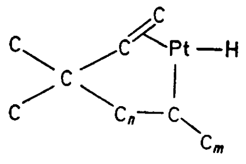
Homogeneous Platinum(II)-catalysed Hydrogen–Deuterium Exchange at a Saturated Carbon Atom

By **Petrus A. Kramer** and **Christopher Masters,*** Koninklijke/Shell-Laboratorium, Badhuisweg 3, Amsterdam (Shell Research B.V.)

Alkenes of the type $RC(CH_3)_2CH{=}CH_2$ (R = Et, Pr, or Bu) undergo hydrogen–deuterium exchange with a deuterium oxide–acetic [$^2H_1$]acid solvent containing perchloric acid in the presence of a homogeneous platinum(II) catalyst. Incorporation of deuterium into the alkyl part of the alkene occurs exclusively at C-5. It is suggested that exchange occurs *via* a dimeric platinum(II) species. Exchange of the olefinic protons is also found; evidence suggests that this latter exchange is essentially an acid-catalysed reaction. Dimeric complexes of the type $[Pt_2Cl_4\{RC(CH_3)_2CH{=}CH_2\}_2]$ have been isolated from the reaction medium.

It has been known for several years that platinum salts in aqueous acetic acid catalyse hydrogen–deuterium (H–D) exchange in aromatic compounds.[1] Recently, a similar effect was reported for hydrogen–deuterium exchange in simple alkanes [2,3] and in the side-chain of alkylbenzenes.[4] The observation [4] that with 1,1-dimethylpropylbenzene H–D exchange in the side-chain occurs almost exclusively at the γ-position prompted us to investigate the H–D exchange in alkenes of type (I), $RC(CH_3)_2CH{=}CH_2$ (R = Me, Et, Pr, or Bu). These substrates were chosen in the belief that co-ordination of the olefinic double-bond to the platinum would bring the alkyl group R into close proximity to the platinum, allowing formation of complexes of type (II) possibly leading to H–D exchange in the moiety R of the alkene.



(II)

---

[1] R. J. Hodges and J. L. Garnett, *J. Catalysis*, 1969, **13**, 83, and refs. therein.

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

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

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

The presence of the geminal methyl groups should prevent formation of a platinum-allyl type complex and isomerization of the alkene. A preliminary communication of our results has already appeared.[5]

RESULTS

Under conditions analogous to those reported by Hodges *et al.*,[3] *i.e.* 1·5 h at 100 °C, solvent 50 mol % CH_3CO_2D in D_2O, 0·2M-$HClO_4$, 0·02M-$K_2[PtCl_4]$, and 0·2M-alkene, we obtained the results shown in Table 1. The position and degree of deuterium incorporation were determined by using a combination of ^{13}C and ^1H magnetic resonance spectroscopy. In the ^1H n.m.r. spectrum (100 MHz in $CDCl_3$) of 3,3-dimethylpent-1-ene the signals due to the alkyl protons were well separated and integration of the spectrum of a deuteriated sample, against a dibromoethane internal standard, revealed that exchange in the alkyl unit had occurred exclusively at C-5. With 3,3-dimethylhex-1-ene integration of the ^1H n.m.r. spectrum showed that exchange had occurred in the alkyl unit; however, it was impossible to distinguish between the protons on C-4 and C-5 by ^1H n.m.r. spectroscopy. In the ^{13}C n.m.r. spectrum of this deuteriated compound there were, after decoupling of the protons, two signals which we assigned to the C-5 carbon, a singlet at $\delta(CS_2)$ = 175·2 p.p.m. from the undeuteriated species, and a 1 : 1 : 1 triplet at $\delta(CS_2)$ = 175·5 p.p.m. ($J_{^{13}C-D}$ = 20 Hz) from the deuteriated form,[6] indicating that: (*a*) deuteriation in the alkyl moiety had occurred predominantly at C-5 (<5% in the other alkyl positions) and (*b*) the predominant deuteriated species was –CHD–. In the case of 3,3-dimethylhept-1-ene the ^1H n.m.r. spectrum (220 MHz) did not show distinct signals for the alkyl protons. The ^{13}C n.m.r. spectrum of the deuteriated sample indicated alkyl deuteriation predominantly at C-5. However, the results were somewhat ambiguous since the signals due to the geminal carbons and C-5 were accidently coincident.[6] With 3,3-dimethylbut-1-ene we observed no incorporation of deuterium into the alkyl moiety. In all cases we found some deuterium incorporation into the olefinic unit. We believe this latter exchange to be basically due to an acid-catalysed protonation/deprotonation reaction since increasing the acid concentration increased the extent of olefinic-proton exchange (but not that of alkyl-proton exchange; see Table 2). Furthermore, even in the absence of platinum exchange of the olefinic protons was found (see Table 3). We have not investigated this olefinic-proton exchange any further. In the absence of platinum no H–D exchange occurred in the alkyl part of the molecule.

TABLE 1

Exchange of hydrogen for deuterium in alkenes of type $RC(CH_3)_2CH=CH_2$; solvent 50 mol % CH_3CO_2D in D_2O; $[HClO_4]$ = 0·2M, $K_2[PtCl_4]$ = 0·02M, [alkene] = 0·2M; temp. = 100 °C; time = $1\frac{1}{2}$ h

	D in		
R	$-CH=CH_2$ % ± 5	$-{}^5CH_2-$ % ± 5	Rest of molecule %
Me	30		<5
Et	15	54	<5
Pr	23	44	<5
Bu	30	*a*	*a*

[a] ^1H N.m.r. spectrum too complex to allow accurate measurement.

Further evidence for the regiospecific nature of the exchange was provided by mass-spectral analysis of the deuteriated alkenes. The pronounced 'peaked' nature of the distribution at D_3 for 3,3-dimethylpent-1-ene and at D_2 for 3,3-dimethylhex-1-ene and 3,3-dimethylhept-1-ene (Table 4) and the virtual absence of deuteriated species above D_6 lend strong support to the n.m.r. findings.

TABLE 2

Effect of $[HClO_4]$ on hydrogen–deuterium exchange in 3,3-dimethylpent-1-ene; conditions as given in Table 1 except for $[HClO_4]$ variation and reaction time of 2 h

	D in	
$[HClO_4]$/M	$-CH=CH_2$ % ±5	Terminal Me (*i.e.* C-5) % ±5
0 [a]	*b*	10
0·2	14	62
0·4	21	65

[a] Solution ceased to be homogeneous after *ca.* 15 min (see text). [b] N.m.r. spectrum indicated some isomerization; it was not possible to calculate %D in $-CH=CH_2$.

TABLE 3

Effect of $[PtCl_4^{2-}]$ on hydrogen–deuterium exchange in 3,3-dimethylpent-1-ene (conditions as given in Table 1 except for $[PtCl_4^{2-}]$ variation and reaction time of 1 h)

	D in	
$\frac{[PtCl_4^{2-}]}{M}$	$-CH=CH_2$ (% ± 5)	Terminal Me (*i.e.* C-5) (% ±5)
0	9	0
0·005	12	15
0·010	10	26
0·015	11	35
0·020	15	41
0·025	18	44
0·030	15	47
0·050	18	57

At the other positions in the alkene <5% deuterium incorporation was found.

TABLE 4

Mass-spectral analysis of deuteriated alkenes of type $RC(CH_3)_2CH=CH_2$ (conditions as given in Table 1 except where indicated)

	% (±5) of D_x species						
R	D_0	D_1	D_2	D_3	D_4	D_5	D_6 [e]
Et [a]	41	7	10	28	10	2	1
Et [b]	33	7	11	32	10	2	1
Pr [c]	15	28	26	13	7	1	1
Bu [d]	10	24	27	17	7	3	1

[a] [Alkene] = 0·3M; reaction time 2 h. [b] [Alkene] = 0·3M; reaction time 3 h. [c] Reaction time 2 h. [d] Reaction time 3 h. [e] <1% Of deuteriated species higher than D_6.

In order to investigate the exchange reaction in more detail we chose 3,3-dimethylpent-1-ene as substrate as this olefin gives rise to an easily interpretable n.m.r. spectrum. We first investigated the effect of perchloric acid on the exchange reaction. In the absence of this acid a considerable amount of platinum metal was deposited during the reaction (2 h, 100 °C) and the mixture ceased to be homogeneous after *ca.* 15 min. This observation was not unexpected since platinum–alkene complexes

---

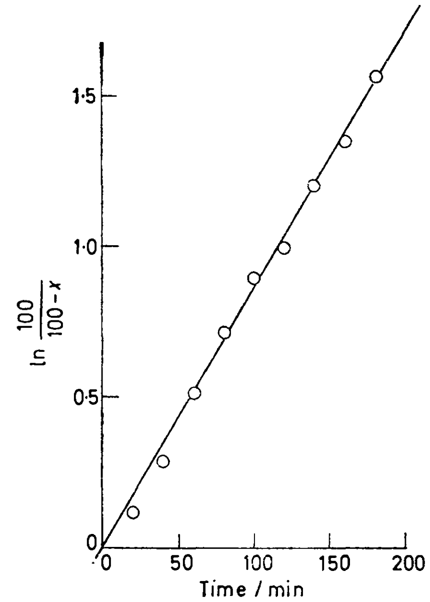
[5] C. Masters, *J.C.S. Chem. Comm.*, 1972, 1258.

[6] A. D. H. Clague and C. Masters, *J.C.S. Dalton*, 1975, 858.

are known to decompose in solutions of low acidity at elevated temperatures;[7] also platinum(II) tetrachloride rapidly disproportionates according to equation (1) in solutions of low acidity.[8] Garnett *et al.* have shown[9]

$$2[PtCl_4]^{2-} \rightleftharpoons Pt\downarrow + [PtCl_6]^{2-} + 2Cl^- \qquad (1)$$

that an acidity equivalent to a pH of -1 is necessary to inhibit this disproportionation. Doubling the concentration of added perchloric acid (from 0·2 to 0·4M) had virtually no effect on the H–D exchange in the alkyl part but resulted in increased enrichment of the olefinic moiety. The results are given in Table 2. We followed the H–D exchange reaction as a function of time during 3 h; the exchange obeyed first-order kinetics, as shown by the linearity of a plot of ln $100/(100 - x)$, where x is the %D at C-5, against t (see Figure). The observed first-order rate constants at various $[PtCl_4]^{2-}$ concentrations are given in Table 5. As can be seen, the rate increases non-linearly as the tetrachloroplatinate(II) concentration is increased. We have measured the first-order rate constants at 80, 100, and 120 °C; the values are given in Table 6. A plot of the Arrhenius equation, ln $k_{obs.}$ *vs.* the inverse of the absolute temperature, gives a reasonably straight line, the slope of which yields a value of 72 ± 10 kJ mol^{-1} for the activation energy.



First-order plot for H–D exchange at C-5 of 3,3-dimethylpent-1-ene; solvent 50 mol % CH_3CO_2D in D_2O; $[HClO_4]$ = 0·2M, $[PtCl_4^{2-}]$ = 0·02M, [alkene] = 0·2M; temp. = 100 °C

TABLE 5

Observed first-order rate constants, $k_{obs.}$, for hydrogen–deuterium exchange at C-5 of 3,3-dimethylpent-1-ene as a function of $[PtCl_4^{2-}]$; solvent 50 mol % CH_3CO_2D in D_2O; $[HClO_4]$ = 0·2M, [alkene] = 0·2M, temp. = 100 °C

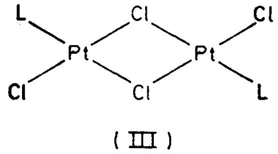
$[PtCl_4^{2-}]$/M	$10^5k_{obs.}$/s^{-1}
0·005	4·5
0·010	8·4
0·015	12·0
0·020	14·6
0·025	16·1
0·030	17·6
0·050	23·4

TABLE 6

Observed first-order rate constants, $k_{obs.}$, for hydrogen–deuterium exchange at C-5 of 3,3-dimethylpent-1-ene as a function of temperature; solvent 50 mol % CH_3CO_2D in D_2O; $[HClO_4]$ = 0·2M, $[PtCl_4^{2-}]$ = 0·02M, [alkene] = 0·2M

Temp./°C	$10^5k_{obs.}$/s^{-1}
80	3·4
100	14·4
120	39·5

During the deuteriation reaction the colour of the solution changed from red to yellow and complexes of type (III), where L = alkene, could be isolated.



(III)

DISCUSSION

Our results show that in the presence of a homogeneous platinum(II) salt alkenes of the type $RC(CH_3)_2CH{=}CH_2$ (R = Et, Pr, or Bu) undergo a regiospecific hydrogen–deuterium exchange in CH_3CO_2D–D_2O containing perchloric acid. We suggest that the first step in the H–D exchange involves co-ordination of the alkene to the platinum with displacement of chloride ion [equation (2)]. In the presence of an excess of alkene (A) this equilibrium lies completely to the right:

$$[PtCl_4]^{2-} + A \overset{K_1}{\rightleftharpoons} \underset{(1)}{[PtCl_3A]^-} + Cl^- \qquad (2)$$

The non-linear dependence of the rate on added $[PtCl_4]^{2-}$ (Table 5) shows that (*1*) is not the catalytically active species. Further possible equilibria are given in equations (3) to (5), where Solv is a solvent molecule (D_2O or CH_3CO_2D) or possibly another alkene molecule, and A stands for alkene:

$$[PtCl_3A]^+ + Solv \overset{K_2}{\rightleftharpoons} \underset{(2)}{[PtCl_2ASolv]} + Cl^- \qquad (3)$$

$$2[PtCl_3A]^- \overset{K_3}{\rightleftharpoons} \underset{(3)}{[PtCl_2A]_2} + 2Cl^- \qquad (4)$$

$$2[PtCl_2ASolv] \overset{K_4}{\rightleftharpoons} \underset{(3)}{[PtCl_2A]_2} + 2Solv \qquad (5)$$

If (2) lies predominantly to the right then

$$[(2)] = \frac{-[PtCl_4^{2-}] + \{[PtCl_4^{2-}]^2 + 4K_2[PtCl_4^{2-}]\}^{\frac{1}{2}}}{2} \qquad (6)$$

Further we may write:

$$k_{obs} = \alpha[(2)]^{\beta} \qquad (7)$$

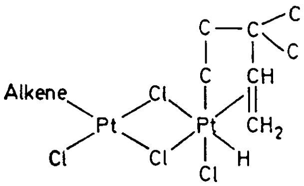
---

[7] I. Leden and J. Chatt, *J. Chem. Soc.*, 1955, 2936.

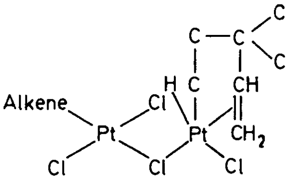
[8] O. Ginstrip and I. Leden, *Acta Chem. Scand.*, 1967, **21**, 2689.

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

If (*2*) is the catalyst then $\beta = 1$ and if the dimeric species (*3*) is the catalyst then $\beta = 2$. Using the data listed in Table 5 and applying a non-linear regressional technique to equation (7) we obtain a value of 2 for β ($\alpha = 0{\cdot}443 \pm 0{\cdot}088$; $K_2 = 0{\cdot}0366 \pm 0{\cdot}0047$ with a $\sigma = 4{\cdot}6 \times 10^{-6}$), indicating that the effective catalyst is a dimeric species such as (*3*).* On the basis of these results we suggest that insertion into the C–H bond at C-5 of the alkene occurs in the dimeric platinum complex either with retention of the chloro-bridge to give an intermediate such as (IV) or with partial rupture of the bridge to afford an intermediate such as (V). Although we cannot distinguish between the two we favour (V) as here the platinum on which insertion has occurred is co-ordinatively unsaturated and this fact could assist in the exchange of the hydrogen bonded to platinum for deuterium. The preferential formation of a five-membered ring in the proposed intermediate is not unexpected since it has been found that internal metallation of tertiary phosphine or phosphite ligands complexed to transition metals preferentially gives rise to complexes containing five-membered rings.[10,11] In contrast to the platinum-catalysed H–D exchange in alkanes[3] the H–D exchange in the alkyl part of alkenes of type (I) is a stepwise process, as evidenced by the predominance of the –CHD– species in an exchanged sample of 3,3-dimethylhex-1-ene. This indicates that exchange between free and co-ordinated alkene is several orders of magnitude faster than the H–D exchange. We have studied[12] the exchange between added free alkene and complexed alkene in complexes of type (III) and found that, in benzene solution, this is the case.



(IV)



(V)

Conclusions.—Two main conclusions can be drawn from these results: (*a*) the H–D exchange occurs in a regiospecific manner, indicating the importance of five-membered ring intermediates; (*b*) the exchange occurs *via* a dimeric platinum intermediate.

EXPERIMENTAL

Acetic [$^2H_1$]acid was prepared from acetic anhydride (acid-free) by reaction with deuterium oxide.[4] For each set of experiments an aqueous solution containing potassium tetrachloroplatinate(II) and perchloric acid in deuterium oxide was prepared. During the preparation of this aqueous solution potassium perchlorate precipitated and this was removed by centrifugation. An aliquot of this solution was transferred to a glass ampoule, after which acetic [$^2H_1$]acid and the alkene were added. The ampoule was sealed without evacuation and then vibrated in an oil-bath at a constant temperature for the required time. Subsequently the alkene was separated from the cooled reaction medium by cautious addition of water. It was washed well with water to remove any residual acid.

Analysis.—Mass-spectral data were obtained with an A.E.I. MS9 spectrometer. For a hydrocarbon containing n hydrogen atoms, the percentage replacement by deuterium (% D) is given by ϕ/n, where the function ϕ is defined by

$$\phi = \sum_{i=0}^{n} i[^2H_i]$$

[^2H_i] being the percentage of the hydrocarbon containing i deuterium atoms.[4] ^{13}C N.m.r. spectra were recorded on a Varian HA 100 spectrometer in the pulse Fourier-transform mode at 25·1 MHz. Solutions were *ca.* 50% in CCl_4; the reference lock was external ^{13}C-enriched CS_2. Spectral assignments were made with the aid of partial decoupling and shift prediction formulae.[13] ^1H N.m.r. spectra were measured on a Varian HA 100 spectrometer at 100 MHz. The amount of deuterium incorporated was determined from the ^1H n.m.r. spectrum by integration against an internal standard (dibromoethane) in $CDCl_3$ containing *ca.* 3% benzene to provide ^1H field-frequency lock.

In all cases the alkenes were recovered after the exchange reaction in greater than 96% purity (g.l.c. analysis).

[4/1178 *Received*, 17*th June*, 1974]

---

* An analogous approach has previously been used by Hodges *et al.*[8] for the platinum(II)-catalysed H–D exchange in alkanes.

[10] A. J. Cheney, B. E. Mann, B. L. Shaw, and R. M. Slade, *J. Chem. Soc.* (*A*), 1971, 3833.

[11] C. Masters, *J.C.S. Chem. Comm.*, 1973, 191.

[12] P. A. Kramer and C. Masters, *Rec. Trav. chim.*, 1975, **94**, 25.

[13] L. P. Lindeman and J. Q. Adams, *Analyt. Chem.*, 1971, **43**, 1245.