Electrochemically generated catalyst system with increased specificity and efficiency for olefin metathesis

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Dedicated to Professor Ernst Otto Fischer on the occasion of his 85th birthday

Abstract

A facile route for the electrochemical generation of an olefin metathesis catalyst from methylene chloride solution of WCl_6 was described. It was found that reductive, oxidative and pulse electrolysis produced the same intermediate. This electrolysis intermediate incorporates olefin into its structure possibly forming a metal–olefin complex, which decomposes into catalytically active metal carbene type species. ESCA, NMR and ESR methods were used to elucidate the structure of the catalyst system. The catalyst was applied in the metathesis of 1-octene and 2-octene without any need for a co-catalyst. Highly specific products with high yields were obtained.
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1. Introduction

The catalyst systems for olefin metathesis reactions usually involve transition metal salts or oxides and their complexes [1–13]. These catalysts are generally used together with some co-catalysts such as organoaluminum compounds which produce the species specifically responsible for the catalytic action [3,4]. In most cases it is difficult to determine the coordination number and the oxidation state of these active species. Co-catalysts increase the activity of the catalysts used. They, on the other hand, cause a reduction in the stability and the selectivity of the catalyst. The loss of selectivity is due to side reactions such as isomerization, alkylation and polymerization [14–17]. The extent of the side reactions can be reduced by the addition of some chemicals such as tertiary amines to the medium or by the optimization of the ratios of the catalyst to co-catalyst and to olefin [18]. The photochemical generation of catalytic action [19] without the need for a co-catalyst is possible but activity is reduced substantially in these cases [20].

It is known that the electrochemical reduction of WCl_6 or $MoCl_5$ using Pt cathode and Al anode in chlorinated solvents under controlled potential conditions produces a stable and active metathesis catalyst. The electrochemical control of the desired oxidation state of the active species thus leads to higher selectivity in metathesis reactions [21–24].

This study describes an investigation of the electrogeneration of an active, stable, efficient and selective catalytic system from the electrolysis of WCl_6 in methylene chloride using a Pt cathode and Al anode. Oxidative, reductive and pulse electrolysis results are

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compared and an electrochemical formation mechanism for the catalyst system is proposed.

2. Results and discussion

The cyclic voltammogram of WCl_6 in methylene chloride-0.01 M tetrabutylammonium tetrafluoroborate (TBABF$_4$) medium on a Pt disc electrode is shown in Fig. 1. The first and second reduction steps are easily observed with a peak potential of $+0.9$ and -0.3 V, respectively. Two oxidation peaks at $+0.3$ and $+1.6$ V are observed when the potential scan is reversed. Constant potential electrolysis at more negative potential than $+0.9$ V produces cathodic currents, whereas the same electrolysis at more positive potential than $+1.6$ V results in anodic currents.

The cathodic peak at $+0.9$ V is due to the one electron reduction of WCl_6 Eq. (1) followed by the splitting of $WCl_6^{\bullet-}$ in to $WCl_5^{\bullet}$ neutral radical and chloride ion Eq. (2)

$$WCl_6 + e^- \rightarrow WCl_6^{\bullet-} \tag{1}$$
$$WCl_6^{\bullet-} \rightarrow WCl_5^{\bullet} + Cl^- \tag{2}$$

The anodic peak at $+1.6$ V, on the other hand, is due to the one electron oxidation Eq. (3) process producing

WCl_5^+ (with the same oxidation state as WCl_6) and chlorine atoms which dimerize to produce chlorine molecules Eq. (4).

$$WCl_6 \rightarrow WCl_5^+ + Cl^{\bullet} + e^- \tag{3}$$
$$2Cl^{\bullet} \rightarrow Cl_2 \tag{4}$$
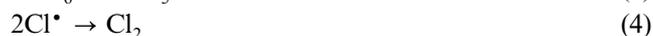
The reductive electrolysis at $+0.9$ V and the oxidative electrolysis at $+1.6$ V both produced the catalytically active species in the metathesis of olefins. This result indicates that the species responsible for the catalytic activity must be generated at the Al counter electrode (anode) in one of the above electrolysis experiments since the products of these electrolysis are different in nature. The possible electrochemical reactions Eqs. (5)– (7) occurring at the Al anode during the cathodic electrolysis at Pt electrode are,

$$Cl^- \rightarrow Cl^{\bullet} + e^- \tag{5}$$
$$Al + 3Cl^- \rightarrow AlCl_3 + 3e^- \tag{6}$$
$$WCl_5^{\bullet} \rightarrow WCl_5^+ + e^- \tag{7}$$
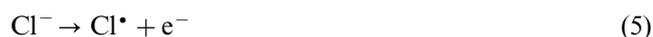
During the oxidative electrolysis at Pt electrode the only possible electrochemical reaction Eq. (8) occurring at the Al counter electrode (cathode) is

$$WCl_6 + e^- \rightarrow WCl_5^{\bullet} + Cl^- \tag{8}$$

The only common species produced during either of these electrolysis experiments is WCl_5^+.

Another evidence for the crucial role of WCl_5^+ in the catalysis was obtained from the pulse electrolysis where the potential applied to the Pt electrode is pulsed between $+0.6$ and $+1.6$ V (pulse duration = 0.2 s). As explained below the yield of the metathesis reaction is increased significantly during the pulse electrolysis. $WCl_5^{\bullet}$ neutral radicals produced at the Pt cathode during the cathodic half cycle of the pulse, get oxidized immediately at the same surface during the subsequent half cycle of the pulse, producing WCl_5^+. Furthermore $WCl_5^{\bullet}$ neutral radical produced at the Al cathode during the first half cycle of the pulse gets oxidized to WCl_5^+ at the same surface during the following half cycle. The absence of any ESR signal indicated that $WCl_5^{\bullet}$ neutral radical does not exist in the solution after a prolonged electrolysis. It can thus be concluded that WCl_5^+ is the only possible active species in the catalysis system. The counter ion which stabilizes WCl_5^+ in the electrolysis solution is probably produced from the reaction between the other electrolysis products such as $AlCl_3$ and Cl^-.

$$AlCl_3 + Cl^- \rightarrow AlCl_4^- \tag{9}$$

The accepted mechanism in literature for several olefin metathesis catalyst systems involve the initial formation of a metal–olefin complex intermediate via π-interaction which then gives a metal carbene structure by 1,2 hydride shift [1,2] Eq. (10)
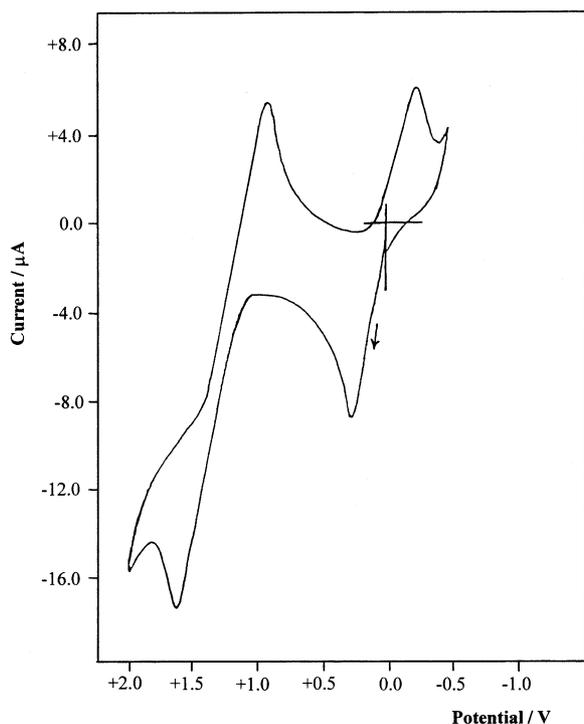
Fig. 1. Cyclic voltammogram of 1.0×10^{-3} M WCl_6 solution in methylene chloride-0,01 M TBABF$_4$ on Pt disc electrode. Scan rate: 100 mV s^{-1}.

$$\left[WCl_5\right]^+\cdots\overset{CH-R_1}{\underset{CH-R_2}{\|}} \longrightarrow \left[WCl_5\right]^+_H\overset{}{\underset{CH-R_2}{\overset{C-R_1}{\|}}} \longrightarrow \longrightarrow \left[WCl_x\right]=C\overset{R_1}{\underset{CH_2-R_2}{}} \qquad (Eq.(10))$$
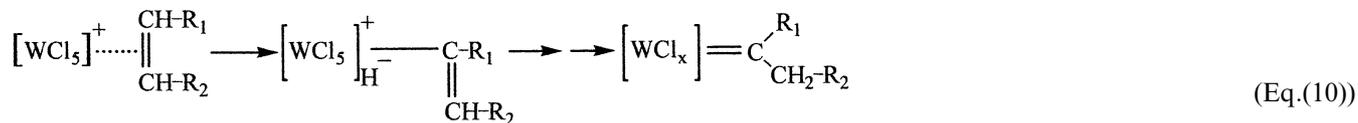
$(R_1 = H, \text{alkyl}; R_2 = \text{alkyl})$

The olefin metathesis proceeds via this metal carbene compound [1,2] according to the well-known following step Eq. (11).

$$\left[WCl_x\right]=C\overset{R_1}{\underset{CH_2-R_2}{}} + \overset{H\quad H}{\underset{R_1\quad R_2}{\|}} \longrightarrow \left[WCl_x\right]\overset{CR_1CH_2-R_2}{\underset{R_1\quad R_2}{|}} \longrightarrow \overset{[WCl_x]}{\underset{CHR_1}{\|}} + \overset{CR_1CH_2-R_2}{\underset{CHR_2}{\|}} \qquad (Eq.(11))$$
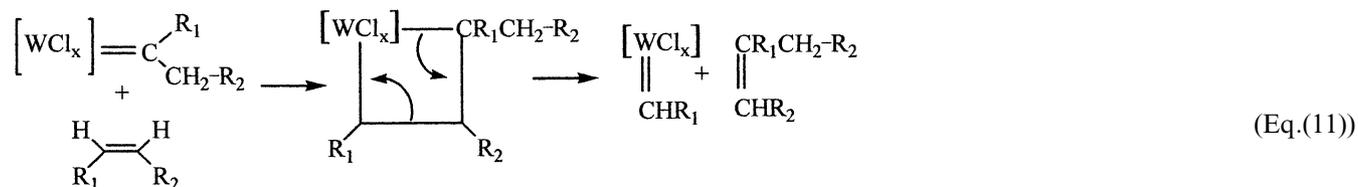
$(R_1 = H, \text{alkyl}; R_2 = \text{alkyl})$

Fig. 2 shows the ESCA spectra of WCl_6, the product obtained after the reductive electrolysis and the product after the olefin addition (before the metathetic activity
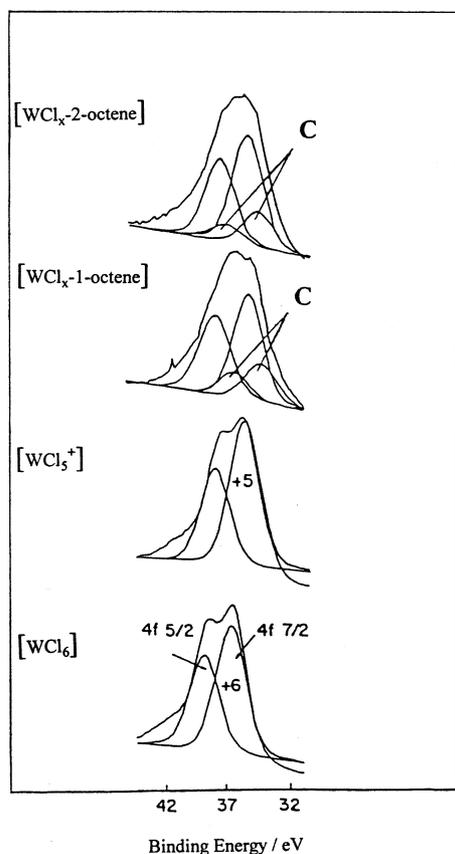
Fig. 2. W4f region of the XPS spectrum of WCl_6, reduced or pulsed WCl_6 and two olefin complexes. The extra peaks denoted by C correspond to W–olefin adduct.

starts; where olefin/$WCl_6 = 0.1$). The binding energies of the $4f_{7/2}$ and $4f_{5/2}$ of WCl_6 electrons (36.6 and 38.7 eV) are in good agreement with the literature values (36.4 and 38.5 eV) [25]. The binding energies of the $4f_{7/2}$ and $4f_{5/2}$ electrons of a compound obtained after the reductive electrolysis however shifted to lower values by about 0.5 eV. For the olefin adduct, these energies are shifted toward even lower values by about 1.4 eV (shown in the figure by C), which shows that the electron density is altered significantly upon incorporation of an olefin into the structure of the tungsten complex.

The absence of the carbene type peaks [26,27] in the ^{1}H-NMR and ^{13}C-NMR spectra obtained from the solution of olefin adduct indicates that the initial olefin adduct is likely a metal–olefin complex.

The solution obtained after the electrolysis of WCl_6 is not active in initiating the metathesis reaction. Upon further addition of olefin to the solution containing the olefin adduct of the electrolyzed tungsten complex, the metathetic activity starts. (The olefin adduct can be kept under nitrogen atmosphere after the solvent is evaporated and is active even after a week when redissolved in dichloromethane).

The primary metathesis product obtained from 1-octene is 7-tetradecene and that from 2-octene is 6-dodecene (other products, ethylene and 2-butene, respectively, are vented off the vessel during the reaction). The metathetic activity obtained with the electrolysis solution leads to the formation of these products which

underlines the high specificity of the reaction. Furthermore the yield of the formation of these products increases significantly if the initial electrolysis is carried out with the application of a pulse instead of a constant potential. For 2-octene the final yield of 6-dodecene was 92.7% in pulse electrolysis experiment while the final yield in constant cathodic potential electrolysis was 62.5% (Products yield: $2n_{product}/[n_{olefin}]_o \times 100$; the ratio of Olefin/Catal. = 80; reaction time 3 h at room temperature). It should also be noted that a much less amount of catalyst is needed with electrolyzed solutions when compared with photochemical systems [20], wherein no co-catalyst is required.

In another experiment, an in situ reductive electrolysis of WCl_6–olefin mixture was carried out. Fig. 3A shows the product distribution obtained after such an electrolysis with 1-octene which is initially present in the WCl_6 solution. The chromatogram shown in Fig. 3B is the one obtained after 1-octene is added to the solution after WCl_6 was electrolyzed. Comparison of the two product distributions clearly indicates that the addition of olefin to the solution after electrolysis is more advantageous. The loss of the specificity in the in situ electrolysis is probably due to the further reduction of the intermediates formed between the initial electrolysis product of WCl_6 and the olefin present in solution.

3. Conclusion

In this electrochemical system, the mechanism proposed in Eq. (10) involving the addition of WCl_5^+ to the alkene followed by 1,2 hydride shift for the first metal–carbene formation is in good agreement with the experimental results. It can be concluded that the catalyst system which is electrochemically generated from WCl_6 solution in dichloromethane acts with higher specificity and is more efficient. The efficiency of the catalyst system is remarkably increased when generated using pulse electrolysis.

4. Experimental details

4.1. Reagents

Olefins were purchased from Aldrich, stored over KOH and then distilled over CaH_2 under nitrogen atmosphere. WCl_6 was purified by sublimation of the more volatile impurities (WO_2Cl_2 and $WClO_4$) under nitrogen at about 200 °C and kept under nitrogen atmosphere [5]. Methylene chloride was washed with concentrated sulfuric acid, then with aqueous carbonate solution and water, followed by drying over calcium chloride [16]. It was then distilled over P_2O_5 under nitrogen, kept under nitrogen.

4.2. Electrochemical procedure and apparatus

The electrochemical measurements were carried out under nitrogen atmosphere in a three-electrode cell having a jacket through which water from a constant temperature bath was circulated. A polished Pt disc electrode with a diameter of 0.10 cm, inlaid in a glass capillary of 0.80 cm, was used in cyclic voltammetric experiments as a working electrode. The counter electrode was a Pt wire (2 cm^2) immersed in CH_2Cl_2/0.1 M $TBABF_4$ separated from the electrolysis solution by a sintered glass disc. The reference electrode consisted of AgCl coated on a Ag wire in CH_2Cl_2/0.1 M $TBABF_4$
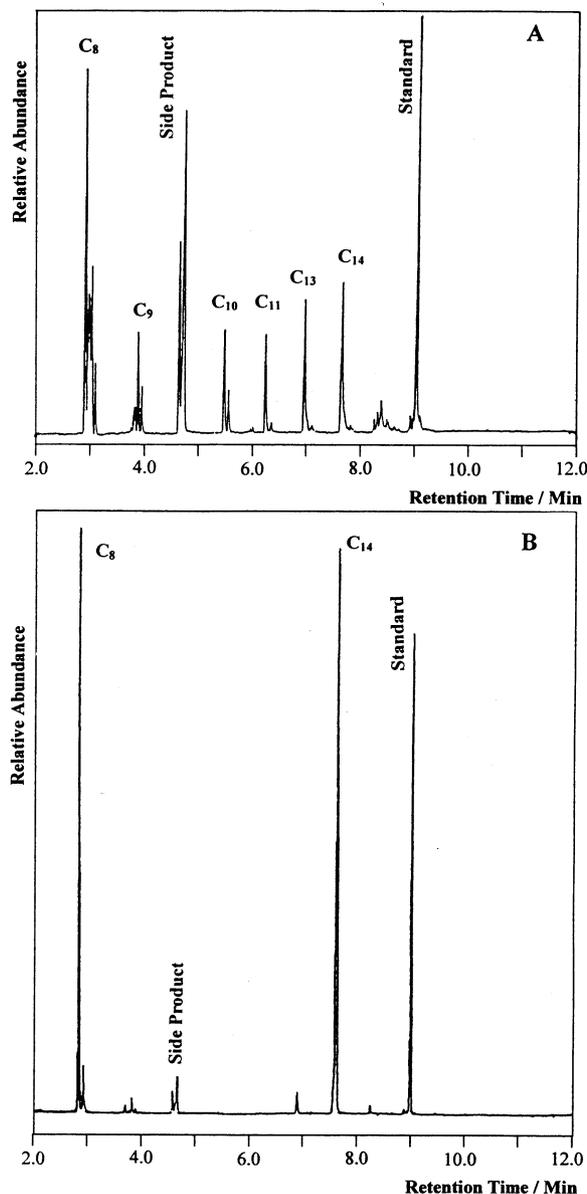
Fig. 3. Gas chromatograms of the solution taken after the solution of (A) WCl_6–olefin mixture is reductively electrolyzed, (B) WCl_6 is reductively electrolyzed and excess olefin is added following electrolysis.

which was also separated from the electrolysis solution by a sintered glass disc.

Exhaustive controlled potential and pulse electrolysis experiments were carried out in an undivided cell with a macro working Pt foil electrode (2.0 cm^2) and a Al foil (2.0 cm^2) counter electrode. Macro electrolysis was carried out without supporting electrolyte due to its deleterious effect on the catalyst system. For this reason the distance between Pt working and Al counter electrode was kept constant and as small as possible (i.e. 2.0 mm) in order to keep the solution resistance at minimum. The electrodes were introduced into the deep red solution (10^{-2} M WCl$_6$ in CH$_2$Cl$_2$) and electrolysis was conducted for 3 h in all reductive, oxidative and pulse experiments. The colour of the resulting solutions was darkened after each electrolysis. An aliquot from this solution was added to the certain amount of olefin along with internal standard (hexadecane) under nitrogen flow. The reactions were then followed by GC–MS.

4.3. Analysis

Electrochemical instrumentation consisted of EGG-PAR Model 273 coupled with a PAR Model Universal Programmer. Current voltage curves were recorded on a Model SE-790 BBC Goerzt Metra-Watt X-Y recorder.

Analysis of the products was performed on a Hewlett Packard Model 5890 GC which was connected to Model 5971 MSD analyser. Separations were performed on 25 mm × 30 m glass capillary columns supported with DB-5 polysiloxane.

ESR measurements were obtained with a VARIAN E-L9 X-band ESR spectrometer with a 100 kHz modulation at room temperature.

NMR spectra were obtained with BRUKER GmbH DPX-400, 400 MHz High Performance Digital FT-NMR Spectrometer.

A KRATOS ES 300 photoelectron spectrometer with Mgkalfa X-rays was used for ESCA.

Acknowledgements

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