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# New Efficient Route to Alkene Metathesis Catalysts. Electrogeneration of Catalytically Active Species from Tungsten Hexachloride

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*Summary* At ambient temperature, an active species generated by the electroreduction of tungsten hexachloride with an aluminium anode catalyses the metathesis of internal olefins in halogenated solvents with good activity and selectivity.

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SINCE the discovery of the homogeneous alkene disproportionation $2\ R^1CH{=}CHR^2 \rightleftharpoons R^1CH{=}CHR^1 + R^2CH{=}CHR^2$,[1] much effort has been made to explain the reaction mechanism and to find more effective and stable catalysts.[2] The most active catalysts are often derived from the combination of transition metal (W, Mo) complexes in high oxidation states with organoaluminium compounds having reducing and acid properties.

To find a new route to species active for metathesis, the electrochemical reduction of W or Mo complexes has been studied. The electrochemical conditions are mild, so that they offer the opportunity of stabilizing the metal in a particular oxidation state.[3]

As the most commonly used homogeneous catalyst is the $WCl_6$–EtOH–$EtAlCl_2$ system, electroreduction of $WCl_6$ with an aluminium anode was performed in halogenated solvents such as PhCl, $CH_2Cl_2$, or $CH_2Cl{\cdot}CH_2Cl$. Reactions (1) and (2) generate *in situ* simultaneously the reduced tungsten species and a Lewis acid.

$$WCl_6 + ne \longrightarrow WCl_{6-n} + n\,Cl^- \qquad (1)$$

$$Al + 3\,Cl^- \longrightarrow AlCl_3 + 3e \qquad (2)$$

Voltamperometric studies were initially conducted on $WCl_6$ under an inert atmosphere in order to determine the half-wave potentials of the reduction steps. The polarogram obtained with a 0·1 M $WCl_6$ –1,2-dichloroethane solution (rotating platinium electrode, $NBu_4^+\ ClO_4^-$ 0·1 M as supporting electrolyte) exhibits three reduction waves at +2·01, +0·63, and −0·27 V (*vs.* Ag–AgCl–$Cl^-$ saturated solution). The preliminary electrochemical experiments were carried out under a controlled potential (+1·5 V *vs.* Ag–AgCl–$Cl^-$) so that only catalytic products arising from the first reduction step could be present. After electrolysis at room temperature under nitrogen (2 h; Al cylindrical anode; Pt cathode; $[WCl_6] = 7{\cdot}5 \times 10^{-3}$ M in dichloroethane), pent-2-ene was injected into the electrolytic cell and the metathesis reaction 2 pent-2-ene $\rightleftharpoons$ but-2-ene + hex-3-ene occurred. The activities of these electrogenerated species compared to those obtained from chemical reductions with an identical aluminium foil are in the Table. In all cases, these results indicate that an equilibrium mixture of olefinic compounds is reached with selectivities as high as 95—100%, and only traces of but-1-ene are detectable by g.l.c. No alkylation products were observed.

TABLE. Catalytic behaviour of chemically and electrochemically reduced $WCl_6$ salts for the metathetic reaction of pent-2-ene.

| Catalytic system | $WCl_6$–Al[a] | $WCl_6$–Al[a] | $WCl_6$–Al[b] | $WCl_6$–Al[b] |
|---|---|---|---|---|
| Olefin/W ratio | 40 | 500 | 40 | 500 |
| Initial rate/$h^{-1}$ | 4·7 | 8·9 | 63·4 | 189 |
| Turnover number per Faraday | — | — | 82 | 1800[c] |

[a] Chemically reduced W salt. [b] Electrochemically reduced W salt. [c] No activity when an iron anode was used.

From these results, the following conclusions can be drawn. (i) Active species are electrochemically generated during the first reducing step of tungsten hexachloride. (ii) As no metathesis was detected with $WCl_6$–$AlCl_3$ under the same chemical conditions, we can assume that the reduction of $WCl_6$ is effected during electrolysis and that this reduction is necessary to provide at least one vacant co-ordination site for the alkene substrate. (iii) Since iron is not a suitable metal for the anode, we suggest that a strong Lewis acid must be present as a cocatalyst. This is reinforced by the fact that the $WCl_6$–Fe system is effective only after addition of $AlCl_3$. (iv) Although good conversions are obtained, these electrocatalytic systems are not yet as active as their chemical $WCl_6$–$EtAlCl_2$ analogues. However they have the advantage of being selective and are able to catalyse the reaction under mild conditions. (v) The very mild formation of active species and the absence of organoaluminium compounds allows their generation and identification to be studied. In particular, it is of interest to know how the carbene intermediate, which is generally accepted as being present in this reaction, is formed under such conditions and why the presence of the strong Lewis acid $AlCl_3$ is also necessary to effect metathesis.

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[2] For a recent review, see J. J. Rooney and A. Stewart, *Catalysis* (*London*), 1977, **1**, 277.
[3] H. Lehmkuhl, in 'Organic Electrochemistry,' Marcel Dekker, New York, 1973, p. 621.