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Stereochemistry and Mechanism of Cleavage of the Platinum–Carbon σ-Bond by Peroxy Acid

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Summary With *m*-chloroperbenzoic acid $[(PhCHD)PtCl(PPh_3)_2]$ yields $[^2H]$benzyl *m*-chlorobenzoate and $[^2H]$-benzyl alcohol with retention of stereochemistry at carbon, and the ratio of *m*-chlorobenzoate: alcohol product on oxidation of $[(ArCH_2)PtCl(PPh_3)_2]$ (Ar = Ph or *p*-$NO_2C_6H_4$) and of *cis*-$[Bu^n_2Pt(PPh_3)_2]$ depends on the polarity of the group which is cleaved; in $[RhH(CO)(PPh_3)_3]$ the hydride is cleaved by Bu^tO_2H.

We have reported[1] oxidative cleavage by hydroperoxides of carbonyl, triphenylphosphine, and carbon σ-bonds in various transition metal complexes. We were led to envisage a process of addition of hydroperoxide RO_2H, as fragments RO and HO, followed by an elimination step. However, the incidence of electron-transfer processes in transition metal complex-catalysed hydroperoxide decomposition,[2] and in other reactions of transition metal complexes[3] raised uncertainty as to the precise reaction mechanism. We have therefore determined the stereochemistry of cleavage of the Pt–carbon σ-bond as being likely to offer more decisive information.

(*S*)-(+)-$[^2H]$ Benzyl chloride,[4] (77% ^2H), $[\alpha]_D$ + 1·22°, with $[Pt(PPh_3)_4]$ gave $[(PhCHD)PtCl(PPh_3)_2]$, m.p. 198—200 °C, τ 2·43 and 7·60 ($J_{Pt\text{-}H}$ 80 Hz). This complex with *m*-chloroperbenzoic acid in benzene under nitrogen gave an orange solution from which *m*-$ClC_6H_4CO_2CHDPh$ (77% ^2H), *m/e* 249 and 247, τ 1·73—2·40 (9H), 4·67 (1·2H), $[\alpha]_D$ −2·18°, could be isolated by chromatography. The parent $[^2H_1]$ benzyl alcohol with *m*-chlorobenzoyl chloride and pyridine gave *m*-$ClC_6H_4CO_2CHDPh$, $[\alpha]_D$ + 2·13°, characterised by mass and n.m.r. spectroscopy.

The oxidation reaction also yielded $[^2H_1]$ benzyl alcohol (m.s., n.m.r.), $[\alpha]_D$ −0·69°, from a sample of the platinum complex derived from PhCHDCl, $[\alpha]_D$ +0·94°.

Stepwise oxidation of $[(PhCH_2)PtCl(PPh_3)_2]$ in benzene, followed by n.m.r. spectroscopy, showed simultaneous progressive formation of benzyl alcohol and benzyl *m*-chlorobenzoate, *i.e.* both appear to be primary products of oxidation, and Pt–carbon bond cleavage competes effectively with phosphine oxidation.

There is sound precedent[5] for anticipating reaction of (*S*)-(+)-PhCHDCl and $[Pt(PPh_3)_4]$ with inversion of stereochemistry at carbon. The (*S*)-benzyl derivatives PhCHDX, where X = OH, Cl, or *m*-$ClC_6H_4CO_2$, exhibit optical rotations in the same sense. The $[\alpha]_D$ values for *m*-$ClC_6H_4CO_2CHDPh$, noted above, therefore indicate oxidative cleavage of the Pt–benzyl bond with retention of configuration, and effectively stereospecifically. The $[\alpha]_D$ of the isolated $[^2H]$ benzyl alcohol also indicates cleavage with retention, and, if allowance is made for the rather lower optical purity of the $[^2H]$benzyl chloride used, and for possible racemisation of the alcohol during chromatography, again with something approaching stereospecificity.[6]

These results sustain an addition–elimination mechanism, and give no support to electron transfer as an important process in this oxidation reaction.

Competitive oxidation of $[(ArCH_2)PtCl(PPh_3)_2]$ (Ar = Ph or *p*-$NO_2C_6H_4$) gave additional information. The complex (Ar = *p*-$NO_2C_6H_4$), m.p. 244—246 °C, τ 2·0—2·7, 6·82 (t of t, *J* 76 and 5 Hz), with *m*-chloroperbenzoic acid gave *p*-$NO_2C_6H_4CH_2X$ (X = HO and *m*-$ClC_6H_4CO_2$) (3 : 1). The two complexes at equimolar concentration were found, by integration of proton n.m.r. signals, to be oxidised competitively by the peracid at almost exactly the same rate, *i.e.* alkyl bond polarity does not markedly influence the rate of the overall process. However, from these two complexes the ratios $ArCH_2OH$: *m*-$ClC_6H_4CO_2CH_2Ar$ differed, *viz.* 0·5 for Ar = Ph, 3 for Ar = *p*-$NO_2C_6H_4$, and *cis*-$[Bu^n{}_2Pt(PPh_3)_2]$[7] on oxidation gave n-butyl *m*-chlorobenzoate and only a trace of n-butanol. Hence alkyl group polarity may influence the relative energetics of transfer of the HO and *m*-$ClC_6H_4CO_2$ groups, or the geometry of addition of peracid.

We have also extended our previous observations[1] of oxidation with t-butyl hydroperoxide to include the hydride ligand. Progressive addition of Bu^tO_2H to $[RhH(CO)(PPh_3)_3]$ in benzene resulted in parallel loss of ν_{RhH} at 2057 cm^{-1}, movement of ν_{CO} from 1914 to 1971 cm^{-1}, and the appearance of bands at 1120 and 1180 cm^{-1} due to Ph_3PO. Excess (3 equiv.) of hydroperoxide led to loss of ν_{CO} at 1971 cm^{-1}. Oxidation was also monitored by disappearance of the Rh–H signal at τ 19·3. t-Butyl hydroperoxide also oxidises the complexes $[(ArCH_2)PtCl(PPh_3)_2]$ with formation of $ArCH_2OH$ (Ar = Ph or *p*-$NO_2C_6H_4$), but less efficiently than *m*-chloroperbenzoic acid.

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