

Orientation of Hydrogen Isotope Exchange in Naphthalene Catalysed by the Platinum Group Metals and Their Salts

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Recently, Preece and Robinson reported [1] hydrogen isotope exchange between naphthalene and deuterium oxide/deuterioacetic acid – CH_3COOD , in the presence of salts of platinum, iridium, osmium, rhodium, ruthenium and palladium and noted that the activity of these catalysts decreased in that order. In agreement with our previous work [2], the exchange in naphthalene catalysed by $\text{Na}_2\text{PtCl}_4 \cdot 4\text{H}_2\text{O}$ at 100 °C occurred predominantly at the β positions whereas at 200 °C with this same catalyst random labelling was observed [1]. In contrast, exchange in the presence of the other less active metals at 200 °C showed a preference for deuteration at the α sites [1]. During these reactions, Preece and Robinson [1] observed precipitation of metal with all chloro com-

plexes except $\text{Na}_2\text{OsCl}_6 \cdot 6\text{H}_2\text{O}$; however they showed that these heterogeneous metals were catalytically inactive in the acetic acid medium used, also in agreement with our observations. They concluded that their observed exchange was catalysed by homogeneous metal species [1] and suggested modifications to the π -dissociative mechanism proposed by us for homogeneous platinum exchange to explain the reversal in the preferred site of deuteration in naphthalene at 200 °C.

However, we believe that there is an alternative, simpler, more plausible explanation for their unexpected α -orientation effects observed with all complexes except platinum. It has been obvious to us in our current work where we are extending our study of homogeneous metal catalysed exchange from platinum [2], iridium [3] and rhodium [4] to the other platinum metals that ruthenium, rhodium, palladium and osmium require temperatures considerably in excess of 80 °C to achieve comparable deuteration rates to PtCl_4^{2-} . At temperatures approaching 200 °C interpretation of the exchange is complicated by the metal precipitation observed by Preece and Robinson [1]. Reduction of the metal chloride to metal liberates mineral acid [5]. In the present exchange work, it is thus necessary to carefully distinguish between the homogeneous process

TABLE I. Orientation of Deuterium in Naphthalene following Acid and Metal Catalysed Exchange.^a

| Run | Catalyst | Solvent | Temp. °C | Time h | %D | % α D | % β D | % Deqm. (Theor) |
|-----|--|-----------------------|----------|--------|------|--------------|-------------|-----------------|
| 1 | DCI (1 M) | D ₂ O/AcOD | 180 | 144 | 44 | 44 | 44 | 44 |
| 2 | DCI (0.1 M) | D ₂ O/AcOD | 200 | 5 | 21 | 35 | 6.7 | 44 |
| 3 | DCI (0.05 M) | D ₂ O/AcOD | 200 | 5 | 16 | 27 | 5.1 | 44 |
| 4 | DCI (0.005 M) | D ₂ O/AcOD | 200 | 5 | 2.6 | – | – | 44 |
| 5 | (NH ₄) ₃ IrCl ₆ (0.02 M) | D ₂ O/AcOD | 130 | 5.5 | 11.8 | 3.5 | 20 | 69 |
| 6 | Na ₂ PtCl ₄ (0.6 M) | D ₂ O/AcOD | 100 | 5 | 36 | 2.5 | 69 | 94 |
| 7 | Pt unsupported | D ₂ O | 130 | 168 | 13 | 2.3 | 24 | 50 |
| 8 | 10%Pd/C | D ₂ O | 150 | 960 | 9.0 | 2.8 | 15 | 50 |
| 9 | 5%Rh/C | D ₂ O | 150 | 528 | 7.7 | 1.5 | 14 | 50 |
| 10 | 5% Ru/C | D ₂ O | 150 | 744 | 11.2 | 3.9 | 18 | 50 |
| 11 | 10% Ir/C | D ₂ O | 150 | 792 | 22 | 6 | 38 | 50 |

^aRun 1–4 50 mol % AcOD, Run 6 67 mol % AcOD. 2 ml of solvent used in each run.

Charcoal supported catalysts were used to obtain enhanced exchange rates but support does not affect deuterium orientation [11].

Typical mass spec. deuterium distributions, D₀D₁.....D₈

| | | | | | | | | | |
|--------|-----|------|------|-----|-----|-----|-----|-----|---|
| run 3: | 75 | 135 | 106 | 44 | 11 | 1.6 | 0 | 0 | 0 |
| run 5: | 60 | 13.0 | 11.8 | 7.1 | 5.2 | 1.6 | 0.9 | 0.4 | 0 |
| run 6: | 0.8 | 6.2 | 19 | 38 | 31 | 4.9 | 0.3 | 0 | 0 |
| run 7: | 38 | 35 | 18 | 5.8 | 1.9 | 1.0 | 0.7 | 0 | 0 |

catalysed by the platinum metal chlorides and exchange induced by mineral acid when temperatures as high as 200 °C are used.

The data in the Table show the catalytic effect of simple hydrochloric acid in the deuteration of naphthalene. With 0.1 M acid, 21% deuteration is found after only five hours at 200 °C. Even acid concentrations as low as 0.005 M yield detectable exchange under these experimental conditions. The deuteration is predominantly at the α positions when the exchange is stopped well short of equilibrium as is expected of simple electrophilic substitution, whereas with *homogeneous* platinum and iridium catalytic systems after deuteration for five hours at 130 °C or less, the exchange is β -oriented (Table). Similar β -orientation is found with platinum [6, 7], iridium, rhodium, ruthenium and palladium when used as *heterogeneous* metal catalysts with water as the isotope source (Table). This *heterogeneous* result is important since, from the mechanistic relationship between *homogeneous* and *heterogeneous* catalysis involving π -complex intermediates [8–10], it would be predicted that under initial conditions all *homogeneous* metal catalysts used in this study would likewise favour β -orientation in naphthalene.

We have observed exchange in naphthalene above 180 °C in the presence of salts of all the platinum metals, but the tendency to α -oriented exchange we believe represents catalysis by mineral acid formed *in situ*. With salts such as OsCl_6^{2-} conversion to a lower oxidation state yields the acid in a manner similar to that proposed for the Pt(IV)/Pt(II) system [5].

It would thus appear that the modifications proposed by Preece and Robinson [1], for the π -dissociative mechanism [8] in order to explain α -oriented exchange in naphthalene at 200 °C are unnecessary. Their observation of metal precipitation, the observed similarity of deuterium distribution patterns and the extent of incorporation with the least active catalysts, together with the possi-

bility of solvation and changes in oxidation state, indicate the presence of mineral acid induced exchange. At 200 °C this would accompany homogeneous metal catalysis and be α -oriented. Our experience indicates that extensive metal precipitation occurs within 5 hours at 200 °C and acid concentrations approaching 0.05 M are possible. Considerable care is necessary to stabilise the homogeneous metal salt if exchange is to be unequivocally catalysed by the metal species. We have reported preliminary results with iridium [3] and rhodium [4] and intend to describe details of our studies with other Group VIII metals shortly.

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