Thermal and Photochemical Catalytic Dehydrogenation of Alkanes with $[IrH_2(CF_3CO_2)(PR_3)_2]$ ($R = C_6H_4F$-*p* and Cyclohexyl)

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$[IrH_2(CF_3CO_2)(Pcy_3)_2]$ (cy = cyclohexyl) catalyses the photochemical dehydrogenation of cyclo-octane both in the presence and absence of a hydrogen-acceptor.

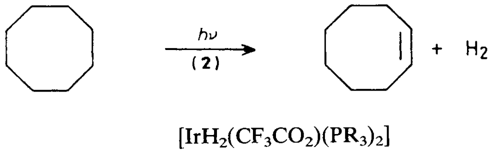
Several catalysts for thermal alkane dehydrogenation have been described recently.[1,2] In each case it has been found necessary to have a hydrogen-acceptor such as the alkene t-butylethylene, which we originally introduced[3] for this purpose. We now report on some new catalysts $[IrH_2(CF_3CO_2)(PR_3)_2]$, (**1**; $R = C_6H_4F$-*p*) and (**2**; R = cyclohexyl). While both give thermal[†] alkane dehydrogenation, (**2**) also gives a novel photochemical catalytic dehydrogenation at ambient temperature, even in the absence of t-butylethylene.

Complex (**1**) is made from the corresponding $[IrH_2(Me_2CO)_2L_2]SbF_6$[3] [$L = P(C_6H_4F\text{-}p)_3$] with $Na(CF_3CO_2)$ in tetrahydrofuran (thf) and resembles the known analogous chelating carboxylate complexes[4] {(**1**): ^1H n.m.r. (CD_2Cl_2): δ −30.4 [t, ^2J(P,H) 16.5 Hz, Ir–H], 6.74, and 7.38 (complex, PAr); i.r.: ν 2254 (Ir–H), 1390, and 1612 cm^{-1} (RCO_2)}. In cyclo-octane (1.5 ml) containing t-butylethylene (50 equiv.) at 150 °C, complex (**1**) (10 mg) gave 16 turnovers of cyclo-octene, as determined by g.c. and g.c.–mass spectroscopy. After 2 days no further cyclo-octene formation was observed and 1 equiv. C_6H_5F was also detected; this arises by P–C cleavage[2,3] of the phosphine and may well be responsible for the deactivation of the catalyst.

Complex (**2**), made by treatment of $[Ir(cod)(CF_3CO_2)]_2$ and Pcy_3 (2 equiv.) (cod = cyclo-octa-1,5-diene; cy = cyclohexyl) in CH_2Cl_2 with H_2, has an analogous structure {(**2**): ^1H n.m.r.: δ −33.3 [t, ^2J(P,H) 16 Hz, Ir–H], 1.2—2.3 (complex, Pcy); i.r. ν 2280 (Ir–H), 1440, and 1619 cm^{-1} (RCO_2)}. Under the thermal conditions described above, only 2 turnovers of cyclo-octene were observed. Photochemically and at room temperature, (**2**) was much more active. Under the same conditions, but at 25 °C and with u.v. illumination at 254 nm (Rayonet reactor), (**2**) gives 28 turnovers of cyclo-octene in 7 days. No P–C cleavage products were detected and *ca.* 30% of the colourless alkane-soluble catalyst was recovered from the very pale yellow products.

Other alkanes were also dehydrogenated under the photochemical conditions, *e.g.*, cyclohexane gave cyclohexene (2.0 turnovers); methylcyclohexane gave methylenecyclohexane (2.75), 1-methyl- (2.19), 3-methyl- (0.85), and 4-methylcyclohexene (1.26); hexane gave hex-1-ene (1.18), *trans*-hex-2-ene (2.48), *cis*-hex-2-ene (0.47), and *trans*-hex-3-ene, (0.52) by capillary g.c. (Carbowax column) and g.c.–mass spectroscopy.

In all the experiments described above the hydrogen removed from the alkane was transferred to t-butylethylene to give t-butylethane. We now find that even in the absence of t-butylethylene, dehydrogenation does take place under the photochemical, but not the thermal conditions: 7 turnovers of cyclo-octene are observed with (**2**) after 7 days. It appears that the photochemical energy provides the thermodynamic driving force necessary for dehydrogenation to take place [equation (1)].[‡]



(1)

$[IrH_2(CF_3CO_2)(PR_3)_2]$

(**1**) $R = C_6H_4F$-*p*
(**2**) R = cyclohexyl

[†] H. Felkin *et al.* simultaneously and independently observed thermal alkane dehydrogenation from $IrH_5(PR_3)_2$ (R = Ph) in the presence of $MeCO_2H$; they considered $[IrH_2(MeCO_2)(PR_3)_2]$ was involved. (H. Felkin, personal communication, 1984).

[‡] The H_2 expected on the basis of equation (1) has also been detected; technical difficulties have prevented us from determining the quantum yields.

We are currently studying the mechanism, which is probably similar to that previously proposed for this type of alkane dehydrogenation.[1—3]

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