

a hydrogen acceptor. The dehydrogenations reported are the first efficient homogeneous dehydrogenations of alkane not using light irradiation (5) or a sacrificial hydrogen acceptor.

When refluxing a cyclooctane solution of (I), with a stream of argon passing over the condenser, the initial rate of cyclooctene formation is 11 turnovers h^{-1} . After 44 hours, 104 turnovers are obtained and after 120 hours, 190 turnovers. These results should be compared with those from $\text{IrH}_2(\text{O}_2\text{CR})(\text{PCy}_3)_2$, the most active soluble 'acceptorless' dehydrogenation catalyst previously investigated. This was reported to give 1.41 turnovers h^{-1} cyclooctene, with a maximum of 28.5 turnovers obtained after 48 hours (6, 7).

The potential for industrial applications of the present iridium catalyst system requires further development, and the chemistry reported to-date needs extending and evaluating (8). It will be necessary to increase the rates achieved so far by two to three orders of magnitude and improve efficiency. As indicated above, conversion drops after several hundred turnovers, probably because the olefinic product bonds to the vacant co-ordination sites on the catalyst. Since the reaction slows down when the product alkene concentration reaches 5 to 10 per cent, continuous removal of product by distillation or by some other means may be possible, so that catalyst activity is maintained. The catalyst also needs evaluating with linear alkanes, since the biggest commercial rewards lie here. For instance, cyclooctane has a dehydrogenation enthalpy of only 23.3 kcal mole^{-1} but alkanes typically require about 28 to 30 kcal mole^{-1} for the elimination of hydrogen from two secondary C-H bonds (4). The ability to promote the conversion of alkenes or cycloalkenes to aromatics by direct dehydrogenation in the absence of a sacrificial hydrogen acceptor, would also constitute a significant advance.

As the iridium system (I) catalyses the hydrogenation of arenes to cycloalkanes, as well as the reverse reaction, the potential of these systems for hydrogen storage could be explored. By coupling the dehydrogenation and hydrogenation reactions, hydrogen could be cyclically stored and released, for applications such as

the supply of hydrogen to the fuel cells used in electric cars. When all the cycloalkanes have been dehydrogenated, the arene products could be 'refuelled' by re-hydrogenation from an external hydrogen source. The idea of using alkanes as a hydrogen storage source is not new, but until now there has been no means of dehydrogenating them at moderate temperatures.

References

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Catalysis Technical Guide

Johnson Matthey Chemicals North America has just published a "Catalysis Technical Guide", containing information on heterogeneous and homogeneous catalysis using the platinum metals.

The "Heterogeneous Catalysis" section begins with a concise description of the critical factors to be considered in the design and selection of the most appropriate catalyst for each application. Commercially significant hydrogenations using powdered and particulate catalysts are described individually and specific catalysts are recommended. Hydrogenation of aromatic rings, aldehydes, ketones, nitro compounds and benzyl protecting groups are only a few examples of the reactions described.

The "Homogeneous Catalysis" section begins with a brief introduction to the concepts and terminology, key to understanding these processes. Among the synthetic reactions individually described are hydrogenation, isomerisation, carbonylation, Heck coupling and allylic alkylation. A section is devoted to the increasingly critical area of chiral homogeneous catalysis.

Each section has guidelines for the safe handling of catalysts. For more information contact: Johnson Matthey, telephone: (+1)(609) 384-7000 or (+1)(800) 444-1411; fax: (+1)(609) 384-7282.