

Autocatalysis and Free Radical Mechanism in a Ruthenium Cluster Catalysed Hydrogen Transfer Reaction

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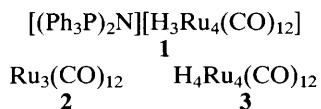
The mechanisms of the $[(\text{Ph}_3\text{P})_2\text{N}][\text{H}_3\text{Ru}_4(\text{CO})_{12}]$ **1** catalysed disproportionation and transfer-hydrogenations of cyclohex-2-en-1-one have been shown to involve free radicals; in the latter reaction **1** is converted to other carbonyl species *via* autocatalysis.

Autoxidations of hydrocarbons are the only reactions where carbonyl clusters are known to catalyse radical initiation steps.¹ To our knowledge radical mechanisms in cluster catalysed hydrogenation or transfer-hydrogenation reactions are unknown. We herein present evidence for the involvement

of free radicals in the $[\text{PPN}][\text{H}_3\text{Ru}_4(\text{CO})_{12}]$ **1** [$\text{PPN} = (\text{Ph}_3\text{P})_2\text{N}$] catalysed disproportionation and transfer-hydrogenations of cyclohex-2-en-1-one. Kinetic simulation studies for the latter reaction indicate that **1** is converted to other carbonyl species in an autocatalytic manner. The

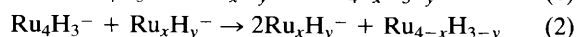
simulated curves agree well with experimentally observed, time-dependent concentration profiles of cyclohex-2-en-1-one and the products, cyclohexanone and cyclohexanol.

The abilities of $\text{Ru}_3(\text{CO})_{12}$ **2** and $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ **3** to act as precatalysts for the transfer-hydrogenation of cyclohex-2-en-1-one to cyclohexanol through the intermediate formation of cyclohexanone have recently been reported.² Cluster **1** is found to be considerably (>3 times) more active than **2** and **3** for this transformation. The mechanistic investigations have therefore been confined to this cluster.



Spectroscopic (IR, ^1H NMR) analyses at the end of a catalytic run (82 °C, 5 h, > 100 turnovers of cyclohexanol) with **1** as the precatalyst indicated that all of **1** was converted into a mixture of soluble carbonyl and hydridic species. One of the components, $[\text{PPN}]_2[\text{Ru}_6(\text{CO})_{18}]$ (<10%), isolated by fractional crystallisation and characterised by spectroscopic comparison with an authentic sample,³ was found to have negligible activity as a precatalyst.

The kinetic behaviour of the catalytic system has been simulated by computer assisted unsteady state kinetic modelling.⁴ The changes in the concentrations of cyclohex-2-en-1-one, cyclohexanone and cyclohexanol were monitored by GC, while the rate of disappearance of **1** was measured from the changes in the IR spectra. As shown in Fig. 1, when the order of the rate of disappearance of **1** with respect to the concentration of **1** is varied from -1 to +2, marked discrepancies between the experimental points and the simulated curves result. This suggests a complex reaction sequence where the overall rate cannot be adequately modelled by a simple $k[\mathbf{1}]^n$ type expression with n having integral or fractional values. The simplest model, which gives an excellent fit, is based on the assumption that **1** is converted in an autocatalytic manner to carbonyl species of different nuclearities, *i.e.* reactions (1) and (2). A linear differential rate law plot (not shown) also validates this assumption.⁵



Ru_4H_3^- represents **1** (CO groups are not included, for clarity); x, y are integers $1 \leq x \leq 3$; $1 \leq y \leq 3$.

To extend the model it has been assumed that reactions (3) and (4) are catalysed by the species Ru_xH_y^- , generated from **1**

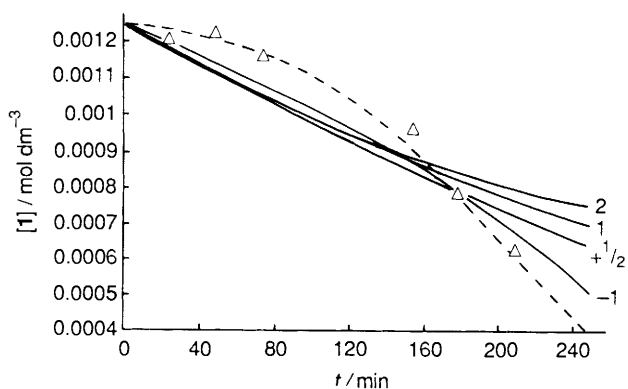
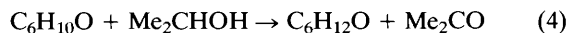
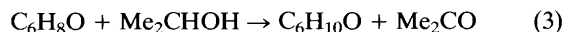


Fig. 1 $[\mathbf{1}]$ vs. t measured by IR spectroscopy. (Δ) Experimental points. (—) Assumed that rate = $-k[\mathbf{1}]^n$, labelled by respective n . (---) Autocatalysis, reactions (1) and (2), assumed

by autocatalysis. It is also reasonable to assume that these reactions are pseudo zero-order with respect to the concentrations of propan-2-ol. The overall model consisting of reactions (1)–(4) describes well the time-dependent concentrations of cyclohex-2-en-1-one ($\text{C}_6\text{H}_8\text{O}$), cyclohexanone ($\text{C}_6\text{H}_{10}\text{O}$) and cyclohexanol ($\text{C}_6\text{H}_{12}\text{O}$) (Fig. 2). It is possible that the other species $\text{Ru}_{4-x}\text{H}_{3-y}$ also acts as a catalyst. However, its inclusion as a catalyst for (3) and (4) arbitrarily increases the number of steps in the model without contributing significantly to its accuracy.



An isotropic ESR signal (g ca. 2.042 at 77 K) is observed when **1** is heated with neat cyclohex-1-en-2-one (ca. 2 min). Product analysis after heating for 3 h indicated formation (ca. 20% conversion) of phenol and a mixture of cyclohexanone and cyclohexanol. However, under similar reaction conditions with only propan-2-ol, it is evident from total analysis of the reaction mixture that there is no observable reaction.

To establish a possible radical chain mechanism, the effect of the known radical inhibitor 2,6-di-*t*-butyl-4-methylphenol on the rate of the hydrogen transfer reaction has been studied. While **1** does not react with 2,6-di-*t*-butyl-4-methylphenol, the initial rates of the hydrogen transfer reactions progressively diminish with increasing the amount of the inhibitor. Similarly the presence of small quantities of carbon tetrachloride is found to have an inhibitory effect on the hydrogen transfer rates.

The radical mechanism, as indicated by the above evidence, is probably initiated by a hydridocarbonyl species in a catalytic manner [reactions (5)–(7)]. In neat cyclohex-2-en-1-one reactions (5) and (6), and in the presence of propan-2-ol reactions (5) and (7), are proposed to be the predominant radical initiation pathway. It is noteworthy that the involvement of radical species has recently been established in the transfer-hydrogenations of aromatic ketones with alkoxides.⁶ The numbers of propagation and termination reactions that must follow the initiation steps are too many to speculate upon meaningfully. However, the sums of all the initiation, propagation and termination reactions would result in steps (3) and (4). These steps, along with steps (1) and (2), give a model that describes the kinetic behaviour of the catalytic system remarkably well (Figs. 1 and 2). Further work is being done to elaborate these reaction schemes with other cluster precatalysts.

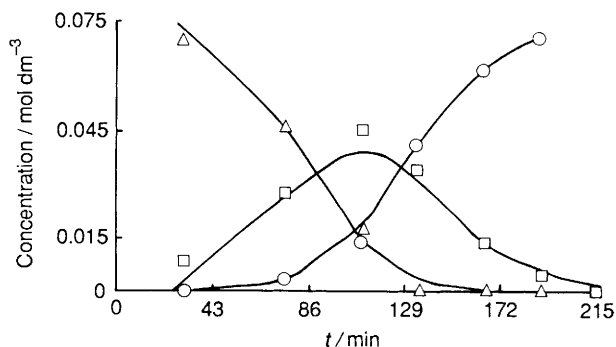
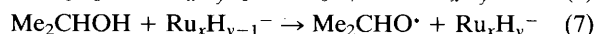
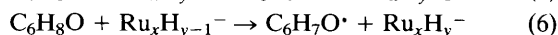
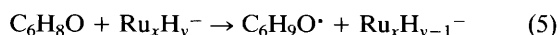


Fig. 2 Concentrations of cyclohex-2-en-1-one (Δ), cyclohexanone (\square) and cyclohexanol (\circ), measured experimentally, vs. t . (—) Simulated concentration profiles

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