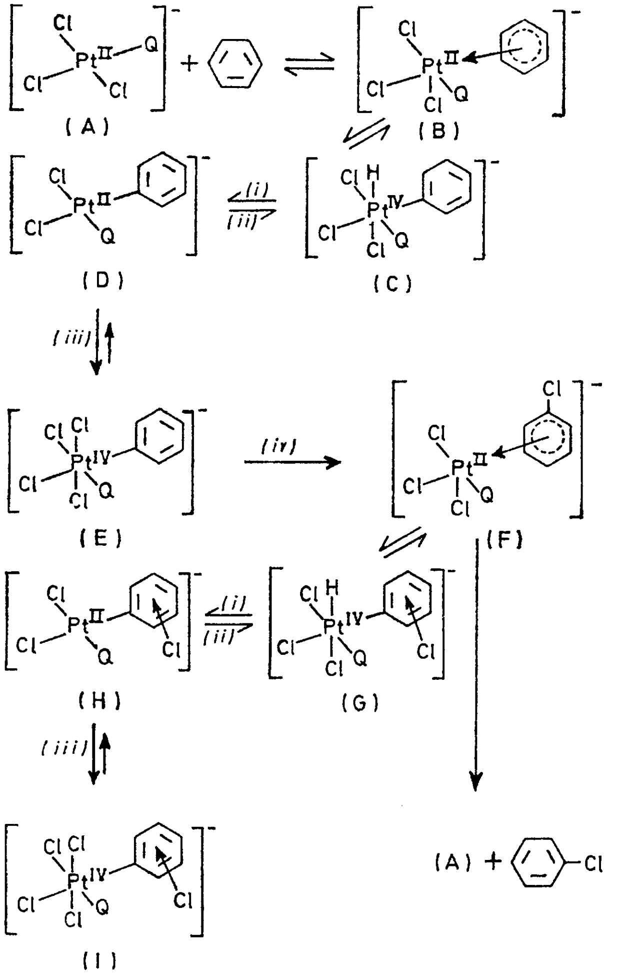
Percentages of free chlorobenzene and of platinum(II) in a typical reaction mixture

t/min	Chlorobenzene		Pt^{II}
	a	b	
32	1·3	1·4	3·4
54	3·0	3·0	6·2
70	4·5	4·6	8·2
84	5·5	5·5	9·4
103	7·9	8·0	12·6
120	9·1	9·1	14·5
130	10·3	10·3	15·8

Reaction conditions: C_6H_6 (672 μmol); H_2PtCl_6 (672 μmol); CF_3CO_2H (1·2 cm^3); H_2O (0·8 cm^3); and 120 °C.

[a] Before Ce^{IV} addition. [b] After Ce^{IV} addition.

These results add considerable support to the reaction scheme favoured by Garnett and West.[9] Our scheme is not identical but contains the three essential steps (*i*) formation of a platinum-benzene complex, (*ii*) its conversion to a platinum–chlorobenzene complex, and



(*i*), −HCl; (*ii*), +HCl; (*iii*), $+[PtCl_6]^{2-} - [PtCl_4]^{2-}$; (*iv*), ligand oxidation; Q = solvent

(*iii*) subsequent formation of chlorobenzene. The initial step is addition of benzene to the square-planar d^8 Pt^{II} species, $[PtCl_4]^{2-}$, or, more likely, a solvolysed chloro-complex (A) as is proposed as the catalyst for hydrogen–deuterium exchange.[2] In the absence of added Pt^{II}, this $[PtCl_4]^{2-}$ will be the small amount present as impurity in H_2PtCl_6, or it may be formed from Pt^{IV} in the reaction mixture. It was found that when solutions of H_2PtCl_6 in aqueous trifluoroacetic acid were heated to 120 °C in the absence of hydrocarbon the solution became red in colour, characteristic of Pt^{II}, and on cooling the colour reverted to the yellow of Pt^{IV}. Benzene may oxidatively add to (A) giving (C) or it may first form the π-complex (B). The hydridophenyl complex so formed, (C), is assumed to occur during Pt^{II}-catalysed H–D exchange and a similar complex of tungsten(IV), $[(\eta\text{-}C_5H_5)_2WHPh]$, has been made by addition of benzene to a solution assumed to contain $[(\eta\text{-}C_5H_5)_2W]$.[13] Complex (C) like all Pt^{IV} hydrides[14] will readily lose HCl to give the phenylplatinum(II) complex (D). This is then transformed into the phenylplatinum(IV) complex, (E), by oxidation with two chlorine atoms from $[PtCl_6]^{2-}$, possibly through a binuclear complex with chloride bridges. We propose that complex (E) is fairly stable and is the major platinum–phenyl complex in the system, but we have no direct evidence that this is so. It is during the next step of the reaction that oxidation of the benzene occurs. The co-ordinated phenyl group of (E) is chlorinated by one of the chloride ligands of the platinum. This gives the π-complex (F) which in turn gives the products chlorobenzene and the $[PtCl_3(\text{solvent})]^-$ ion. However, not all the π-complex (F) will decompose into products. Oxidative addition to give a (chlorophenyl)platinum(IV) hydride, (G), loss of HCl to form complex (H), and oxidation by H_2PtCl_6 to give the (chlorophenyl)platinum(IV) complex (I) also occurs. These last three reactions are exact analogues of those leading to complex (E). Complex (I) will, like (E), be fairly stable and be the main (chlorophenyl)platinum complex in the system. Chlorination of (I) can occur to give dichlorobenzene and a further cycle of (dichlorophenyl)platinum complexes. We found free *m*- and *p*-dichlorobenzene in our reaction mixtures after 6 h.

This reaction scheme is further supported by the effects on the reaction of changes in the initial concentrations of Pt^{IV}, Pt^{II}, and chloride. The initial rate of loss of benzene was found to be approximately first order in $[Pt^{IV}]$ as expected, since Pt^{IV} enters the scheme to convert complex (D) to (E). Addition of $K_2[PtCl_4]$ to the reactants increased both the rate of loss of benzene and the rate of formation of chlorobenzene (Figure 2), Pt^{II} being necessary as the initial interaction of benzene is with a Pt^{II} species. Finally, added chloride ion retarded the reaction (Figure 2) either by inhibiting the conversion of complex (C) to (D) or, if the catalytic form of Pt^{II} is not the $[PtCl_4]^{2-}$ ion but some solvolysed species such as (A), by inhibiting the formation of these catalytically active molecules.

Reaction of Hexane.—Figure 3 shows the quantities of hexane remaining in typical reaction mixtures, at 120 °C, using aqueous trifluoroacetic acid as the solvent, after various reaction times and under various conditions. The initial rate of disappearance of hexane was increased by addition of Pt^{IV} or Pt^{II} and was retarded by the addition of chloride ion. These effects are the same as for the benzene reaction and indicate close similarity for the reactions of the two compounds, and we would expect chlorohexanes to be the major products of reaction (1). This was not so. Figure 3 shows that a reaction mixture which initially contained 460 μmol hexane and 460 μmol H_2PtCl_6 had lost 50 ± 5 μmol hexane after 2 h. At this time the reaction mixture contained only 3 μmol (0·7%) 1-chlorohexane. It contained less than 0·1% of other isomers of chlorohexane, isomers of dichlorohexane, all

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[13] C. Giannotti and M. L. H. Green, *J.C.S. Chem. Comm.*, 1972, 1114.

[14] See F. R. Hartley, 'The Chemistry of Platinum and Palladium,' Applied Science Publishers Ltd., London, 1973, p. 252.

isomers of hexanols, hexanones, and hexyl trifluoroacetates, hexanoic acid, dodecane or isomerisation or dehydrogenation products of hexane. Signals in the alkyl proton region of the ^1H n.m.r. spectrum of the red oil formed by evaporation of the ether layer obtained during analysis [see procedure (C), Experimental section] were no more intense than those of blanks from reaction mixtures that had not been heated; hence substantial polymerisation of the hexane (*via* dehydrogenation) to give involatile products did not occur.

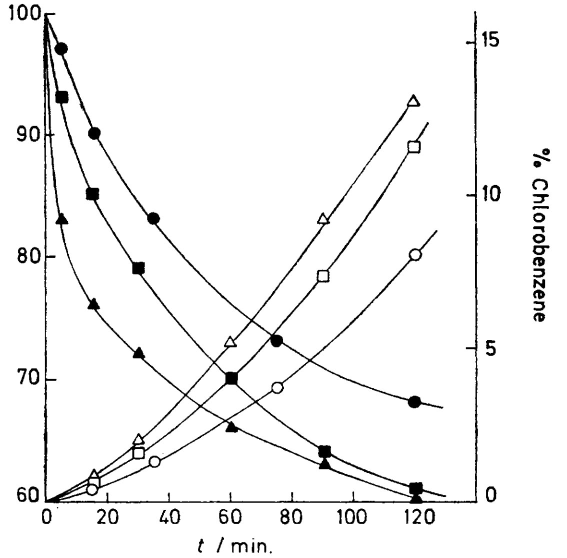

FIGURE 2 Molar percentages of free benzene (filled symbols) and chlorobenzene (open symbols) present in reaction mixtures at 120 °C with reactants H_2PtCl_6 (672 μmol) and C_6H_6 (672 μmol) in H_2O (0·8 cm³) and CF_3CO_2H (1·2 cm³): (■) and (□), no additional reagents; (▲) and (△), $K_2[PtCl_4]$ (67 μmol); (●) and (○), NaCl (134 μmol)

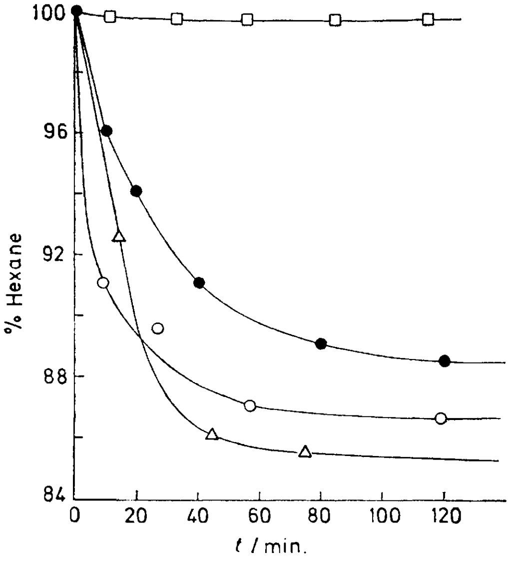

FIGURE 3 Molar percentages of free hexane found in various reaction mixtures at 120 °C with reactants: (●), hexane (460 μmol), H_2PtCl_6 (460 μmol); (△), hexane (460 μmol), H_2PtCl_6 (725 μmol); (□), hexane (460 μmol), H_2PtCl_6 (460 μmol), NaCl (230 μmol); and (○), hexane (460 μmol), H_2PtCl_6 (460 μmol), $K_2[PtCl_4]$ (92 μmol). The solvent was H_2O (0·8 cm³) and CF_3CO_2H (1·2 cm³)

Analysis of the aqueous layer obtained during the work-up of the reaction mixture using procedure (A) (see Experimental section) showed no trace of hexane or of any of the oxidation products given above. Aqueous layers were also treated with nitric acid, hydrogen peroxide, hydrogen, or 1,2-bis(diphenylphosphino)-ethane in attempts to displace the organic moiety from any organometallic complexes in solution, but no organic products were found. Analyses of samples of untreated reaction mixtures [which still contained water, trifluoroacetic acid, and hexachloroplatinic(IV) acid] on columns that separate aliphatic carboxylic acids also showed no trace of such compounds.

Analysis of the ether layer from the work-up using procedure (C) (Experimental section) gave 5 μmol (1·0%) of hexane. We suspect that this hexane comes from a platinum-containing complex, possibly a platinum–hexene complex, the hexene being most probably formed by dehydrohalogenation of the chlorohexane. Several such complexes are known, for example the binuclear diethyl ether-soluble $[\{PtCl_2(C_2H_4)\}_2]$ which is reduced to platinum metal and ethane by hydrogen.[15] We verified that, under our experimental conditions, a platinum–hexene complex can be formed and hexane produced when the complex is treated with hydrogen gas. Hex-1-ene (460 μmol) and H_2PtCl_6 (460 μmol) were heated in aqueous trifluoroacetic acid at 120 °C for 5 min and the reaction mixture was worked-up as described in the Experimental section. The resulting ether layer, when analysed by procedure (C), gave 120 μmol (27%) of hexane that must have come from an involatile platinum–hexene complex.

We found, therefore, that after 2 h a reaction mixture which originally contained 460 μmol (100%) hexane and 460 μmol H_2PtCl_6 contained 89 ± 1% hexane, 0·7% 1-chlorohexane, and 1% of a hexene–platinum complex. We were unable to find any other organic products or the ultimate oxidation product carbon dioxide. Thus 8—10% of the hexane has been lost. These results were confirmed by many other measurements made at various reaction times, some longer and some shorter than 2 h. The yield of 1-chlorohexane gradually increased with time.

A study of the formation of Pt^{II} in the system provides evidence as to how this loss occurred. Every conversion of Pt^{IV} to Pt^{II} causes two-electron oxidation of hexane or one of its reaction products; similarly, formation of a chlorohexane molecule requires formation of one Pt^{II} and each further oxidation step will require the formation of a further Pt^{II} species. Table 3 shows the percentages of hexane lost and of Pt^{II} formed in the reaction mixture at various times. For every mol of hexane consumed 5—6 mol of Pt^{II} were produced by reduction of Pt^{IV}; on average each hexane molecule that reacts undergoes five to six two-electron oxidations. We suggest that hexane is first chlorinated and the chlorohexane formed then reacts with more Pt^{IV}.

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[15] J. S. Anderson, *J. Chem. Soc.*, 1934, 971.

To investigate this suggestion we heated a mixture of 1-chlorohexane (60 μmol), octane (400 μmol), H_2PtCl_6 (400 μmol), and $K_2[PtCl_4]$ (60 μmol) in aqueous trifluoroacetic acid at 120 °C for 2 h. This mixture was designed to simulate a reaction of hexane (460 μmol) and H_2PtCl_6 (460 μmol) in which 60 μmol of the hexane had been converted to 1-chlorohexane. After reaction, 45 μmol (75%) of the 1-chlorohexane was recovered unchanged. This is much more than found after a normal reaction of hexane with H_2PtCl_6, and indicates that the initial reaction of hexane cannot be exclusively chlorination in the terminal position. On repeating the above reaction using a mixture of 2- and 3-chlorohexanes * instead of 1-chlorohexane it was found that after 2 h at 120 °C no chlorohexanes were left in the reaction mixture, suggesting that chlorination of hexane by H_2PtCl_6 takes place at both terminal and internal positions. Only the 1-chlorohexane survives further oxidation in sufficient quantity to be detected.

TABLE 3

Percentages of reactant lost and Pt^{II} formed *

Reactant	t/min	Reactant lost	Pt^{II} formed
Hexane	20	7	25
	45	8	37
	80	10	44
	150	12	70
	210	11	65
	270	14	74
	390	14	75
Octane	120	9	54
Decane	120	7	48
2,2-Dimethylbutane	30	3	5
	90	7	20
	120	15	34
	145	9	26
	180	19	40
2,2-Dimethylpropane	150	0	
2,2,3,3-Tetramethylbutane	120	0	
Hexanoic acid	100	13	48
	120	13	49
	220	20	61
	220	22	61

Reaction conditions: reactant (460 μmol); H_2PtCl_6 (460 μmol); CF_3CO_2H (1·2 cm^3); H_2O (0·8 cm^3); and 120 °C.

* Each entry refers to a separate experiment.

We also studied the reactions of the chlorohexane isomers (215 μmol) with hydrogen chloride (300 μmol) and lithium chloride (600 μmol) in aqueous trifluoroacetic acid at 120 °C for 30 min. No isomerisation or hydrolysis of the 1-chlorohexane occurred, but 20% of the mixture of 2- and 3-chlorohexanes was converted into the hexyl trifluoroacetates. The oxidation of the internal isomers of chlorohexane may therefore occur *via* the corresponding trifluoroacetates, these being more easily formed by hydrolysis than the terminal isomer.

The possibility that the first reaction of hexane with H_2PtCl_6 is dehydrogenation to a hexene that then reacts with hydrogen chloride to give a chlorohexane was investigated by treating hex-1-ene with either hexachloroplatinic(IV) acid or with hydrogen chloride and lithium chloride in aqueous trifluoroacetic acid. 1-Chlorohexane was not formed in either case, indicating that reaction does not occur by this route. Hence, hexane is chlorinated by H_2PtCl_6 to give both terminal and internal chlorohexanes. The internal isomers are rapidly oxidised *via* C–C bond cleavage to smaller organic molecules, probably carboxylic acids, which are further chlorinated. It is known that acetic acid is rapidly chlorinated under the reaction conditions [10] and Table 3 shows that, when hexanoic acid was used as the reactant, each mol reduced on average 3—4 mol of Pt^{IV} to Pt^{II}.

The ratio of Pt^{II} formed to alkane lost was found to be dependent on the alkane used (Table 3). For octane and decane the ratio was higher than for hexane, presumably because there is greater scope for multiple attack on the longer alkyl chains. 2,2-Dimethylbutane has a Pt^{II} : 'alkane lost' ratio of less than 3 : 1, because of the difficulty of substitution on the bulky t-butyl group. Neither 2,2-dimethylpropane nor 2,2,3,3-tetramethylbutane was oxidised at all by Pt^{IV}. This observation is of significance in support of the close similarity between the initial processes involved in hydrogen–deuterium exchange and in oxidation; it has been shown earlier that the rate of hydrogen–deuterium exchange in 2,2-dimethylpropane catalysed by Pt^{II} is very slow.[2]

The oxidation of cyclohexane is more complicated. From a reaction mixture containing initially cyclohexane (930 μmol), H_2PtCl_6 (440 μmol), and $K_2[PtCl_4]$ (20 μmol) there was found, after 40 h at 100 °C, cyclohexane (765 μmol), benzene (56 μmol), chlorobenzene and chlorocyclohexane (17 μmol), and cyclohexanone (5 μmol). Dehydrogenation to benzene had occurred and the system became a mixed alkane–benzene system. These results broadly confirm those of Shilov,[10] and we carried out no further studies with cyclohexane.

We briefly investigated the reaction of H_2PtCl_6 with hexane in other solvents. In water, and in aqueous nitromethane, where under our conditions a two-phase system existed even at 120 °C, no significant reaction occurred after 7·5 h. No oxidation occurred in aqueous acetonitrile at 120 °C for 2 h; the platinum formed a yellow complex ammine salt due to hydrolysis of the acetonitrile.

Conclusion.—The reactions of benzene and of hexane with H_2PtCl_6 are therefore very different after close similarity in the early stages of the reaction sequence. For benzene, π-complexes that lead to stable phenylplatinum complexes are formed, and for alkanes there must be initial interaction of the platinum with the σ electrons of the alkane that leads on to oxidative addition to give an alkylplatinum complex analogous to (C) in the scheme. Benzene gives chlorobenzene as a fairly stable reaction product, but for hexane and other alkanes multiple oxidation occurs leading to polychlorinated carboxylic acids which may equilibrate with

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* The published preparation of 2-chlorohexane [16] gives a mixture of the 2- and 3-chlorohexanes. These are inseparable by g.l.c., but the mixture is quite suitable for our purposes.

[16] See A. I. Vogel, 'Practical Organic Chemistry,' 3rd edn., Longmans, London, 1956, p. 273.

the aqueous trifluoroacetic acid solvent and then be further oxidised. Despite strenuous efforts, we were unable to identify the final reaction products which must be highly polar compounds.

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