

Ligand Effects on the Aerobic Oxidation of Cyclohexene Catalysed by Aqua(phosphine)ruthenium(II) Complexes

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The multistep nature of the aerobic oxidation of cyclohexene catalysed by a series of aqua(phosphine)ruthenium(II) complexes can clearly be demonstrated from the correlation of catalyst turnovers with the rate constants of ligand substitution, and the correlation of catalyst turnovers with Hammett σ_p values.

The activation of molecular oxygen by ruthenium-containing complexes, with a focus on the aerobic oxidation of organic substrates, is a topic of current interest.¹⁻⁵ This study represents the first report where the rate-determining step of the aerobic oxidation of an organic substrate can be changed

from one step of a serial catalysis mechanism to another step of the same mechanism, by ligand modification of the catalyst. Thus, this novel study illustrates the profound phosphine ligand effects in the aerobic oxidation of cyclohexene catalysed by aqua(phosphine)ruthenium(II) complexes.

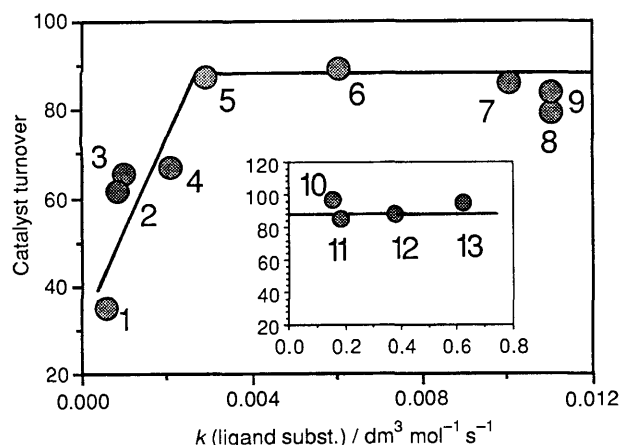


Fig. 1 A plot of catalyst turnovers (catalyst turnover = moles of oxidized products formed moles⁻¹ of ruthenium catalyst added) as a function of the second-order rate constants of ligand substitution, for the aerobic oxidation of cyclohexene catalysed by $[\text{Ru}(\text{OH}_2)(\text{bpy})_2(\text{PR}_3)_2]^{2+}$ complexes at 25 °C and 1 atm $\text{O}_2(\text{g})$ for 8 h. The phosphine ligands utilized in these complexes are plotted as: 1 = $\text{P}(p\text{-C}_6\text{H}_4\text{CF}_3)_3$, 2 = PEt_3 , 3 = PPri^n_3 , 4 = $\text{P}(p\text{-C}_6\text{H}_4\text{F})_3$, 5 = PBu^n_3 , 6 = PPh_3 , 7 = $\text{P}(p\text{-C}_6\text{H}_4\text{Me})_3$, 8 = $\text{P}(p\text{-C}_6\text{H}_4\text{OMe})_3$, 9 = $\text{P}(m\text{-C}_6\text{H}_4\text{Me})_3$, 10 = $\text{P}(\text{CH}_2\text{Ph})_3$, 11 = PPri^i_3 , 12 = $\text{PPh}_2(o\text{-C}_6\text{H}_4\text{Me})$, 13 = $\text{P}(\text{Cyclohexyl})_3$.

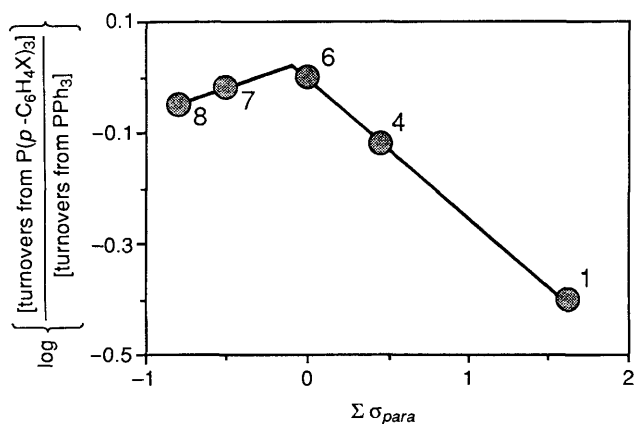
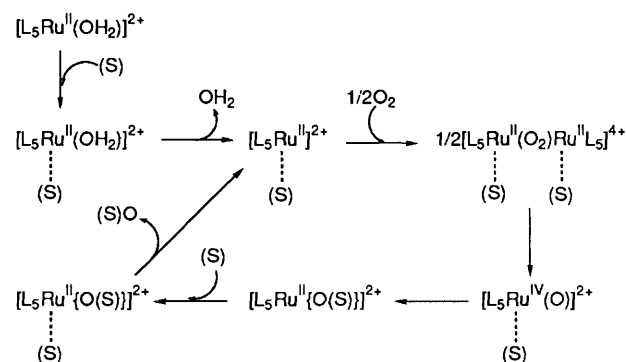


Fig. 2 A plot of the $\log\{\text{catalyst turnovers produced in 8 h by } [\text{Ru}(\text{OH}_2)(\text{bpy})_2(\text{P}(p\text{-C}_6\text{H}_4\text{X})_3)]^{2+} \text{ complexes/catalyst turnovers produced in 8 h by } [\text{Ru}(\text{OH}_2)(\text{bpy})_2(\text{PPh}_3)_2]^{2+}\}$ vs. Σ Hammett σ_p values, for the aerobic oxidation of cyclohexene in *o*-dichlorobenzene at 25 °C and 1 atm $\text{O}_2(\text{g})$. The ligand numbers correspond to those in Fig. 1.

We have plotted the catalyst turnovers[†] for the aerobic oxidation of cyclohexene catalysed by a series of aqua(phosphine)ruthenium(II) complexes as a function of the second-order rate constants⁶ for the substitution of water by acetonitrile for the same series of aqua(phosphine)ruthenium(II) complexes (see Fig. 1). The plot shows a change in functionality, where a linear relationship between catalyst turnovers and the rate constants for ligand substitution is observed for the very slowly substituting ruthenium(II) complexes (points 1–4), while the catalyst turnovers for the faster substituting ruthenium(II) complexes (points 7–13), show no dependence on the rate constants for ligand substitution. Since points 5 and

[†] Catalyst turnovers = $\{[2(\text{moles cyclohex-2-en-1-one}) + \text{moles of cyclohex-2-en-1-ol} + \text{moles of cyclohexene oxide}] \text{ produced in 8 h moles}^{-1} \text{ of ruthenium catalyst added}\}$. The formation of cyclohex-2-en-1-one requires a 4-electron oxidation and thus is expected to require 2 equivalents of ruthenium complex for each mole of ketone produced.



Scheme 1 The aerobic oxidation of cyclohexene catalysed by $[\text{Ru}(\text{OH}_2)(\text{bpy})_2(\text{PR}_3)_2]^{2+}$ complexes. The dotted lines (---) represent a weak association between the substrate (S) and the ruthenium centre. For an example of a weak association between a molecule and a ruthenium centre, see ref. 6.

6 occur where the functionality of the plot changes, these two points probably involve mechanisms associated with both sets of points of Fig. 1. From these results, we suggest (see Scheme 1) that the dissociation of either water or oxidized substrate (both utilize an oxygen donor atom) from a ruthenium(II) centre is the rate-determining step for the aerobic oxidation of cyclohexene catalysed by aqua(phosphine)ruthenium(II) complexes which have very slow rate constants of ligand substitution (complexes 1–4). For the aqua(phosphine)ruthenium(II) complexes which have higher rate constants of ligand substitution (complexes 7–13), we propose that the rate-determining step for the aerobic oxidation of cyclohexene is shifted to another step in the catalytic cycle (*vide infra*).

By considering only aqua(phosphine)ruthenium(II) complexes which contain phosphine ligands of constant cone angle $[\text{P}(p\text{-C}_6\text{H}_4\text{X})_3]$,⁷ we can utilize Hammett σ_p parameters^{8,9} to focus primarily on the electronic ligand effects on the aerobic oxidation of cyclohexene, by keeping the steric ligand effects constant. The values of $\log\{\text{catalyst turnovers produced in 8 h by } [\text{Ru}(\text{H}_2\text{O})(\text{bpy})_2(\text{P}(p\text{-C}_6\text{H}_4\text{X})_3)]^{2+} \text{ complexes/catalyst turnovers produced in 8 h by } [\text{Ru}(\text{H}_2\text{O})(\text{bpy})_2(\text{PPh}_3)_2]^{2+}\}$; bpy = 2,2'-bipyridyl) were plotted as a function of Σ (Hammett σ_p) values, yielding a concave down-shaped graph (see Fig. 2). It has been suggested for non-catalytic reactions that the concave down shape of the graph of $\log(k_X/k_H)$ values vs. σ values is indicative of a change in the rate-determining step from one step to another in a serial mechanism.¹⁰ Note in Fig. 2 that for points 7 and 8, the amount of products increases as the electron-withdrawing nature of the phosphine ligand increases, while for points 1 and 4, the amount of products decreases as the electron-withdrawing nature of the phosphine ligand increases. Thus, it can be suggested from Fig. 2 that within the same mechanism, one rate-determining step is accessed with points 7 and 8, while another rate-determining step occurs with points 1 and 4. Since point 6 occurs where the functionality of the plot changes, this point probably involves mechanisms associated with both sets of points of Fig. 2.

Points 1 and 4 of Fig. 2 can be interpreted in a manner similar to points 1–4 of Fig. 1. The rate constant of dissociation of a ligand (either water or oxidized substrate) from a ruthenium(II) centre would be decreased by electron-withdrawing substituents, and thus for points 1 and 4, the catalyst turnovers decrease as the electron-withdrawing nature of the phosphine ligand increases. However, points 7 and 8 of Fig. 2 should be interpreted in terms of a new rate-determining step. We propose that the rate-determining step for points 7 and 8 involves the oxidation of cyclohexene by the redox active form of the ruthenium catalyst (see Scheme 1), since an increase in the electron-withdrawing nature of the phosphine substituent would result in the increase in rate constant of the oxidation of

cyclohexene. In addition, we suggest that points 7–13 of Fig. 1 involve the same rate-determining step as points 7 and 8 of Fig. 2. We previously proposed that the redox-active form of the ruthenium catalyst is the $[\text{Ru}(\text{bpy})_2(\text{O})(\text{PR}_3)]^{2+}$ complex,⁵ and the electronic data of points 7 and 8 of Fig. 2, along with ligand substitution data of points 7–13 of Fig. 1, corroborate this assertion.

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