Activation of Simple Alkanes by a Platinum(II) Complex; Homogeneously Catalysed Hydrogen–Deuterium Exchange

By R. J. HODGES, D. E. WEBSTER, and P. B. WELLS
(*The University, Hull, Yorkshire* HU6 7RX)

Summary Simple alkanes interact with platinum(II) in solution; carbon–hydrogen bond cleavage occurs, and protium in the alkane is substituted by deuterium from the solvent.

WE report extensive protium (called hydrogen)–deuterium exchange in a range of simple alkanes (C_1—C_6) catalysed by solutions of potassium tetrachloroplatinate(II) in aqueous acetic acid. The present reaction conditions have been developed from those used for exchange reactions in aromatic compounds.[1] Shilov and his co-workers,[2] reported a very small amount of exchange in methane and ethane; the conditions appear to be similar to those used for aromatic compounds.[1]

TABLE 1. *Exchange of hydrogen for deuterium in alkanes*

Alkane	Time (h)	D found (%)	D in Me– (%)	D in –CH_2– (%)	D in –CH– (%)	D calc. (%)
Methane ..	95	25	—	—	—	96
Ethane ..	137	91	91	—	—	95
Pentane ..	137	75	92	57	—	92
2-Methylbutane	137	69	83	37	9	92
Cyclohexane[a]	110	70	—	70	—	92

[a] $[PtCl_4^{2-}] = 0{\cdot}01$M.

The reaction medium used in this work consists of a 1 : 1 molar mixture of CH_3CO_2D (or CD_3CO_2D) and D_2O containing (*a*) the catalyst K_2PtCl_4 (typically 0·04M), (*b*) $DClO_4$ (typically 0·2M) to increase the acidity of the solution and thereby inhibit disproportionation of the platinum(II) to platinum(IV) and metallic platinum, (*c*) an aromatic compound (typically 0·05M pyrene) also to inhibit disproportionation, and (*d*) the alkane (typically 0·5M). The reactions were carried out in sealed tubes and the alkanes were analysed by mass spectrometry. The exchange reaction is catalysed homogeneously; platinum metal as formed in this acidic medium was not catalytically active.†

TABLE 2
Relative rates of deuteriation of alkanes. (*Solvent* 50 *mol* % CH_3CO_2D *in* D_2O, [alkane] = 0·3M, [aromatic][a] = 0·05M, $[DClO_4]$ = 0·2M, $[K_2PtCl_4]$ = 0·02M, T = 100°).

Alkane	Exchange rate[b] (%/h)	M value[c]	Ionization potential (eV)[d]
Methane	0·2	—	12·99
Ethane	4·0	1·7	11·65
Propane	7·2	1·6	11·08
Butane	9·5	1·6	10·65
Pentane	11·7	1·5	10·33
Hexane	12·7	1·5	10·17
2-Methylpropane ..	3·8	1·8	10·55
2-Methylbutane ..	6·6	1·5	10·30
2-Methylpentane ..	10·8	1·6	10·09
3-Methylpentane ..	9·7	1·5	10·06
2,2-Dimethylpropane	0·4	—	10·37
2,2-Dimethylbutane ..	3·8	1·4	10·04
2,3-Dimethylbutane ..	4·3	1·4	10·00
Cyclopentane	18·8	1·7	10·51
Cyclohexane	25·2	1·4	9·88

[a] Benzene or pyrene.
[b] Rate of disappearance of $[^2H_0]$alkane.[4]
[c] Multiple exchange parameter.[4]
[d] Photoionisation potentials.[5]

The results in Table 1, obtained using the above conditions, with CD_3CO_2D, at 120°, show the percentage of deuterium in the molecules and its distribution. The rate of exchange is primary C–H > secondary C–H > tertiary C–H. In the last column (calc. %D) is given the amount of deuterium to be expected if all the deuterium and hydrogen

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† Although acid-catalysed exchange reactions occur in alkanes in solvents such as mixtures of anhydrous fluorosulphuric acid and anhydrous antimony pentafluoride,[3] our solvent system is totally inactive. No exchange was detected in a study with aromatic compounds in a similar solvent mixture,[1] although aromatic compounds are more sensitive to acid-catalysed exchange than are alkanes. Also, acid-catalysed exchange would be expected to proceed by a stepwise substitution (M = 1), whereas the results show that for the alkanes M is greater than unity. Furthermore, by using perchloric acid in glacial acetic acid, we have increased the acidity of the solution by >1000 over that used in these studies and exchange in pentane was not observed.

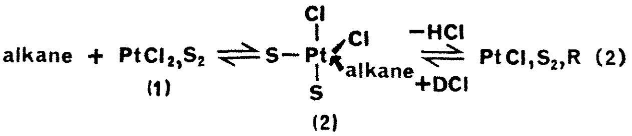
in the reaction mixture is equilibrated. The hydrogen atoms of the methyl groups of pentane and of ethane are at, or near, equilibrium with the reaction mixture.

For a comparison of the reactivities of the alkanes, the data are best analysed in terms of the initial rate of disappearance of the $[^2H_0]$alkane.[4] Such exthange rates for a range of simple alkanes are given in Table 2. The exchange rate increases with increase in the chain length of the alkane, decreases with increase in branching, and is highest for the cyclic alkanes. In these reactions M, the mean number of hydrogen atoms exchanged for deuterium during each encounter of the alkane with the catalyst, exceeds unity (typically M = 1·7, see Table 2) and any proposed reaction mechanism must account for this. The initial rates of reaction show inverse dependence on added chloride ion, and we deduce that the catalytic species is $PtCl_2,S_2$ (**1**) (S is solvent or the aromatic compounds) *i.e.* $PtCl_4^{2-}$ that has lost two chloride ions by solvolysis [equation (1)].

For the linear alkanes the rates are inversely related to their ionization potentials.[5] This may mean that some process of electron transfer is important in the reaction intermediate which we picture as (**2**). The interaction between the alkane and the platinum(II) is thought to involve the delocalised molecular orbitals of the alkane, as these results are difficult to explain using the localised-bond model.

Subsequent steps in the reaction, after the formation of (**2**), are not clear, but we favour oxidative addition of a C–H bond of the alkane to give a platinum(IV) complex which loses HCl to, and gains DCl from, the solution [equation (2)].

$$PtCl_4^{2-} + 2S \rightleftharpoons PtCl_2,S_2 + 2Cl^- \quad (1)$$



$$\text{alkane} + \underset{(1)}{PtCl_2,S_2} \rightleftharpoons \underset{(2)}{S-\overset{Cl}{\underset{S}{Pt}}\begin{smallmatrix}\swarrow Cl\\ \nwarrow \text{alkane}\end{smallmatrix}} \underset{+DCl}{\overset{-HCl}{\rightleftharpoons}} PtCl,S_2,R \quad (2)$$

$$2PtCl_2,S_2 \rightleftharpoons (PtCl_2,S)_2 + 2S \quad (3)$$

It is also possible to interpret the multiple exchange (Table 2) by the formation of a catalytically active dimeric platinum(II) complex [equation (3)].

The implications and extensions of the reaction reported above are now under study in our laboratory.

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