

Homogeneous Catalyst for Alkane Dehydrogenation

AN IRIIDIUM CATALYST NEEDING NO HYDROGEN RECEPTOR

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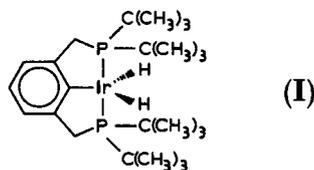
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The removal of hydrogen from alkanes to give alkenes is an important commercial objective, as alkenes are widely used as organic feedstocks in industrial processes involving chemical synthesis and polymerisation. This reaction is, however, significantly endothermic, needing up to 30 kcal per mole, and normally occurring at temperatures exceeding 400°C in the presence of heterogeneous supported metal catalyst systems in the gas phase. The conversion of alkanes to aromatic molecules (as part of 'catalytic reforming') is even more important and is also effected using supported metal catalysts, such as platinum on high surface area alumina. For these kinds of reactions to be achieved with a homogeneous catalyst in solution, under milder conditions, the use of hydrogen acceptors has been thought essential; that is, the conversions have been achieved via 'transfer hydrogenation'. A possible alternative means for achieving the dehydrogenation reaction would be irradiation with UV light, but this is not usually industrially attractive.

In early work, R. H. Crabtree and co-workers (1) used $\text{IrH}_2\{\text{O}_2\text{CCF}_3\}(\text{PPr}^i)_2$ to effect the dehydrogenation of alkanes to arenes via oxidative addition at 150°C in the presence of the hydrogen acceptor, *tert*-butylethylene. However, it was thought that this system was not catalytic because hydrogenolysis of the phosphine P-C bonds occurs at temperatures of 135°C or above: the temperatures needed to release arenes from the intermediate complexes.

The five-co-ordinate iridium P-C-P pincer complex $(\text{PCP})\text{IrH}_2$ (I), where $\text{PCP} = \eta^3\text{-C}_6\text{H}_3\text{-}[\text{CH}_2\text{P}(\textit{tert}\text{-C}_4\text{H}_9)_2]_{2-1,3}$, was reported by Jensen, Kaska and their colleagues (2) to be a highly active homogeneous catalyst for the transfer dehydrogenation of cyclooctane, with unusually

long-term stability for temperatures as high as 200°C. This catalyst was subsequently demonstrated to be useful for the catalytic transfer dehydrogenation of cycloalkanes to arenes (3). For example, cyclohexane was dehydrogenated to cyclohexene and benzene in the presence of (I) and *tert*-butylethylene, the latter being converted almost quantitatively into *tert*-butylethane. This special reactivity is ascribed to the presence of the P-C-P ligand, which renders the metal centre reactive with saturated hydrocarbons, but restricts its access to the ligand P-C bonds. It was claimed that the P-C-P pincer complex could promote accessibility to previously unattainable catalytic pathways.



In collaborative research between members of the Chemistry Departments of Rutgers, New Jersey, the University of Hawaii and the University of California, Santa Barbara, Goldman, Jensen, Kaska and co-workers (4) have now shown that cycloalkanes can be efficiently dehydrogenated using (I) as catalyst to give the corresponding cycloalkene and dihydrogen, without using a hydrogen acceptor; and several hundred mol product are produced per mol catalyst. However, after several hundred catalytic cycles, conversion decreases, and this is thought to be due to the alkene product increasingly inhibiting the catalyst by co-ordination to catalyst sites, as its concentration increases.

In principle, the temperatures used are sufficiently high to overcome the large positive enthalpy of dehydrogenation without the use of

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.

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