Inorganica Chimica Acta, 29 (1978) L199–L200
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Substitution Patterns in the Homogeneous Catalysis of Hydrogen Isotope Exchange at Naphthalene by the Platinum Group Metals

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Received April 15, 1978

The formal analogy between cyclometallation reactions involving aromatic rings bound to coordinated ligands [1] and the metal catalysed hydrogen isotope exchange between aromatic hydrocarbons and deuterium oxide [2] has frequently been noted [3]. However, whereas the cyclometallation reactions have been observed to occur readily with all six platinum group metals [1], studies on the homogeneous catalysis of the hydrogen isotope exchange reactions have been restricted almost exclusively to platinum [4], and have only recently been extended to iridium [5] and rhodium [6].

Having previously observed facile cyclometallation of triphenylphosphite ligands coordinated to each of the six platinum metals [7], we have now undertaken a comparative study of the ability of these metals to catalyse homogeneous hydrogen isotope exchange between naphthalene and deuterium oxide/deuterioacetic acid–CH_3COOD.

Homogeneous solutions of naphthalene (0.65 g, 5 mmol) and platinum metal chloro complex (0.25 mmol) in deuterium oxide and deuterioacetic acid – CH_3COOD (12.5 ml 1:1 mol mixture) were sealed in Carius tubes and heated at a constant temperature (100–200 °C) for 5 hours. The platinum samples were stabilised by addition of trifluoromethane sulphonic acid (0.375 g); addition of acid to the other systems did not give any detectable improvement in stability and was therefore omitted. The recovered naphthalene was purified by sublimation and examined by infrared, proton n.m.r. and mass spectroscopy.

The results obtained indicate that, whereas at 100 °C only $Na_2PtCl_4 \cdot 4H_2O$ catalyses appreciable deuteriation of the naphthalene, at temperatures above 130 °C all six platinum group metal chlorides catalyse significant amounts of hydrogen–deuterium exchange. Data collected at 100 and 200 °C are summarised in the Table. All the chloro complexes except $Na_2OsCl_6 \cdot 6H_2O$ deposited small amounts of metal during the catalysis runs at 200 °C. However, control experiments using freshly precipitated (borohydride reduced [8]) platinum group metals indicated that metallic ruthenium, rhodium and palladium do not catalyse the isotope exchange reaction in naphthalene under the conditions employed in this study, and that metallic iridium and platinum induce only very slow rates of exchange. Moreover, naphthalene is known to strongly poison heterogeneous hydrogen isotope exchange catalysts [9]. We therefore conclude that the systems studied in this work involve essentially homogeneous platinum metal species.

Good agreement between our results and those of Garnett and Hodges [4] for catalysis by $Na_2PtCl_4 \cdot 4H_2O$ at 100 °C confirms the validity of our data. Furthermore, our sequence of catalyst efficiency $Na_2PtCl_4 \cdot 4H_2O \gg Na_2IrCl_6 \cdot 6H_2O > Na_2OsCl_6 \cdot 6H_2O \gg RhCl_3 \cdot 3H_2O > RuCl_3 \cdot 3H_2O > Na_2PdCl_4 \cdot 4H_2O$, is consistent with the less extensive sequence Pt $\gg$ Ir $>$ Rh obtained by Garnett *et al.* [5, 6].

The isotope distribution patterns observed (Table) are consistent with a stepwise deuteriation sequence

TABLE. Deuteriation of Naphthalene. Product Distribution.

System	Temp. °C	Time h	Analysis of Deuterium Content											
			D_0	D_1	D_2	D_3	D_4	D_5	D_6	D_7	D_8	%D	% α_D	% β_D
$Na_2PtCl_4 \cdot 4H_2O$[a]	100	5	8.9	13.8	16.8	23.1	29.5	7.1	0.8	–	–	34.4	5.0	63.8
$Na_2PtCl_4 \cdot 4H_2O$[a]	200	5	2.8	7.7	16.5	24.3	24.4	15.8	6.8	1.6	0.1	42.9	44.2	41.6
$Na_2IrCl_6 \cdot 6H_2O$	200	5	15.3	26.3	26.2	18.0	9.2	3.6	1.1	0.3	–	24.5	31.4	17.6
$RhCl_3 \cdot 3H_2O$	200	5	33.0	32.9	18.4	9.1	4.0	1.8	0.6	0.2	–	15.9	25.0	6.8
$RuCl_3 \cdot 3H_2O$	200	5	28.9	37.6	23.3	8.0	1.7	0.2	–	0.3	–	14.8	23.6	6.0
$Na_2OsCl_6 \cdot 6H_2O$	200	5	36.4	33.3	19.0	5.3	0.8	–	–	0.1	0.1	16.5	28.4	4.6
$Na_2PdCl_4 \cdot 4H_2O$	200	5	31.9	37.8	21.7	7.0	1.3	0.2	–	–	0.1	13.9	25.2	2.4
Blank Run	200	5	98.5	1.5	–	–	–	–	–	–	–	0.2	–	–

[a] In the presence of added CF_3SO_3H.

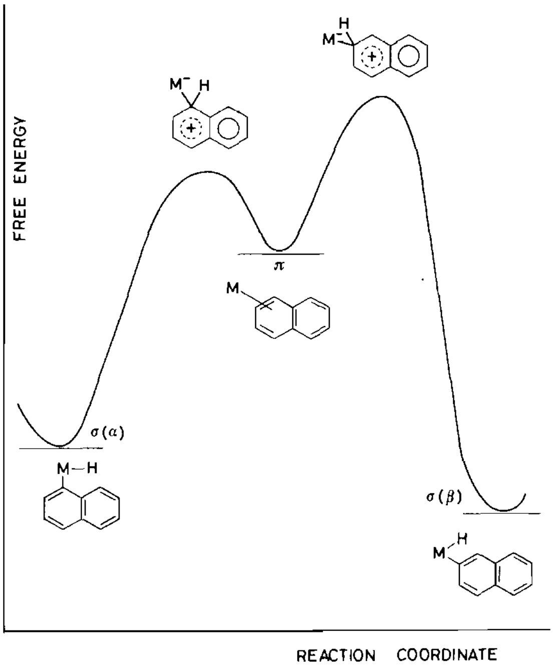

Figure. Mechanism of the exchange process.

presumably involving a π-dissociative mechanism [2]. Moreover, they clearly indicate that, whereas $Na_2PtCl_4{\cdot}4H_2O$ at 100 °C catalyses preferential hydrogen isotope exchange at the β-sites, at 200 °C all six platinum metal chloro species apparently favour deuteriation at the less accessible α-sites [10]. In the case of $Na_2PtCl_4{\cdot}4H_2O$ at 200 °C the α/β deuteriation ratio is unity within experimental error, and the increase in the proportion of α-deuteriation at the higher temperature can therefore be attributed to thermally induced statistical redistribution of hydrogen isotopes within the naphthalene. However, with the other five metals the α/β deuteriation ratio is significantly greater than unity and therefore must reflect a measure of α-selectivity. Moreover, comparison of catalytic activity for the six metal salts at a given temperature (200 °C) reveals that as the overall rate of deuteriation (as measured by % deuterium content) *decreases* the α/β substitution ratio *increases.*

To account for these observations we commence with the premise that the exchange proceeds by a dissociative mechanism involving a rate-determining π–σ conversion step (Figure). With the more efficient catalysts equilibrium between π and σ forms should be rapidly attained and the α/β deuteriation ratio, which should reflect the steric preference for the σ-bonded β-naphthyl metal complex relative to its α-analogue [11], should favour isotope exchange at the β-position, as observed for $Na_2PtCl_4{\cdot}4H_2O$ at 100 °C. However, with the less efficient catalysts involving higher activation energies for the π–σ transition, kinetic control is likely to become increasingly significant and, since the α-transition state is expected to be more stable than its β analogue [12], should progressively favour α-substitution. Thus the hypothesis predicts that for different platinum metal catalysts operating at the same temperature an *increase* in the α/β deuteriation ratio should accompany a *decrease* in the overall rate of deuteriation, and is therefore in accord with our experimental data.

Acknowledgement

We thank British Petroleum Research Limited for use of facilities and for financial support (to MP).

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