

PT(II) - CATALYSED  $^1\text{H}$ - $^2\text{H}$  EXCHANGE IN ALKANES AND CYCLOALKANES

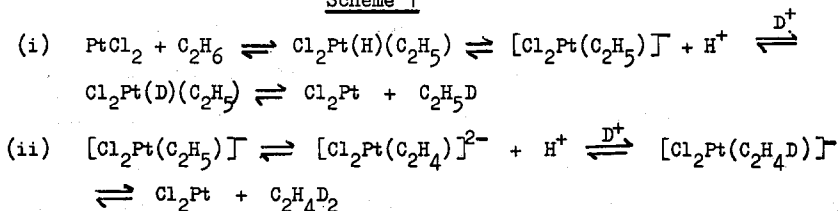
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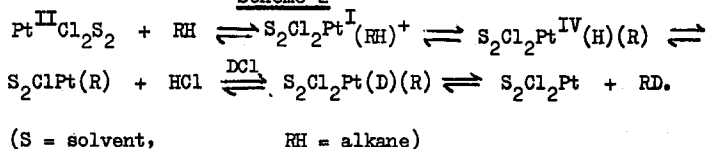
Gol'dshleyer, Tyabin, Shilov and Steinman (1) proposed a reaction Scheme 1 for  $^1\text{H}$  -  $^2\text{H}$  exchange of alkanes catalysed by Pt(II) chloride in AcOD and  $\text{D}_2\text{O}$ .

Scheme 1



Hodges, Webster and Wells (2) outline an alternative, Scheme 2, which omits the Pt-alkene complex, and involves an initial alkane to platinum electron transfer.

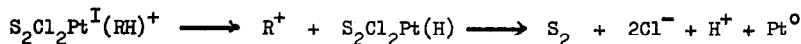
Scheme 2



In both schemes the hydridoplatinum alkyl corresponds to the intermediate in hydrogenation of an alkene, which it is known may revert to the parent alkene. This parallel led us to examine the exchange reaction.

n-Decane (0.3 M), (in a sealed tube,  $100^\circ$ ) in AcOD and  $\text{D}_2\text{O}$  (1:1, 5 ml),  $\text{K}_2\text{PtCl}_4$  (0.02 M),  $\text{DClO}_4$  (0.2 M) and pyrene as stabiliser (0.05 M) showed progressive, but non-selective  $^2\text{H}$  incorporation: 17h. 2.9%, 45h. 9.1%, 66h. 18.5%  $^2\text{H}$ , with  $^2\text{H}_0$  to  $^2\text{H}_8$  isomers.  $\text{K}_2\text{PtCl}_4$  with  $\text{F}_3\text{CCO}_2\text{D}$  in place of AcOD gave 17.9%, and with  $\text{D}_2\text{SO}_4$  in place of  $\text{DClO}_4$ , 17.5%  $^2\text{H}$  in n-decane, but  $\text{Ac}_2\text{O}$  in place of AcOD with  $\text{DClO}_4$  and  $\text{D}_2\text{O}$  led to incorporation of only 3%  $^2\text{H}$  (all at  $100^\circ$ , 65h.). Carbazole is an effective stabiliser in place of pyrene.

In considering Schemes 1 and 2, it appeared that a Pt-alkene intermediate could in principle give rise to the alkyl or vinyl acetate, that a Pt-alkyl might be oxidisable, and that the suggested  $S_2Cl_2Pt^I(RH)^+$  intermediate could alternatively undergo hydride transfer:



particularly where  $R^+$  is a stable carbenium ion.

Processes of this kind could lead to functionalisation of the alkane. However, n-decane gave no decyl acetate or other derivative in the exchange reaction as above, or when carried out in presence of  $V_2O_5$ , chloranil, or in a stream of oxygen. Oxidising conditions retarded, but did not inhibit exchange, viz. with  $V_2O_5$ , 7.5%, with chloranil 16.6%, and in oxygen 9.2%  $^2H$  incorporation in n-decane after 65h at  $100^\circ$ .

With bibenzyl in place of n-decane we were able to recognise trans-stilbene ( $\lambda_{max}$  294, 307 nm) in the  $^2H$ -bibenzyl (38.9%  $^2H$ ) which, however, formed the major product (3).

The electron transfer proposed in Scheme 2 has analogies with electrochemical oxidation which for adamantane (4) and cyclohexane (5) has been shown to lead to products of carbenium ion substitution or rearrangement. This analogy and the possible hydride transfer noted above led us to examine exchange in adamantane and norbornane where the derived carbenium ions show some stability.

Adamantane, treated as for n-decane, (65h.  $100^\circ$ ) gave  $^2H$ -adamantane (10.24%  $^2H$ ),  $^2H_0$  20.02,  $^2H_1$  30.01,  $^2H_2$  24.9,  $^2H_3$  15.7,  $^2H_4$  6.22,  $^2H_5$  2.41%, a distribution somewhat different from that found for heterogeneous exchange (6). We found no adamantanol or the acetate, but an expanded n.m.r. spectrum (90 MHz) of the  $^2H$ -adamantane showed the  $\tau$  8.1 and 8.2 signals in an intensity ratio of 1:4.7. Since the  $\tau$  8.1 signal has reasonably been attributed to the bridgehead protons (7), this indicates preferential bridgehead exchange, and necessarily with retention of stereochemistry.

Norbornane treated similarly gave  $^2H$ -norbornane (15.3%  $^2H$ ),  $^2H_0$  14.9,  $^2H_1$  28.7,  $^2H_2$  24.6,  $^2H_3$  15.9,  $^2H_4$  10.7,  $^2H_5$  5.1%, but no norbornyl acetate.

Protoadamantane, which if carbenium character is generated at  $C_4$  should rearrange to adamantane, was also examined. However, treated as for adamantane, it gave unisomerised protoadamantane (glc examination),  $^2H_0$  22.5,  $^2H_1$  28.3,  $^2H_2$  23.1,  $^2H_3$  12.7,  $^2H_4$  5.7,  $^2H_5$  2.7%.

The total incorporation, 9.3%  $^2\text{H}$ , is somewhat smaller than for adamantane, and we note a similar difference in reactivity towards bromine (8).

Triphenylmethane and triptycene when treated similarly showed very similar  $^2\text{H}$  incorporation, respectively 28.3 and 32.8%  $^2\text{H}$ , but there was no evidence of triphenylmethanol being formed.

The lack of evidence for products derived from carbon-platinum electron transfer led us to reconsider the significance of the reported (2) parallel between rate of exchange and hydrocarbon ionisation potential. We note a similar parallel between hydrocarbon chain length and rate of heterogeneous  $^1\text{H}$ - $^2\text{H}$  exchange (9). Also the correlation is limited: cyclohexane (ip 10.3 eV), norbornane (9.8 eV) (11), adamantane (9.25 eV) (11) and adamantan-2-one (8.76 eV) (11) show  $^2\text{H}$  incorporation of 34.2, 15.3, 10.2, and 6% respectively after 65h. at  $100^\circ$ . Some of these differences in reaction rate may, however, be related to a multiple exchange process. Thus the isolated  $^2\text{H}$ -cyclohexane showed a distribution:  $^2\text{H}_0$  12.04,  $^2\text{H}_1$  26.15,  $^2\text{H}_2$  2.15,  $^2\text{H}_3$  3.45,  $^2\text{H}_4$  5.94,  $^2\text{H}_5$  7.16,  $^2\text{H}_6$  5.89,  $^2\text{H}_7$  20.27,  $^2\text{H}_8$  17.09 suggesting single and multiple exchange, which again is a characteristic of the heterogeneous reaction (9,10). It appears, therefore, that the ionisation potential correlation for linear hydrocarbons is more reasonably regarded as an index of polarisability of the CH bonds towards electrophilic insertion, which may indeed be a synchronous process of  $^2\text{H}$  insertion and  $^1\text{H}$  acceptance by a catalyst species such as  $[\text{D PtCl}_2]^+$ .

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