The Activation of Saturated Hydrocarbons by Transition-metal Complexes in Solution. Part III.[1] Use of Photoelectron Spectra of Halogen-substituted Hydrocarbons and Hydrocarbons containing Quaternary Carbon Atoms to interpret the Nature of Platinum(II)-catalysed Hydrogen–Deuterium Exchange

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Representative fluoro-, chloro-, bromo-, and iodo-substituted alkanes and aromatic compounds, and two branched-chain hydrocarbons that contain an ethyl group adjacent to a quaternary carbon atom, have been studied both by photoelectron spectroscopy and in hydrogen–deuterium exchange reactions catalysed by $PtCl_4^{2-}$ in 50 mol % acetic [$^2H_1$]acid–deuterium oxide. For the halogen-substituted compounds, H–D exchange occurs in those molecules for which the first ionisation potential in the photoelectron spectrum is associated with a molecular orbital centred on carbon–hydrogen bonds. For these compounds, an exponential relationship exists between the rate constant for exchange and this potential. When the first ionisation potential is associated with electrons of the halogen atom, then displacement of the halogen occurs. For the branched-chain hydrocarbons, the rate constant for exchange in the ethyl group correlates with the rate constants for the linear alkanes, provided an ionisation potential attributable to electrons of the ethyl group is used.

PLATINUM(II) complexes with ligands of low *trans*-effect will catalyse hydrogen–deuterium exchange in alkanes and aromatic compounds (preceding paper). Rate constants for exchange in a series of hydrocarbons were found to correlate with ionisation potential, and it was suggested that the mechanism of the reaction is essentially the same both for alkanes and for aromatic compounds. The relationship with ionisation potential has indicated that electron transfer from the highest occupied orbital in either an alkane or an aromatic compound to the platinum(II) produces the activated complex. This will be a π-orbital for the aromatic compounds,[2] and must be a delocalised σ-orbital for the alkane.[3] Subsequent interaction with the deuteriated solvent gives deuteriated products.[3] Such a relationship between the reactivity and ionisation potential may be tested by examining the behaviour of substituted hydrocarbons. For example there are several halogen derivatives of the alkanes for which the first ionisation potential is associated with the removal of a halogen *p*-electron rather than an electron associated with the hydrocarbon part of the molecule.[4-6] We would predict that for these molecules the first ionisation potential should not correlate with the rate constant for hydrogen–deuterium exchange. Another series of molecules, which contain a quaternary carbon atom, have their lowest ionisation potentials associated with molecular orbitals that are centred mainly on carbon–carbon bonds[7] and hydrogen–deuterium exchange in these molecules is not so related to this ionisation potential.[3] Here we consider the involvement of orbitals of higher ionisation energy in this context. The ionisation energies of the various orbitals in a molecule can, in principle, be obtained by photoelectron spectroscopy although with the alkanes and their derivatives, some difficulty is encountered in the interpretation of the spectra.

For halogen-substituted hydrocarbons, the first ionisation potential is associated with halogen *p*-electrons or with carbon 2*p*-electrons. Since in halogenoalkanes and halogenoaromatic compounds, the halogens have *p*-electrons that are non-bonding or only weakly bonding, it is generally possible to obtain the energy of ionisation both of halogen *p*-electrons and of carbon 2*p*-electrons by photoelectron spectroscopy.[8] We shall now discuss the effect of each of the halogens in turn.

In organic fluorine compounds, the 2*p*-electrons of fluorine have ionisation energies in the region 13—17 eV.[8] These energies are higher than the ionisation energies of the alkanes and aromatic hydrocarbons considered in the preceding paper, for which values ranged from 7·46 to 12·70 eV. The first ionisation potential of fluorine-substituted hydrocarbons should not involve removal of a fluorine 2*p*-electron and, as shown later, fluorine in the organic molecule exerts only a minor influence upon hydrogen–deuterium exchange.

The *p*-electrons of chlorine, bromine, and iodine in halogen-substituted hydrocarbons have ionisation energies in the regions 11—12, 10—11, and 9—10 eV respectively.[4-6,8] These values all lie within the range of ionisation energies of alkanes and aromatic hydrocarbons. It is therefore possible to select representative chlorine-, bromine-, and iodine-substituted hydrocarbons and divide them into two groups depending upon the relative energies of ionisation of the non-bonding halogen *p*-electrons and the bonding carbon 2*p*-electrons. For one group, where the first ionisation potential involves the non-bonding halogen *p*-electrons, the rate constants for hydrogen-deuterium exchange are not expected to be related to the first ionisation energy. In the second group, where the halogen *p*-electrons ionise at

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[1] Part II, preceding paper.

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

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[6] A. D. Baker, D. Betteridge, N. R. Kemp, and R. E. Kirby, *Analyt. Chem.*, 1971, **43**, 375.

[7] W. C. Price, personal communication.

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

a higher potential than a molecular orbital involving the organic moiety, hydrogen–deuterium exchange is expected to follow the previously observed pattern for hydrocarbons (preceding paper). The actual place in each series at which the change from group one to group two behaviour occurs should vary from the organic chlorides, to the bromides, to the iodides.

For branched alkanes, the relationship between hydrogen–deuterium exchange rate and ionisation energy is less clear than for halogen-substituted alkanes because photoelectron spectra of alkanes contain broad ionisation bands whereas the spectra of the halogenoalkanes often contain sharp peaks.[8-10] With the exception of methane, it is still not known with certainty which of the molecular orbitals in an alkane has the highest energy (and hence the lowest ionisation energy),[11] whether it is one that involves principally carbon–hydrogen bonds [9-11] or carbon–carbon bonds.[12] However, the evidence indicates that the occupied molecular orbital of highest energy in an alkane is dependent upon the branching in the molecule.[7] For linear alkanes, *e.g.*, ethane and propane, the lowest ionisation potential is due to electrons in delocalised orbitals that are principally carbon–hydrogen bonding,[11] whereas for the branched alkanes, *e.g.*, 2,2-dimethylpropane, it is due to electrons in delocalised orbitals that are principally carbon–carbon bonding.[7] Similar effects due to branching are also observed in mass-spectrometry, *e.g.*, in ethane and in propane, carbon–hydrogen bonds are readily broken by electron impact, whereas in 2,2-dimethylpropane the first ionisation process is accompanied by the breaking of a carbon–carbon bond.[13] Any interaction between a carbon–carbon bond in 2,2-dimethylpropane and the platinum would be expected to be sterically hindered since previous studies showed pronounced steric hindrance to exchange in all *ortho*-positions of aromatic compounds.[2] Consequently, the first ionisation energy of a branched alkane would not be expected to give an indication of the hydrogen–deuterium exchange rate, but this rate would be expected to correlate with the energy of an orbital associated with carbon–hydrogen bonds. The latter energy can be obtained by photoelectron spectroscopy for several branched alkanes.

This paper presents the results for hydrogen–deuterium exchange in the two series of compounds just discussed, *viz.*, halogen-substituted hydrocarbons and hydrocarbons containing quaternary carbon atoms. The basis for the use of ionisation potential as a suitable parameter for predicting reactivity in this system is established.

EXPERIMENTAL

Preparation.—The catalyst solution, 0·02M-$PtCl_4^{2-}$ in 50 mol % AcOD in D_2O containing 0·2M-$DClO_4$, was prepared as before.[3]

Analyses.—Deuterium distributions were computed from individual mass peaks by correction where applicable for natural abundances of ^{13}C, ^{37}Cl, and ^{81}Br, and for ion-fragmentation. Deuterium contents (%D), multiple exchange parameters (M), and rate constants for the disappearance of the parent compound (k_b), were then calculated as before.[3]

In several cases it was necessary to identify products formed in the exchange reaction and to estimate lability of the halogen in the halogenoalkanes. For identification of products, a temperature-programmed Pye g.l.c. with flame ionisation detector and SE 30 column was used. Chlorine exchange in the chloroalkanes was studied by liquid scintillation counting of ^{36}Cl.

Photoelectron spectra for several 1-fluoroalkanes, 1-chloroalkanes, 1-bromoalkanes, iodoaromatic compounds, and hydrocarbons containing quaternary carbon atoms were obtained with a Perkin-Elmer PS-16 Photoelectron Spectrometer fitted with a heated probe. To ensure accurate calibration, traces of oxygen and of argon were admitted while each sample was being scanned. Oxygen lines at 12·08 and 18·17 eV and the argon line at 15·75 eV were used to correct the spectrum for contact potential errors. A He I source was used and the resolving power of the instrument was *ca.* 0·3% of the kinetic energy of the photoelectron, *i.e.*, *ca.* 40 MeV for the first ionisation potential of 1-iodonaphthalene. Adiabatic first ionisation potentials for the compounds whose photoelectron spectra are reported here, together with literature values for the other compounds studied, are given in Tables 1 and 4. The i.p. values for compounds that do not have a fine line structure are very difficult to deduce. Those given here are 0·05 eV above the extrapolated inflexion points shown on the spectra (supplementary data).

RESULTS

Preliminary experiments showed that all linear mono-iodoalkanes and monobromoalkanes containing from three to ten carbon atoms did not undergo hydrogen–deuterium exchange. In addition, it was found that 1-chloropropane and iodobenzene could not be deuteriated catalytically in solutions containing tetrachloroplatinate(II) anions. Exchange results (%D, M, and k_b) for other compounds studied (fluoroalkanes, chloroalkanes, and halogen-substituted aromatic compounds) are in Table 1. These results were obtained by use of mass spectrometric analysis at *ca.* 12 eV; parent ion spectra were obtained for the aromatic compounds, but elimination of HX (X = halogen) occurred for most of the halogenoalkanes.

The three fluoroalkanes studied and fluorobenzene (Table 1) could be deuteriated catalytically, although the rates were slower than those of corresponding hydrocarbons (preceding paper). 1-Chloropropane lost HCl and the propene formed reacted with the platinum(II) catalyst to produce a solution of a yellow complex and exchange was inhibited in the initial stages of the reaction. All the remaining 1-chloroalkanes studied and chlorobenzene underwent exchange without appreciable decomposition at rates comparable with those of the corresponding fluorohydrocarbons. For all the chloroalkanes containing more than four carbon atoms, a fragment $C_4H_xD_{8-x}Cl^+$ occurred in the mass spectrum. As indicated in Table 1, the deuterium

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

[10] W. C. Price, in 'Molecular Spectroscopy,' ed. P. Hepple, Elsevier, 1968, p. 221.

[11] A. D. Baker, D. Betteridge, N. R. Kemp, and R. E. Kirby, *J. Mol. Structure*, 1971, **8**, 75.

[12] H. D. Beckey and F. J. Comes, *Adv. Analyt. Chem. Instrumen.*, 1970, **8**, 1.

[13] F. H. Field and J. L. Franklin, 'Electron Impact Phenomena,' Academic Press Inc., New York, 1957, p. 119.

content of this fragment was less than that of the fragment $C_nH_xD_{2n-x}^+$. For example 1-chlorohexane ($C_6H_{13}Cl$) produces two major sets of fragments at low energies in the mass spectrometer; a fragment by elimination of an ethyl group ($C_4H_8Cl^+$) and a fragment by elimination of HCl ($C_6H_{12}^+$). The rate constant (k_b) obtained by use of the fragment $C_6H_xD_{12-x}^+$ is *ca.* 5 times that calculated by use of the fragment $C_4H_xD_{8-x}Cl^+$ (Table 1). This difference is found also for 1-chloropentane (where the group eliminated is methyl or HCl), 1-chloroheptane (where the group eliminated is propyl or HCl), and 1-chlorodecane (where the group eliminated is hexyl or HCl). The results indicate that deuterium is not randomised by migration in the mass-spectrometer. It appears that the predominant exchange occurred in the methyl group as was observed for the normal alkanes.[3]

TABLE 1

Exchange in halogen-substituted hydrocarbons with 0·02M-$PtCl_4^{2-}$ in 50 mol % AcOD in D_2O at 100 °C; [$DClO_4$] = 0·2M, [pyrene] = 0·05M, [compound] = 0·3M), and ionisation potentials

Code	Compound	Time/h	Method of analysis[a]	% D	*M*	k_b/% h^{-1}	Ionisation potential eV (±0·05 eV)
1	1-Fluoropentane	20·08	B	6·50	1·57	2·25	10·65
2	1-Fluorohexane	20·08	B	6·86	1·59	2·82	10·42
3	1-Fluorooctane	20·08	B	5·16	1·38	3·21	10·28
4	Fluorobenzene	0·83	A	18·23	2·01	41·7	9·15[e]
5	1-Chloropropane	20·08	—	Decomposed to propene			10·65
6	1-Chlorobutane	20·08	B	6·99	1·54	2·14	10·60
7	1-Chloropentane	20·08	B	6·92	1·58	2·49	10·52
			C	3·06	1·47	0·85	
8	1-Chlorohexane	20·08	B	5·54	1·38	2·49	10·42
			C	1·86	1·38	0·54	
9	1-Chloroheptane	20·08	B	4·99	1·29	2·77	10·35
			C	2·21	1·09	0·82	
10	1-Chlorodecane	20·08	B	3·96	1·28	3·15	10·05
			C	0·61	1·08	0·23	
11	Chlorobenzene	0·83	A	21·1	2·00	47·1	9·00[e]
12	1-Bromobutane	10·00	—	Chloroalkanes and $PtBr_4^{2-}$ formed			10·15
13	1-Bromoheptane	10·00	—				9·95
14	1-Bromodecane	10·00	—				10·05
15	Bromobenzene	0·83	A	22·1	1·86	55·3	9·00[e]
16	1-Iodoalkanes and iodobenzene	1·00	—	Red-black precipitate formed			—
17	1-Iodonaphthalene	4·0	A	12·53	1·05	137·0[b]	8·06
		2·0	A	40·6[c]	—	—	
18	2-Iodobiphenyl	4·0	A	20·8	1·12	288·0[b]	8·35
		1·25	A	10·2	1·18	275·0[b]	
		2·0	A	52·0[d]	—	—	

[a] A = Analysis by use of molecular ions; B = analysis by use of the fragment ions $C_nH_xD_{2n-{}^1x}^+$; C = analysis by use of the fragment ions $C_4H_xD_{8-x}Cl^+$. [b] Results at 80 °C; k_b adjusted to correspond with results at 100 °C by use of benzene as a standard. [c] Mass spectrum shows 3 exchangeable sites. [d] Mass spectrum shows 5 exchangeable sites. [e] From ref. 8.

Hydrogen–deuterium exchange in bromobenzene (and chlorobenzene) occurred in three positions, presumably those *meta* and *para* to the halogen, and the rate was only slightly higher than that for exchange in fluorobenzene. The linear 1-bromoalkanes from 1-bromobutane to 1-bromodecane reacted with the catalyst to produce stoicheiometric amounts of the corresponding chloroalkane and $PtBr_4^{2-}$ (see later), and very little hydrogen–deuterium exchange occurred. A similar inhibition occurred with the iodoalkanes and iodobenzene where a dark red precipitate was formed. By contrast, both 1-iodonaphthalene and 2-iodobiphenyl were readily deuteriated at rates comparable with those for naphthalene and biphenyl respectively and, indeed, very high percentages of deuterium can be introduced into these compounds. N.m.r. and mass analyses together indicated that 1-iodonaphthalene underwent exchange at the 3-, 6-, and 7-positions, and 2-iodobiphenyl at the 4-, 5-, 3′-, 4′-, and 5′-positions. This is in line with the general pattern for platinum(II)-catalysed exchange reactions.[2]

The preceding paper showed that the logarithm of the rate constant for exchange increased with decreasing ionisation potential for a series of hydrocarbons which include methane, ethane, propane, n-butane, n-pentane, cyclohexane, benzene, naphthalene, and phenanthrene. For the halogen-substituted analogues of these compounds results in Table 1 show that a change in behaviour in the hydrogen–deuterium exchange reaction occurs on going from 1-chloropropane to 1-chlorobutane in the series of chloro-compounds, from bromoalkanes to bromobenzene in the bromo-series, and from iodobenzene to 1-iodonaphthalene in the iodo-series. All of the fluoro-compounds studied readily undergo hydrogen-deuterium exchange. It now remains to correlate these trends in reactivity with ionisation energies.

Photoelectron spectra have been obtained for 14 halogen-containing hydrocarbons. The spectra have been deposited with the N.L.L. in Supplementary Publication No. 20523 (17 pp., 1 microfiche).* In this paper these have been used together with published spectra. For each of the fluoroalkanes (1-fluoropentane, 1-fluorohexane, and 1-fluorooctane; Figures 1—3, supplementary data) * it is not possible to assign any band in the spectrum to the ionisation of the fluorine 2*p*-electrons. Apparently, these electrons are in delocalised molecular orbitals. Turner has been able to assign ionisation energies of 13·68 and 16—18 eV to the fluorine 2*p*-electrons in fluorobenzene and fluoromethane respectively.[8] In the spectra of the chloroalkanes (1-chloropropane to 1-chloroheptane and 1-chlorodecane; Figures 4—9, supplementary data) * the band due to the chlorine 3*p*-electrons becomes progressively broader and

* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

overlaps the bands due to carbon 2*p*-electrons as the alkyl chain length increases. This could indicate that the chlorine electrons become delocalised over the whole molecule. For chloromethane and chlorobenzene sharp peaks assignable to the chlorine electrons are observed.[8] Only in 1-chloropropane, in the spectra reported here, is the band due to the chlorine 3*p*-electrons completely isolated from, and at a lower energy than, the bands due to carbon 2*p*-electrons. These spectra correspond with the exchange results. 1-Chloropropane is the only chloroalkane of the series (Table 1) for which the photoelectron spectrum shows that electrons from the chlorine are more readily removed than from the alkyl group, and in which exchange does not occur. The photoelectron spectra of three representative bromoalkanes have been analysed (1-bromobutane, 1-bromoheptane, and 1-bromodecane; Figures 10—12, supplementary data). In each case, two sharp peaks assignable to the bromine 4*p*-electrons were observed. No overlap of peaks due to bromine 4*p*-electrons and carbon 2*p*-electrons was observed for 1-bromobutane. Some broadening of the peak of highest ionisation potential due to the bromine 4*p*-electrons was observed in the spectrum of 1-bromoheptane and, to a greater extent, in the spectrum of 1-bromodecane, but the lower-energy bromine peak remained clearly defined and it is this peak that gives the ionisation potential in all cases. The adiabatic ionisation energy for n-decane is 9·76 eV,[12] whereas for 1-bromodecane, rather surprisingly, it is due to the bromine 4*p*-electrons at the higher value of 10·06 eV. Thus the bromine atom remains the most reactive part of the molecule for the series of bromoalkanes and this explains why hydrogen–deuterium exchange is not favoured. The iodoalkanes behave in a like manner; photoelectron spectra have been published.[4–6] The adiabatic ionisation energies range from 9·54 eV for iodomethane to 9·18 eV for 1-iodopentane.[5] It is clear from the spectra [6] that the iodine 5*p*-electrons ionise at a considerably lower potential than the carbon 2*p*-electrons, and hydrogen–deuterium exchange does not occur in these molecules. The photoelectron spectra of the two iodine-substituted polycyclic aromatic compounds studied (2-iodobiphenyl and 1-iodonaphthalene; Figures 13 and 14, supplementary data) can be compared with the published spectra of biphenyl and naphthalene.[14] In the iodo-compounds additional peaks appear in the region 9—10 eV, well above the lowest-energy peaks at 8·35 and 8·06 eV respectively. This indicates that the first ionisation potential of the iodo-derivatives is due to the carbon 2*p*-electrons. Both 2-iodobiphenyl and 1-iodonaphthalene undergo hydrogen–deuterium exchange uninhibited by the presence in the molecule of the iodine atom (Table 1).

To gain further insight into the system under study, several monobromoalkanes (which did not undergo hydrogen–deuterium exchange) were allowed to react with $PtCl_4^{2-}$ in an acetic acid–water mixture. Using g.l.c. analysis, we found that the corresponding chloroalkanes were produced [equation (1)]. Tetrabromoplatinate(II) ions are almost inactive for catalysing hydrogen–deuterium exchange in alkanes (Table 2), hence exchange in the bromoalkanes was quickly inhibited. Apparently, all the chloride ligands are

$$4RBr + PtCl_4^{2-} \longrightarrow PtBr_4^{2-} + 4RCl \qquad (1)$$

labile in the platinum complex and stoicheiometrically react according to equation (1). This halogen exchange was not platinum-catalysed, since it was found that Cl^- ions in this solvent mixture (50 mol % acetic acid in water containing 0·2M-$HClO_4$) in the absence of Pt^{II} would replace bromine in the bromoalkanes without skeletal rearrangement taking place.

Table 2

Comparison of rate constants for hydrogen–deuterium exchange in a series of alkanes with $PtBr_4^{2-}$ and $PtCl_4^{2-}$ as catalysts at 100 °C; $[DClO_4] = 0{\cdot}2$M, $[Pt^{II}] = 0{\cdot}02$M, [pyrene] = 0·05M, [alkane] = 0·5M, solvent = 50 mol% AcOD in D_2O

	k_b/% h^{-1}	
Compound	$PtBr_4^{2-}$	$PtCl_4^{2-}$
Ethane	0·87	3·99
Butane	1·02	10·46
Pentane	1·44	12·00
Hexane	1·45	13·8

A brief study has been made of the exchange of chlorine in chloroalkanes with Cl^- ions. Chlorine exchange does not inhibit hydrogen–deuterium exchange; however HCl elimination, as occurs for 1-chloropropane, will affect the reaction because alkenes are produced. It was found that ^{36}Cl (as $H^{36}Cl$) could be incorporated into 1-chlorodecane at a similar rate to the hydrogen-deuterium exchange rate. The significance of this result will be considered in the Discussion section.

Previous studies have shown that isolated methyl groups in molecules such as 2,2-dimethylbutane [3] and 1,1-dimethylpropylbenzene [3,15] undergo hydrogen–deuterium exchange at significant rates, whereas the methyl groups in 2,2-dimethylpropane [3] and 1,1-dimethylethylbenzene [16] do not. The similarity of these pairs of molecules allow an accurate comparison of the rate constants for exchange (as well as allowing a study of the differences in the photoelectron spectra) when one methyl group is replaced by an ethyl group. Rate constants for hydrogen–deuterium exchange in 2,2-dimethylbutane and in 1,1-dimethylpropylbenzene are given in Table 3 and photoelectron spectra are given in the supplementary data (Figures 15 and 16). These four molecules, each of which contain a quaternary carbon atom, readily fragment in the mass spectrometer with the elimination of a methyl or an ethyl group. There is not a peak due to the molecular ion in the mass spectrum of deuteriated 2,2-dimethylbutane ($C_6H_xD_{14-x}$), obtained at low ionisation energy; peaks corresponding to $C_5H_xD_{11-x}^+$ and $C_4H_xD_{9-x}^+$ are obtained. Comparisons of deuterium distributions in these fragments give an accurate value for the exchange that has occurred in the ethyl group. In a previous study [3] the values calculated by this method agreed precisely with values calculated from the n.m.r. spectrum of the same sample. This suggests that deuterium migration does not occur on fragmentation in the mass spectrometer.

In the mass spectrum of deuteriated 1,1-dimethylpropylbenzene ($C_{11}H_xD_{16-x}$) at a low ionisation energy, a set of peaks due to the parent ion ($C_{11}H_xD_{16-x}^+$) *is* obtained. This permits the deuterium distribution for the whole molecule, including the exchangeable ring hydrogens, to be calculated (Table 3). A set of peaks is also obtained for $C_9H_xD_{11-x}^+$, *i.e.*, the molecular ion that has lost an ethyl group. The deuterium distribution for this fragment shows that exchange occurred in three positions only, presumably the

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[14] J. H. D. Eland and C. J. Danby, *Z. Naturforsch.*, 1968, **23a**, 355.

[15] J. L. Garnett and R. J. Kenyon, *Chem. Comm.*, 1971, 1227.

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

meta- and *para*-positions of the benzene ring. By solution of a set of simultaneous equations the deuterium distribution in the ethyl group was calculated from the differences between these two spectra (Table 3). The full procedure used for this unconventional analysis is given in the Appendix. Thus rate constants for hydrogen–deuterium exchange in both the molecule as a whole and in the ethyl group alone were obtained for 2,2-dimethylbutane and 1,1-dimethylpropylbenzene.

There is a reduction in the values of the ionisation potential as given by the first two bands in the photoelectron spectrum of 2,2-dimethylbutane compared with that of 2,2-dimethylpropane [7] (Table 4). This effect also occurs for the ionisation energies as given by the first three bands in the spectrum of 1,1-dimethylpropylbenzene when compared with that of 1,1-dimethylethylbenzene.[8] A correlation with the exchange reaction will be considered in the Discussion section.

TABLE 3

Rate constants for $PtCl_4^{2-}$ catalysed hydrogen–deuterium exchange in hydrocarbons containing quaternary carbon atoms at 100 °C; $[PtCl_4^{2-}] = 0{\cdot}02$M, [pyrene] = 0·05M, $[DClO_4] = 0{\cdot}2$M, [hydrocarbon] = 0·3M, solvent = 50 mol % AcOD in D_2O

			Deuterium distribution (%)										
Code	Compound	*t*/h	D_0	D_1	D_2	D_3	D_4	D_5	D_6	D_7	D_8	% D	k_b/ % h^{-1}
19	2,2-Dimethylbutane												
	$C_5H_xD_{11\ x}^+$	22·58	49·5	27·9	14·2	7·2	0·6	0·3	0·2			7·58	3·11
	$C_4H_xD_{9-x}^+$	22·58	94·6	3·2	1·1	0·9	0·1					0·99	0·25
	Ethyl group, calc.[a]	22·58										15·2	2·35
20	1,1-Dimethylpropylbenzene												
	$C_{11}H_xD_{16-x}^+$	0·83	55·0	14·9	14·0	13·5	1·7	0·7	0·1			5·9	71·8
	$C_9H_xD_{11-x}^+$	0·83	57·0	14·5	13·5	14·2	0·6					7·9	67·8
	$C_{11}H_xD_{16-x}^+$	22·58	0·4	4·0	16·3	31·3	25·2	16·0	6·4	0·4	0·1	22·0	
	$C_9H_xD_{11-x}^+$	22·58	0·5	9·5	36·7	49·6	3·0	0·4	0·2			22·5	
	Ethyl group, calc.[a]	22·58	36	31	19	15	0					23·0	3·6

[a] See text and Appendix.

TABLE 4

A comparison of the photoelectron ionisation energies of 2,2-dimethylpropane and 2,2-dimethylbutane, and of 1,1-dimethylethylbenzene and of 1,1-dimethylpropylbenzene

	Adiabatic ionisation energies ± 0·05/eV			
Compound	1st	2nd	3rd	Ref.
2,2-Dimethylpropane	10·2	12·2	—	7
2,2-Dimethylbutane	10·10	11·85	—	Figure 15; Supplementary data
1,1-Dimethylethylbenzene	8·8	10·5	11·8	8
1,1-Dimethylpropylbenzene	8·63	10·12	11·54	Figure 16; Supplementary data

DISCUSSION

The above results with halogen-substituted hydrocarbons indicate that the photoelectron spectra provide a novel means of interpreting the behaviour of such compounds in hydrogen–deuterium exchange reactions. Where the halogen *p*-electrons are clearly responsible for the first ionisation potential, either elimination of HX (where X = Cl, Br, or I) occurs with the formation of an alkene, or the chloride ligands of the $PtCl_4^{2-}$ will exchange with the halogen of the organic compound. In either case, exchange is inhibited, since if alkene complexes of platinum(II) are formed, these are of low catalytic reactivity,[3] as are $PtBr_4^{2-}$ (Table 2) and PtI_4^{2-}.[17]

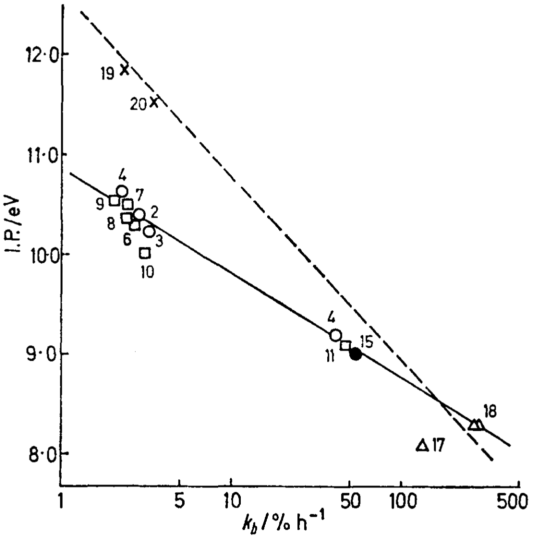
In molecules where the halogen *p*-electrons ionise at higher energies than the carbon 2*p*-electrons, then exchange occurs most readily with hydrogen of terminal methyl groups, and with aromatic hydrogens that are not sterically hindered. In the Figure rate constants for exchange in these molecules are plotted on a logarithmic scale against first ionisation potential and compared with the plot obtained for hydrogen–deuterium exchange in unsubstituted hydrocarbons (dashed line) taken from the preceding paper. These results give a linear correlation for $\log(k_b)$ against ionisation potential; the relationship applies to molecules containing F, Cl, Br, or I. However the slope for the halogenoalkanes is different from that for the unsubstituted hydrocarbons. Substituted aromatic compounds exchange at approximately the same rate as, whereas the halogenoalkanes exchange at a slower rate than, the corresponding hydrocarbon. For example 1-fluoropentane, where exchange occurs predominantly in the methyl group, exchanges at 1/5 the rate for n-pentane where exchange also occurs predominantly in the methyl groups.[3] The reason for these differences in reaction rate is not known.

Photoelectron spectra of bromobenzene [8] and the 1-bromoalkanes (Figures 10—12, supplementary data) give sharp peaks which are attributed to the bromine 4*p*-electrons. In bromobenzene, the ionisation energies of these electrons are at 10·61 and 11·1 eV, clearly above the ionisation energies of the carbon 2*p*-electrons of the aromatic ring, *viz.*, 9·05 and 9·67 eV. The well defined first ionisation potentials of bromomethane,[8] 1-bromobutane, 1-bromoheptane, and 1-bromodecane (Figures 10—12, supplementary data) are due to the bromine 4*p*-electrons and range from 10·08 eV in 1-bromodecane to 10·54 eV in bromomethane. Our results, that bromobenzene undergoes exchange, and that carbon–bromine

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

bonds react in the bromoalkanes, are thus readily explained. The photoelectron spectra could have a wider application than to exchange studies (since it was observed that the breaking of C–Br bonds was not platinum-catalysed), *e.g.*, to halogen substitutions which have been well documented.[18]

First ionisation potentials of the iodoalkanes are due to iodine 5*p*-electrons. In the reaction medium used for hydrogen–deuterium exchange, C–I bonds are broken and no platinum(II)-catalysed exchange is observed. For 2-iodobiphenyl and 1-iodonaphthalene, photoelectron spectra (Figures **13** and **14**, supplementary data) show that the highest-energy molecular orbital is associated with the aromatic π-system; first adiabatic ionisation energies occur at 8·30 and 8·06 eV respectively. Hydrogen–deuterium exchange occurs readily without the breaking of C–I bonds (Table 1).



A plot of ionisation potential (I.P.) and rate constant for exchange (k_b) for ○, fluorohydrocarbons; □, chlorohydrocarbons; ●, bromohydrocarbons; △, iodohydrocarbons; and ×, hydrocarbons containing ethyl groups adjacent to a quaternary carbon atom. Numbers refer to the code in Tables 1 and 3

The interpretation of the photoelectron spectrum of iodobenzene[8] is more difficult. Four sharp peaks are observed at 8·67, 9·38, 9·64, and 10·45 eV.[8] Benzene has two degenerate orbitals from which electrons ionise at 9·25 eV,[8] and iodine electrons, in 1-iodopentane for example, ionise in the same region, namely 9·18 and 9·72 eV.[5] The peak at lowest energy in the iodobenzene spectrum is most likely due to an orbital that is delocalised over the benzene ring and the iodine atom. This suggests that, in the exchange reaction, C–I bonds would be broken and hydrogen–deuterium exchange would not be observed. Table 1 shows that this is the case.

In the series of chloro-compounds studied, 1-chloropropane does not undergo hydrogen-deuterium exchange, but 1-chlorobutane and the higher homologues do. Adiabatic ionisation potentials for propane and n-butane are 11·07 and 10·50 eV respectively,[9,11] whereas in 1-chloroalkanes the broad band for ionisation of chlorine 3*p*-electrons occurs at an intermediate potential, namely *ca.* 10·9 eV. These values and the photoelectron spectra for 1-chloropropane (Figure 4, supplementary data) readily explain why the C–Cl bond is broken in 1-chloropropane. However, the broad bands obtained for the other 1-chloroalkanes (Figures 5—9, supplementary data) suggest that the first ionisation potential in all the remaining chloroalkanes involves removal of an electron from delocalised orbitals which include the chlorine 3*p*-electrons. Since exchange of chlorine of the chloroalkane with $PtCl_4^{2-}$ would not inhibit the hydrogen–deuterium exchange, a separate experiment was carried out to see if such chlorine exchange occurred. It was found that ^{36}Cl could be incorporated into 1-chlorodecane. This substitution was slow and is in agreement with the photoelectron spectrum which indicates that the chlorine 3*p*-electrons and the carbon 2*p*-electrons could form delocalised molecular orbitals responsible for the first ionisation potential, and thus both C–H and C–Cl bonds should be reactive.

We conclude that a knowledge of the energy levels of electrons in halogen-substituted hydrocarbons assists the understanding of the results obtained for platinum(II) catalysed hydrogen–deuterium exchange. This information is at present best obtained by photoelectron spectroscopy.

Since an alkane can undergo ionisation to give any one of a large number of vibrational energy levels in the excited state, the photoelectron spectrum does not contain discrete lines. For simple molecules of high symmetry, such as the normal alkanes and 2,2-dimethylpropane, it is possible to interpret the broad bands in the spectrum on the basis of orbital symmetry. The spectrum of ethane has several uniformly spaced but poorly resolved lines in the region 11·56 to *ca.* 12 eV. Price[10] has attributed this feature of the spectrum to a delocalised molecular orbital of a pseudo-π-type involving the electrons centred on the C–H bonds. Baker *et al.*[11] have studied ethane, propane, and butane and they also attribute the first ionisation potential in these molecules to the electrons of the C–H bonds. For 2,2-dimethylpropane however, Price[7] has assigned the first band in the spectrum (beginning at 10·3 eV) to the molecular orbitals involving C–C bonds, and the second prominent band beginning at 12·2 eV) to a set of orbitals which are centred on the four methyl groups with a node through the central carbon atom (t_1 symmetry). These orbitals are associated with the C–H bonds and are therefore important when considering hydrogen–deuterium exchange in this molecule.

In the preceding paper, hydrogen–deuterium exchange in the alkanes (methane, ethane, propane, and butane) correlates with the first ionisation potential of the molecule (*i.e.*, with the energy of removal of an electron from a molecular orbital involving the C–H bonds[11]). The co-ordinates of the point relating the exchange rate

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[18] N. B. S. monograph No. 34, ' Tables of Chemical Kinetics—Homogeneous Reactions,' Supplementary Tables, U.S.A. 1961.

in 2,2-dimethylpropane [3] and its first ionisation potential (0·37% h^{-1}, 10·3 eV) fall considerably below the correlation line for the normal alkanes. The point is closer to the line if the adiabatic energy of the electrons in the t_1 orbitals discussed above are used. However, this point (0·37% h^{-1}, 12·2 eV) is still not on the correlation line. This may be due to steric hindrance to exchange, thus giving a slow exchange rate as was found for all *ortho*-positions of substituted aromatic compounds.[2]

To avoid the complication that sterically hindered groups might reduce the exchange rate, two molecules, namely 2,2-dimethylbutane and 1,1-dimethylpropylbenzene, were chosen for study. In these molecules it is possible to have exchange in the ethyl groups,[3] and they are molecules where the first ionisation potential is due to electrons from C–C bonds and not from C–H bonds. Rates of exchange in these ethyl groups are given in Table 3. The interpretation of the photoelectron spectra of these two compounds (Figures 15 and 16, supplementary data) is assisted by comparison with the spectra of similar molecules, *viz.*, 2,2-dimethylpropane [7] and 1,1-dimethylethylbenzene,[8] respectively. In both pairs of molecules, one of the methyl groups adjacent to a quaternary carbon atom is replaced by an ethyl group. Since the t_1 band in the spectrum of 2,2-dimethylpropane is due to electrons from four methyl groups that behave as though they were independent, it might be expected that the electrons of the C–H bonds of an ethyl group adjacent to a quaternary carbon atom will ionise independently of the rest of the molecule and give some spectral features similar to ethane.[11,19] Figures 15 and 16 (supplementary data) show that in the region 11·5 to *ca.* 12 eV, as in ethane, uniformly spaced but poorly resolved lines do occur. The adiabatic energies of the prominent spectral features are given in Table 4. We think that the second ionisation potential (at 11·85 eV) in 2,2-dimethylbutane and the third ionisation potential (at 11·54 eV) in 1,1-dimethylpropylbenzene are due to electrons displaced from the C–H bonds in the ethyl group. The co-ordinates of the points (Figure, points 19 and 20) relating the exchange rates (k_b, Table 3) and these ionisation potentials fall quite close to the dashed line representing the correlation for the hydrocarbons of the previous paper.

By this procedure it appears possible to extend the correlation, developed in the preceding paper for normal alkanes and aromatic compounds, to other hydrocarbons.

APPENDIX

Calculation of rate constants for exchange in the ethyl groups of (*a*) 2,2-dimethylbutane and (*b*) 1,1-dimethylpropylbenzene.

(*a*) 2,2-*Dimethylbutane.*—Assuming that the ion $C_5H_xD_{11-x}^+$ contains one ethyl group and two methyl groups, whereas the ion $C_4H_xD_{9-x}^+$ contains 3 methyl groups, and that in the mass-spectrometer, C–C bonds are broken without deuterium rearrangement, we can calculate the rate constants (k_b) from the deuterium distributions for these ions (Table 3). If the rate constant per methyl group is y% h^{-1} and the rate constant for the ethyl group is z% h^{-1}, then $3y = 0{\cdot}25$ and $2y + z = 3{\cdot}11$, giving $z = 2{\cdot}95$% h^{-1}. Correction of the calculated k_b value to allow for the variation from the ' standard ' value for the concurrently run pentane sample gives $k_b = 2{\cdot}35$% h^{-1} (Table 3).

(*b*) 1,1-*Dimethylpropylbenzene.*—The ion $C_{11}H_xD_{16-x}^+$ contains one ethyl group, two methyl groups, and a phenyl group, whereas the ion $C_9H_xD_{11-x}^+$ contains two methyl groups and a phenyl group. For the sample with a reaction time of 22·58 h (Table 3), the deuterium distributions for the two groups of ions show that 3 positions (in the phenyl group) undergo substantial H–D exchange, and that much of the deuterium in the $D_{11}H_xD_{16-x}^+$ ion is in the ethyl group. The distributions show that little or no deuterium is randomised in the formation of the $C_9H_xD_{11-x}^+$ ion in the mass spectrometer. Assuming that the normalised distribution of deuterium in the ethyl group is as given by equation (1) where u, v, w, y, and z are the percentages containing 0, 1, 2, 3, or 4 deuterium atoms respectively. This equation may be combined with the four equations (2)—(5) linking the $C_9H_xD_{11-x}^+$ ion with the $C_{11}H_xD_{16-x}^+$ ion. Equations (2)—(5) use the most abundant deuterium distributions of Table 3.

$$u + v + w + y + z = 100 \quad (1)$$

$$0{\cdot}367u + 0{\cdot}0953v + 0{\cdot}0053w = 16{\cdot}3 \quad (2)$$

$$0{\cdot}4957u + 0{\cdot}367v + 0{\cdot}0953w + 0{\cdot}0053y = 31{\cdot}3 \quad (3)$$

$$0{\cdot}0303u + 0{\cdot}4957v + 0{\cdot}367w + 0{\cdot}0953y + 0{\cdot}0053z = 25{\cdot}2 \quad (4)$$

$$0{\cdot}004u + 0{\cdot}0303v + 0{\cdot}4957w + 0{\cdot}367y + 0{\cdot}0953z = 16{\cdot}0 \quad (5)$$

Solution of these equations gives $u = 36{\cdot}0$, $v = 31{\cdot}5$, $w = 19{\cdot}3$, $y = 15{\cdot}0$, and $z = -1{\cdot}7$. The rate constant, k_b, for the ethyl group, calculated from this deuterium distribution is 4·4% h^{-1}. This value is approximately equal to the difference between the k_b values calculated for each of the two ions, when the reaction time was 0·83 h (Table 3). Correction of the calculated k_b value to allow for the variation from the ' standard ' value of the concurrently run pentane sample gives $k_b = 3{\cdot}6$% h^{-1} (Table 3).

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[2/549 *Received, 8th March*, 1972]

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[19] A. D. Baker, C. Baker, C. R. Brundle, and D. W. Turner, *J. Mass Spectrometry and Ion Phys.*, 1968, **1**, 285.