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Cyclovoltammetric studies on the dimerization of methyl acrylate by ruthenium complexes

Claudia Strehblow, Thomas Schupp, Reiner Sustmann *

Institut für Organische Chemie der Universität Essen, D-45117 Essen, Germany

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Abstract

Electrochemical measurements are described on transition metal complexes which are or might be catalyst precursors for the tail-to-tail dimerization of methyl acrylate (MA). Thus, $RuH_2(PPh_3)_4$ and $RuHCl(CO)(PPh_3)_3$ are studied electrochemically by cyclic voltammetry (CV) in various solvents including neat MA. It is shown that the activation of the catalyst precursor $RuH_2(PPh_3)_4$ with trifluoromethanesulfonic acid and of $RuHCl(CO)(PPh_3)_3$ with triethyloxonium tetrafluoroborate generates new complexes that are easy to reduce and rather difficult to oxidize. The electrochemical measurements provide information on the deactivation of the catalyst. $CpRuH(PPH_3)_2$, which can easily be oxidized but can not be reduced, even at -2.5 V versus SCE, does not act as a catalyst precursor neither in pure form nor in the presence of activating compounds. The ease of reduction or oxidation seems to be connected to a possible catalytic activity. It is, therefore, postulated that cyclic voltammetry can be a useful tool in the study of homogeneous transition metal catalysis. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Ruthenium; Cyclovoltammetry; Dimerization

1. Introduction

Methyl acrylate (MA) can be dimerized by a number of transition metal complexes as catalyst precursors, e.g. palladium [1], nickel [2], rhodium [3,4] and ruthenium [5,6], yielding mainly the linear tail-to-tail dimer *trans*-Δ^2-hexene-1,6-dioicacid dimethylester (HDM). Several investigations on the mechanism of the dimerization have been published. Oehme ([1]a) studied the mechanism of the palladium-catalyzed dimerization of MA by deuterium labelling and by the analysis of the thermal decomposition products of model complexes. A key step in the proposed catalytic cycle is an oxidative addition of a π-coordinated MA to a hydrido-(β-methoxycarbonyl)vinyl palladium complex. The latter is supposed to insert MA into the metal–hydride bond. Wilke [2] studied the catalytic dimerization of MA in the presence of η^3-allyltrimethylphosphane-nickel tetrafluoroborate at 0°C. An essential feature of this process is assumed to be a metal–hydride bond into which MA is inserted. The most effective catalytic system so far, (η^5-1,2,3-trimethylindenyl)-bis(ethene)-rhodium in the presence of a proton source, was developed by Brookhart [3]. Prior to our own studies on the dimerization of MA [4–6] with ruthenium-based catalysts, this metal had been used by McKinney for this purpose [7]. The catalyst was generated in situ by reduction of ruthenium trichloride with zinc. Mechanistic studies were not reported.

Amatore et al. [8] have shown that the combination of electrochemical techniques with NMR spectroscopic methods can lead to information about individual elementary steps in transition metal-catalyzed reactions. Prior to the present studies we reported that the dihydrido complex $RuH_2(PPh_3)_4$ (**1**) produces $Ru(0)(MA)_2(PPh_3)_2$ (**2**) on dissolving in MA. Complex **2** was isolated and the structure of a water adduct was determined by X-ray crystallography [9]. Electrochemi-

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* Corresponding author. Tel.: +49 201 1833097.

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cal studies on this reaction reported in the preceding contribution [10] revealed that MA undergoes oxidative addition to Ru(0) via cleavage of a vinylic C–H bond, a fact that could not be taken into account in the original formulation of the catalytic cycle of the dimerization of MA ([5]a) as it became evident only by the electrochemical measurements.

Here we describe cyclovoltammetric experiments on the dimerization of methyl acrylate using ruthenium-based catalytic systems developed in our laboratory [4–6]. According to these processes, MA is dimerized to miscellaneous C-6 units yielding *trans*-Δ^2-HDM as a main product (90%) in the presence of $RuH_2(PPh_3)_4$ and CF_3SO_3H as activating acid ([5]a). Turn over numbers (TON) range from 200 to 600 at ca. 80°C. By CV experiments we investigate the role of the activating acid CF_3SO_3H, which is necessary to initiate the catalytic cycle. Electrochemical studies are reported for a second catalytic system, $RuHCl(CO)(PPh_3)_3$ (**3**)/Et_3OBF_4 (TON: 50–150), where the oxonium salt abstracts a chloride ion from the complex yielding a free coordination site. The influence of the oxonium salt on the electrochemical behavior of the catalyst precursor bearing chloride as a ligand is studied. Electrochemical studies are further carried out on $Ru(CH_2CH_2CO_2Me)(CO)Cl(PPh_3)_2$ (**4**), the complex which is the insertion product of MA into the ruthenium–hydride bond of **3** [11] and which can be activated by Et_3OBF_4, to produce dimers of MA [6]. The catalytically inactive complex $CpRuH(PPh_3)_2$ (**5**) [6] is included in our study in order to correlate its electrochemical behavior with its catalytic potential with respect to the dimerization of MA.

2. Experimental

2.1. Instrumentation

^1H-, $^1H\{^{31}P\}$-, ^{31}P- and ^{13}C-NMR spectra were recorded on a Bruker AMX 300 spectrometer. ^{31}P-NMR spectra chemical shifts were referenced against external 85% H_3PO_4. IR spectra were recorded on a Perkin-Elmer FT-IR 1600.

2.2. Electrochemical experiments

Cyclic voltammetry was performed on a modified polarograph E 310 (Bruker). Data aquisition was realized by a PC with the software package DigiS (GfS, Aachen) [12]. A platinum button was used as the working electrode, a platinum foil as auxiliary electrode. Apart from three electrodes, the electrochemical cell (Metrohm) was equipped with an argon inlet tube, a bypass tube and was filled with 15 ml solvent. CVs with scan rates $> 1\ V\ s^{-1}$ were obtained with platinum disc electrodes (0.5 mm–10 μm diameter). In this case, a five-necked flask was used as the electrochemical cell, which contained 5 ml of solvent. All potentials were measured against a saturated calomel electrode (Metrohm) using ferrocene as an internal standard [13]. The concentration of the supporting electrolyte tetrabutylammonium hexafluorophosphate (Merck) was 0.1 M. The concentration of the complex was 1×10^{-3} M if not indicated otherwise. The reported potentials are taken from measurements with a scan rate of 100 $mV\ s^{-1}$ if not indicated otherwise.

2.3. Materials

All solvents were thoroughly degassed, dried over sodium (toluene, methanol and *n*-hexane), over CaH_2 (MA), and distilled. Tetrabutylammonium hexafluorophosphate used as the supporting electrolyte in the cyclovoltammetric studies was obtained from Merck, used as-supplied by the manufacturer, and kept under dry argon.

2.4. Preparation of metal complexes

$Ru(0)(MA)_2(PPh_3)_2$ [9], $RuH_2(PPh_3)_4$ [14], $RuHCl(CO)(PPh_3)_3$ [15], $Ru(CH_2CH_2CO_2Me)(CO)Cl(PPh_3)_2$ [11], and $CpRuH(PPh_3)_2$ [16] were prepared according to literature procedures.

2.5. Dimerization of MA

All experiments were carried out four times in order to secure reproducibility. Products were identified by comparison with authentic samples. $4\text{-}HOC_6H_4OCH_3$ was added as inhibitor to prevent free radical polymerization. Details on the dimerization of MA in the presence of $RuH_2(PPh_3)_4/CF_3SO_3H$ have been described before [5].

2.5.1. $RuHCl(CO)(PPh_3)_3$/four eqvivalents Et_3OBF_4

A solution of 39.9 mg (0.21 mmol) Et_3OBF_4, 47.6 mg (0.05 mmol) **3** and 3.3 mg (0.03 mmol) $4\text{-}HOC_6H_4OCH_3$ in 1.93 g (22.4 mmol) MA was heated to 80°C for 48 h. GLC analysis: 85.2% *trans*-Δ^2-HDM, 4.3% *trans*-Δ^3-HDM, 1.9% *cis*-Δ^3-HDM, 1.8% *cis*-Δ^2-HDM, 5.3% 4-methyl-Δ^2-pentene-1,5-dioicacid dimethylester, 1.8% *cis*-Δ^2-hexene-1,6-dioicacid dimethylester, and 0.3% muconicacid dimethylester. TON: 46.

2.5.2. $Ru(CH_2CH_2CO_2Me)(CO)Cl(PPh_3)_2$/three equivalents Et_3OBF_4

A solution of 30.6 mg (0.16 mmol) Et_3OBF_4, 40.1 mg (0.05 mmol) **4**, and 4.0 mg (0.03 mmol) $4\text{-}HOC_6H_4OCH_3$ in 1.93 9 (22.4 mmol) MA was heated to 90°C for 24 h. GLC analysis: 81.4% *trans*-Δ^2-HDM, 3.7% *trans*-Δ^3-HDM, 2.2% *cis*-Δ^3-HDM, 3.1% *cis*-Δ^2-

HDM, 5.9% Δ^2-4-methyl-pentene-1,5-dioicacid dimethylester, 3.0% 2-methylene-pentanedioicacid dimethylester, 0.7% muconicacid dimethylester. TON: 90.

2.5.3. *TONs as a function of activation after predetermined time intervals*

Solutions of the catalyst precursor **1** and 4-$HOC_6H_4OCH_3$ as inhibitor in MA were prepared according to the following example and activated by CF_3SO_3H after the indicated time intervals. TONs for the dimers of methylacrylate were determined by GLC. Example: 0.12 mmol **1** and 0.14 mmol 4-$HOC_6H_4OCH_3$ were dissolved in 112 mmol (933 equivalents) of MA. After 1 h, 0.384 mmol (3.2 equivalents) of CF_3SO_3H were added and the solution was heated to 80°C for 72 h. All operations were carried out in argon atmosphere. The following TONs, given in brackets, were obtained when the solutions were activated after (h): 0.5 (406), 1.0 (418), 3.0 (402), 5.0 (411), 7.0 (409), 24 (401), 72 (411).

2.5.4. *Experiments with $CpRuH(PPh_3)_2$ (**5**)*

Complex **5** (0.05 mmol) and 2–5 mg 4-$HOC_6H_4OCH_3$ as inhibitor were dissolved in 2.0 ml MA and heated to 90°C. No dimers had been formed after several hours. A similar experiment in the presence of four equivalents CF_3SO_3H provided identical results.

A solution of 0.074 mmol of **5** in 1.0 ml THF showed the Ru–H vibration in the IR at 1950 cm^{-1}. MA (1.10 mmol) was added and the spectrum again recorded after 24 h. The intensity of the Ru–H vibration had not changed. The CO-vibration (1734 cm^{-1}), however, appeared in emission when the spectrum of a solution of 1.10 mmol MA in 1.0 ml THF was subtracted. This indicates coordination of MA to ruthenium. At the same time 0.07 mmol (0.95 equivalents) of free triphenylphosphane could be detected in solution by GLC. Electrochemical studies revealed that one equivalent of triphenylphosphane dissociates from $CpRuH(PPh_3)_2$ on dissolving in MA. This was determined from the current density of the oxidation of the complex compared with that of liberated triphenylphosphane. An exchange of one phosphane ligand against one molecule of MA has taken place.

3. Results

3.1. *CV studies on $RuH_2(PPh_3)_4$ (**1**) in the presence of CF_3SO_3H*

In the preceding contribution, the electrochemical behavior of **1** in MA was studied. It was found that MA undergoes an oxidative addition to **1**, producing a ruthenium–hydride complex (**6**) which further inserts a molecule of MA into the ruthenium–hydride bond (**7**). Fig. 1 shows the CV of a solution of $RuH_2(PPh_3)_4$ (**1**) (0.01 M) in MA 1 min after dissolving the complex (trace 1). The first oxidation process (O^1) at 0.85 V had been assigned to the oxidation of **6**, O^2 as due to the oxidation of **7**, and O^{TPP} as corresponding to the oxidation of two equivalents of triphenylphosphane liberated on dissolving **1** [10]. Trace 2 in Fig. 1(a) shows the CV after the addition of 3.2 equivalents CF_3SO_3H to the solution that produced trace 1, conditions which had proved to be optimal for the dimerization of MA. The sulfonic acid itself displays no electrochemical activity in the accessible potential range of −2.5 to +2.0 V versus SCE. Thus, the redox activities in the voltammogram of the activated catalyst precursor must result from ruthenium complexes or products derived from them. After the addition of the activating acid, the current density of O^1 decreases. The oxidation of free triphenylphosphane O^{TPP} can no longer be observed. This is in agreement with the fact that triphenylphosphane adds to MA under these conditions and produces a phosphonium salt with CF_3SO_3H that had been isolated and characterized ([5]a). The latter is not electroactive within the potential window of Fig. 1. The oxidation peak O^1 disappears completely within a few minutes after the activation in favor of the new peak O^3. The current density of O^3, i.e. the concentration of the new species, then corresponds to the initial current density of O^1 showing complete conversion of **6** and **7** to a new complex. Scan rate-dependent measurements reveal that O^2 is irreversible up to 10 V s^{-1}. O^3 is irreversible at 100 mV s^{-1}, it becomes quasi-reversible at scan rates >100 mV s^{-1}, and reversible at scan rates >500 mV s^{-1}.

In the reductive potential range of the activated solution (Fig. 1(b)) two barely separated reduction pro-

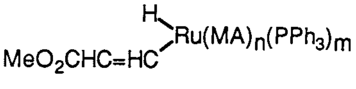
$RuH_2(PPh_3)_4$ **1**

$Ru(MA)_2(PPh_3)_2$ **2**

$RuHCl(CO)(PPh_3)_3$ **3**

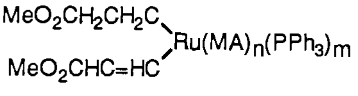
$Ru(CH_2CH_2CO_2Me)(CO)Cl(PPh_3)_2$ **4**

$CpRuH(PPh_3)_2$ **5**



$$(H)(MeO_2CHC{=}HC)Ru(MA)_n(PPh_3)_m$$

6



$$(MeO_2CH_2CH_2C)(MeO_2CHC{=}HC)Ru(MA)_n(PPh_3)_m$$

7

cesses appear at ca. −0.5 V with a total current density that corresponds to the initial current density of O^1. Scan rate-dependent measurements at a scan rate of $>1\ V\,s^{-1}$ reveal only one reduction process that is quasi-reversible up to $10\ V\,s^{-1}$. The reversibility increases with higher scan rates. We interpret the reduction as an electron transfer with a chemical follow up reaction.

In a further experiment, the activation of **1** ($c = 0.001$ M) in MA was carried out with only 1.5 equivalents of CF_3SO_3H (Fig. 2). Under these conditions complexes **2** (O^0) and **6** (O^1) can be identified besides the activated complex (O^3). Apparently this amount of acid does not completely convert complexes **2** and **6** to the species oxidized at 1.2 V and reduced at −0.5 V. As the voltammogram was not recorded up to the potential where **7** is oxidized its possible presence can not be seen in the voltammogram. Due to the smaller absolute concentration of the catalyst precursor as compared with the conditions where Fig. 1 had been recorded the oxidation peaks O^0 and O^1 can be separated. O^0 disappears in favor of O^1.

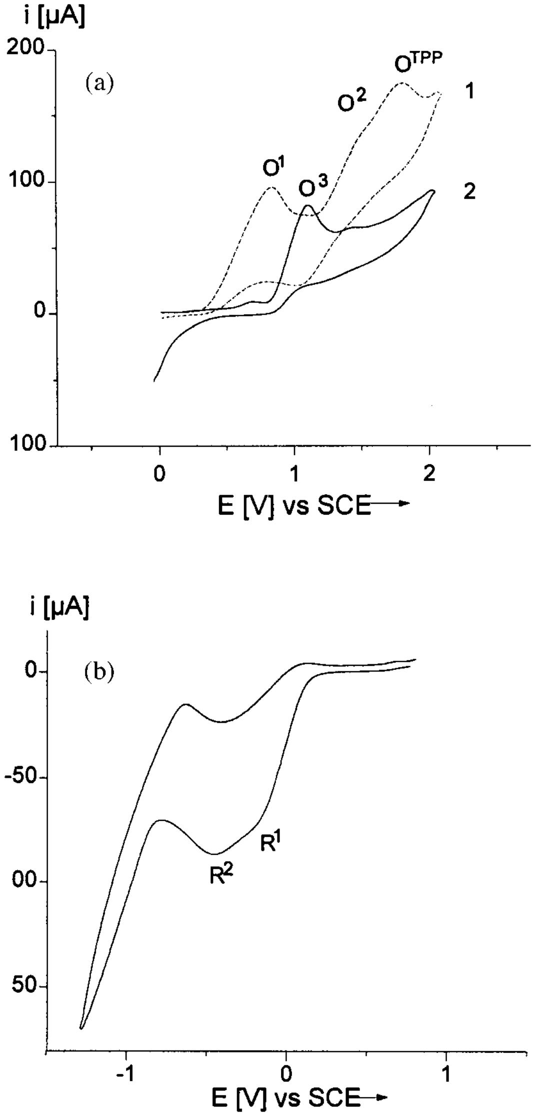


Fig. 1. CV of $RuH_2(PPh_3)_4$ in MA, 1 min after dissolving the complex (trace 1) and after addition of 3.2 equivalents of CF_3SO_3H (trace 2) (a); reductive potential range (b).

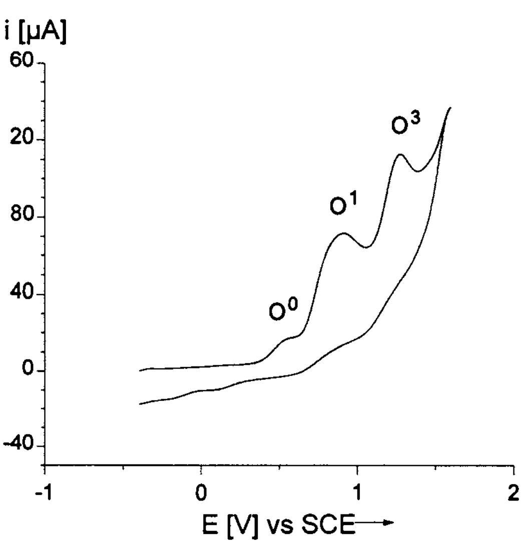


Fig. 2. CV of $RuH_2(PPh_3)_4$ ($c = 0.001$ M) in MA in the presence of 1.5 equivalents of CF_3SO_3H.

The catalytic dimerization of MA in the presence of $RuH_2(PPh_3)_4/CF_3SO_3H$ depends on temperature. Highest conversions are reached at ca. 80°C. Fig. 3 displays temperature-dependent voltammograms of the system $RuH_2(PPh_3)_4$ (0.01 M)/3.2 equivalents CF_3SO_3H in MA. These were recorded at a scan rate of $1.0\ V\,s^{-1}$ because high temperature causes bubbles at the electrode that lead to CVs of bad quality at a scan rate of 100 mV. The CV recorded at 20°C shows the oxidation of the ruthenium complex that is formed after the activation with CF_3SO_3H (O^3) and that of the product of insertion of MA into the Ru–H bond of **3**, namely **7**

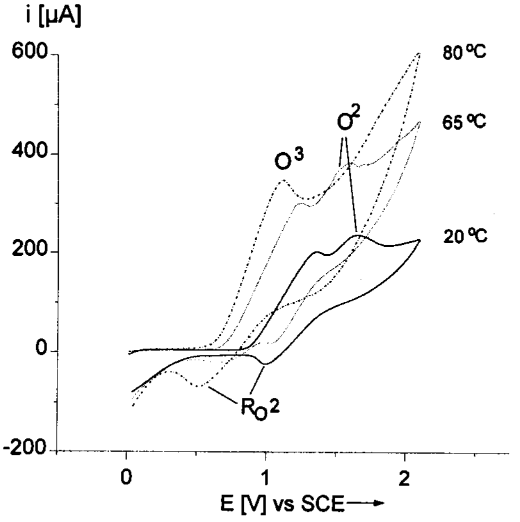


Fig. 3. Temperature-dependent CVs of $RuH_2(PPh_3)_4$ in MA in the presence of 3.2 equivalents of CF_3SO_3H.

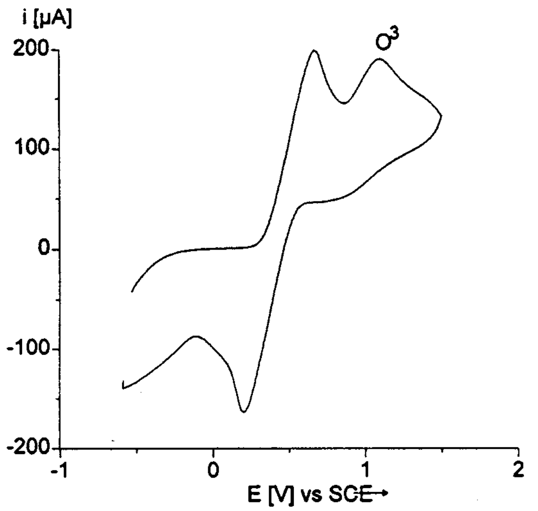


Fig. 4. CV of $RuH_2(PPh_3)_4$ in MA in the presence of 3.2 equivalents of CF_3SO_3H after heating to 80°C for 18 h.

(O^2) with a low current density. The process O^2 is reversible at a scan rate of 1.0 V s^{-1}. With increasing temperature the potential of the saturated calomel electrode shifts to lower values and the current density increases, which is in accordance with general electrochemical laws [17] and is not due to a change of the concentration of the activated catalyst precursor. The voltammogram obtained at 80°C differs from the CV obtained at lower temperatures. The oxidation of **7** can no longer be seen.

Shortly after heating the activated complex to 80°C, the solution was again cooled to r.t. At a scan rate of 1.0 V s^{-1} only the activated complex is identified in a quasi-reversible CV. If this solution is again heated to 80°C, kept at this tempeature for 18 h and cooled to r.t., the voltammogram shown in Fig. 4 is measured. The activated complex is present only in small concentration. Instead, the major wave describes a reversible process at $E_{1/2} = 0.5$ V. It should be noted that generally the catalytic activity has decreased after 18 h at 80°C ([5]a). Therefore, the main wave must represent a catalytic non-active ruthenium complex. On further heating to 80°C for 4 h, the reversible wave at 0.5 V is recorded only at r.t. It will be demonstrated that such redox potentials are typical for catalytically non-active complexes (see below).

Experiments were carried out in order to study the influence of the time-lag between dissolving **1** in MA and the activation with CF_3SO_3H on the catalytic activity. Thus, we determined the maximum TON of solutions of **1** in MA that were activated after 0.5, 1, 5, 24 and 72 h. These experiments always led to the same overall TONs. Thus, the point of time of activation has no influence on the TONs. In view of the mechanistic interpretation of our results this is of importance. An electrochemical experiment of similar nature was carried out. A solution of **1** in MA showed after 12 h only a wave for complex **7** (trace 1 in Fig. 5). If this solution is activated with 3.2 equivalents of CF_3SO_3H, **7** disappears immediately in favor of the activated complex (trace 2). It is therefore postulated, that the main pathway of generating a catalytically active species proceeds via complex **7**, which in turn is formed from **1** via the intermediate complexes **2** and **6**.

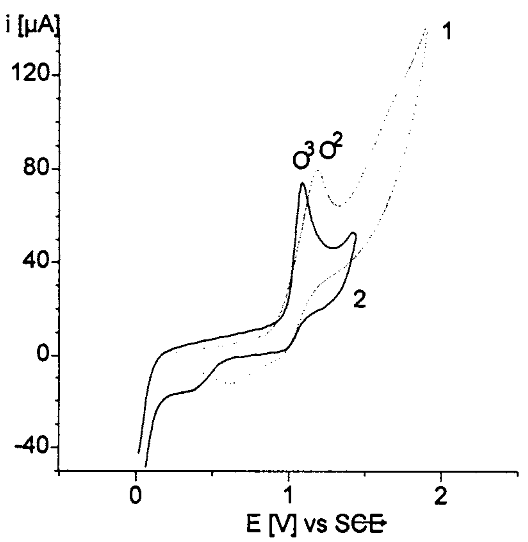


Fig. 5. CV of $RuH_2(PPh_3)_4$ in MA after a reaction time of 12 h (trace 1) and after subsequent additions of 3.2 equivalents of CF_3SO_3H.

3.2. CV studies on the system $BuH_2(PPh_3)_4/CF_3SO_3H$ after termination of the catalysis

The electrochemical behavior of the catalytic system $RuH_2(PPh_3)_4/CF_3SO_3H$ was studied after having reached the maximum TON. Fig. 6 displays the CV of a solution at r.t. that had been activated and heated to 80°C for 24 h. The current density of the quasi-re-

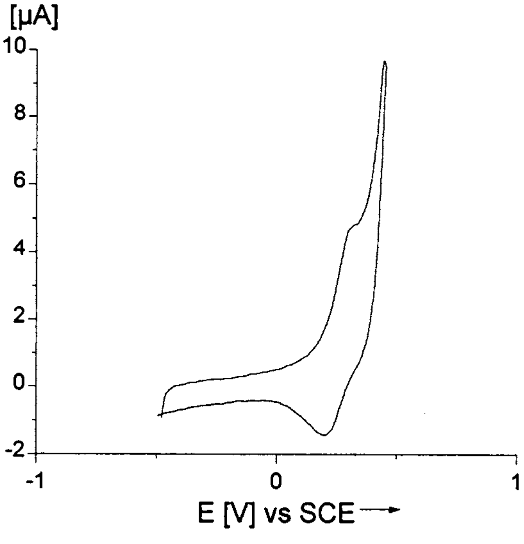


Fig. 6. CV of $RuH_2(PPh_3)_4$ and 3.2 equivalents of CF_3SO_3H in MA after heating to 80°C for 24 h.

versible process after activation with CF_3SO_3H has decreased enormously compared with the initial concentration of the catalyst precursor. No other redox processes can be seen. Thus, the concentration of ruthenium complexes that are left in solution seems to be very low. No reduction processes can be observed in this voltammogram either. We assume that the remainders of ruthenium complexes that showed redoxactivites in the freshly activated solution ($RuH_2(PPh_3)_4$ with 3.2 equivalents CF_3SO_3H) before heating to 80°C are no longer dissolved. Indeed, the preparative experiments proved that the solutions were heterogeneous after the termination of the catalysis. The complex that remains in solution in low concentration shows a reversible oxidation at a low potential (Fig. 6). The CV is identical to that of the experiment where the catalytic solution had been heated to 80°C for 18 h and cooled to r.t. (see Fig. 4 above). This result was interpreted as demonstrating the generation of a complex that is no longer catalytically active in the dimerization of MA.

The low current density at the end of the catalysis is due to traces of oxygen that penetrated the reaction vessel and led to nonsoluble ruthenium complexes. The higher current density in Fig. 5 must be due to the fact that the electrolysis cell was purged permanently with argon during 18 h, thus excluding oxygen completely. Intentional contamination of a catalytic solution with traces of oxygen shows a decrease in the maximum TON. A voltammogram of such a contaminated solution displays an enormous decrease in the current density.

3.3. Influence of an excess CF_3SO_3H (ten equivalents)

It had been found that the addition of more than 3.2 equivalents CF_3SO_3H to the catalyst precursor **1** influences the catalytic activity in a negative way. Therefore, we investigated the electrochemical behavior of an 'overactivated' catalytic system. In the CV after the addition of ten equivalents CF_3SO_3H we observe an irreversible oxidation wave at 1.1 V with a very low (10 μA) current density.

This is not the same result as for the catalytic system after the addition of 3.2 equivalents of activating acid (Fig. 1). Our interpretation is that only a very small concentration of the activated complex is left in solution (O^3 in Fig. 1(a)). Other electrochemically active complexes can not be discovered.

3.4. CV studies on $RuHCl(CO)(PPh_3)_3$ (3) and $Ru(CH_2CH_2CO_2Me)(CO)Cl(PPh_3)_2$ (4)

The catalyst precursor **3** which dimerizes MA in the presence of Et_3OBF_4 dissolves slowly in MA and inserts MA into the Ru–H bond with the loss of one phosphane, yielding **4**. A voltammogram of $RuHCl(CO)(PPh_3)_3$ in MA is displayed in Fig. 7 (trace 1). Two irreversible oxidation steps O^4 and O^5 are observed. O^4 at 0.62 V with a small current density that disappears within 15 min is assigned to the oxidation of the hydrido complex **3**. This could be confirmed by a measurement in dimethyl formamide where **3** is stable. Only one irreversible oxidation wave at 0.6 V is observed. The process O^5 can be attributed to the oxidation of the insertion complex $Ru(CH_2CH_2CO_2Me)(CO)Cl(PPh_3)_2$ (**4**), because a voltammogram of isolated **4** in MA shows the same oxidation peak.

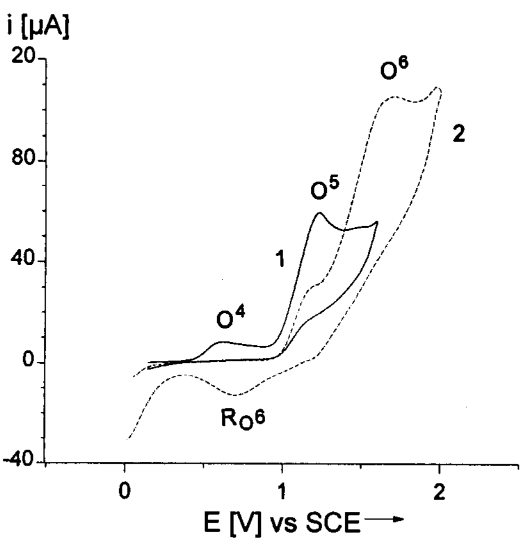


Fig. 7. CV of $RuHCl(CO)(PPh_3)_3$ in MA (trace 1) and CV of the solution after activation with Et_3BF_4 (trace 2) (oxidative part).

A voltammogram of $RuHCl(CO)(PPh_3)_3$ (**3**) in MA shows no reduction peak in the negative potential range. The current density increases at potentials of < -1 V, however. If the potential range is extended to more negative values the current density increases enormously, indicating an electrocatalytic step at potentials < -1 V. Therefore, it is not possible to decide whether there is a reduction step at low potentials (< -1 V). The reductive part of the voltammogram of isolated $Ru(CH_2CH_2CO_2Me)(CO)Cl(PPh_3)_2$ (**4**) shows an irreversible reduction wave at -0.88 V that is a reduction of the dissolved complex and no follow up reduction of an oxidized complex. Although in a solution of dissolved **3** a large portion of the complex has already been converted to **4**, its reduction can not be seen in the CV due to the electrocatalytic reaction. Thus, the reduction behavior of the insertion complex **4** is different from that of 3.

The activation of $RuHCl(CO)(PPh_3)_3$ or of $Ru(CH_2CH_2CO_2Me)(CO)Cl(PPh_3)_2$ with Et_3OBF_4 leads to identical results. Trace 2 in Fig. 7 shows a CV shortly after activating **4** with Et_3OBF_4. The oxidation of **4** is still visible, disappears, however, within 35 min. There is an oxidation wave at 1.5 V (O^6) that is assigned to a complex which is produced on addition of the oxonium salt. This complex is more difficult to oxidize than either **3** or **4**. The current density of O^6 is ca. 15 μA higher than in the activated solution of **3**.Fig. 8 displays voltammograms of $RuHCl(CO)(PPh_3)_3$ and of $Ru(CH_2CH_2CO_2Me)(CO)Cl(PPh_3)_2$ after the activation with oxonium salt starting at ca. 0.5 V. The addition of Et_3OBF_4 either to 3 or 4 leads to an easily reducible complex ($E^{red} = -0.13$ V).

3.5. CV studies on $CpRuH(PPh_3)_2$ (5)

It was found that **5** has no catalytic acitvity in the dimerization of MA, neither when heating the complex in MA nor after the addition of either trifluoromethanesulfonic acid or triethyloxonium tetrafluoroborate. We studied the electrochemical behavior of **5** in MA. The CVs obtained when using the olefin as the solvent were in good agreement with the results of Tilset [18] in tetrahydrofurane. We found no reduction down to −2.5 V, however a reversible one-electron oxidation at 0.22 V, and an irreversible oxidation at 0.77 V. Furthermore, the oxidation of liberated phosphane appeared at 1.45 V in MA. Quantitative GC investigations revealed the liberation of 0.95 equivalents triphenylphosphane. We further subtracted the IR spectrum of neat MA from that of **5** in MA. In the difference spectrum we observe a Ru–H vibration at 1950 cm^{-1}, and an inverse stretching of the MA carbonyl group. Presumably, one liberated phosphane has been replaced by x-coordinated MA on dissolving **5** in MA, thus leading to a reduction of the concentration of MA. No insertion of MA into the Ru–H bond takes place.

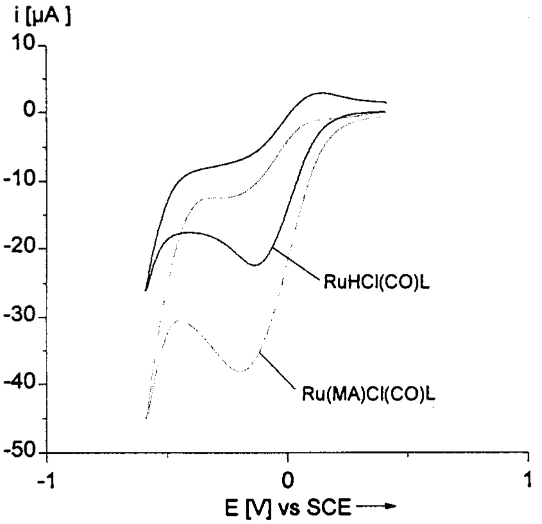


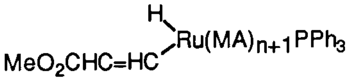
Fig. 8. CVs of $RuHCl(CO)(PPh_3)_3$ and of $Ru(CH_2CH_2CO_2Me)(CO)Cl(PPh_3)_2$ in MA after activation with Et_3OBF_4 (reductive part).

4. Discussion

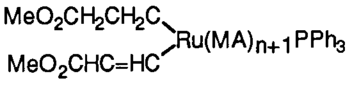
The investigation of the mechanisms of transition metal-catalyzed reactions is difficult because the active species are often generated in situ from precatalysts, constitute in many cases labile complexes, and are normally present in low concentration. In many cases, indirect methods have to be applied to establish catalytic cycles. However, there remains a deficit which complements spectroscopic methods like NMR or IR spectroscopy. Electrochemistry might be such a tool because the redox behavior of metals depends on their oxidation state and the ligands surrounding the metal center. In this investigation it has been shown that cyclic voltammetry can be used as such an analytical tool. Current density can be taken as a measure of concentration and the potentials at which complexes are reduced or oxidized yield information on the nature of the complexes in solution.

Which is the knowledge gained by our studies on the dimerization of methyl acrylate by ruthenium complexes? The preceding contribution confirmed our earlier finding based on the isolation of **2** that two equivalents of triphenylphosphane are liberated on dissolving **1** in MA. The CV studies revealed further that a new complex, representing Ru(II), is generated by oxidative addition of MA which then reacts to a third complex. The latter is presumably the insertion complex **7** of MA into the Ru–H bond of **6**. As no further triphenylphosphane is liberated during these transformations, the complexes **6** and **7** should still be coordinated with two molecules of phosphane. No information is obtained as to the number of coordinated molecules of MA. In case of a 16-electron complex, it should be two molecules, possible is also an 18-electron complex with three π-coordinated molecules of MA.

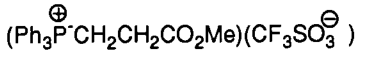
Addition of trifluoromethanesulfonic acid (3.2 equivalents) produces a complex that is more difficult to oxidize than either **2** or **3** but can be reduced easily. Earlier ([5]a) we had shown that three equivalents of the acid remove three molecules of phosphane. Thus, the catalytic active complex holds still one phosphane. If it is formed from **6** or **7**, the active species should be either **8** or **9** (Scheme 1) where one phosphane in **6** or **7** has been replaced by a molecule of MA. The experiments where the activation by CF_3SO_3H was carried out at a time when complexes **2** and **6** had disappeared almost completely in favor of **7** suggests that **9** rather than **8** describes the catalytic active species (however, see below). The activation by CF_3SO_3H then consists in removing a molecule of phosphane from **6** or **7** and transforming this phosphane together with the two molecules that were generated on formation of **2** from **1** to the phosphonium salt **10**.



8 n = 2 or 3



9 n = 2 or 3



$(\mathrm{Ph_3\overset{\oplus}{P}CH_2CH_2CO_2Me})(\mathrm{CF_3SO_3^{\ominus}})$

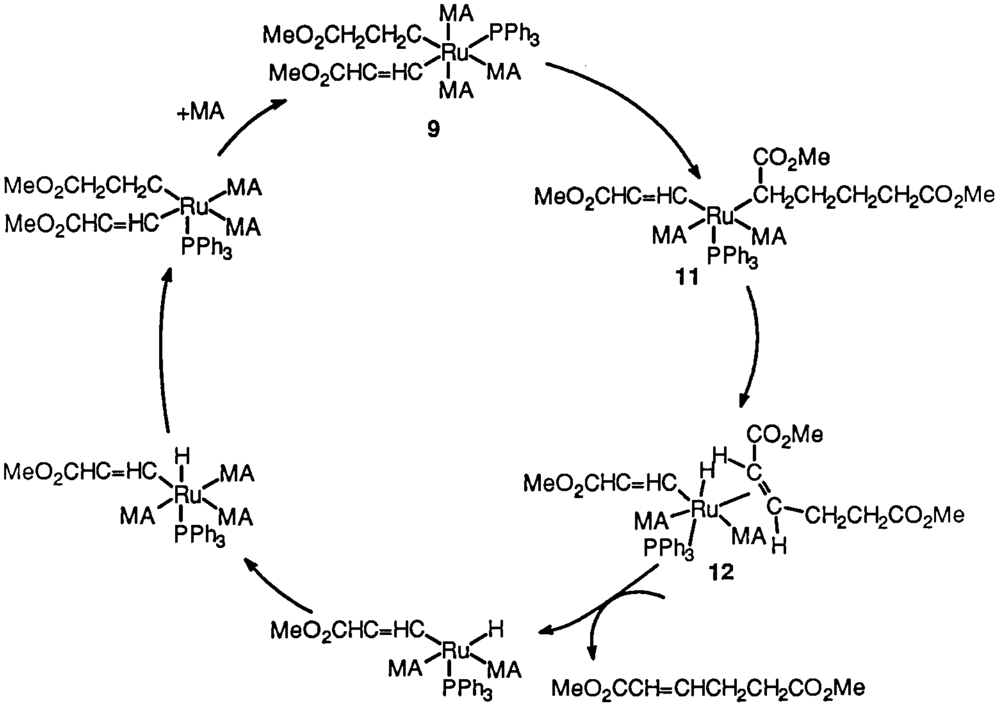
10

On the basis of these findings a plausible catalytic cycle can be written with **9** as starting point. In contrast to our earlier proposal, the sulfonic acid is not necessary to produce the catalytically active ruthenium(II)–hydride complex by protonation. The catalytic cycle includes both **8** and **9** as necessary intermediates.

How does the deactivation proceed? The electrochemical analysis of a 'dead' catalysis showed a low concentration of a complex which can be oxidized reversibly. No other redox processes can be observed. Thus, most of the ruthenium 'disappeared', i.e. was deposited as insoluble and, therefore, electrochemically inactive complexes. The nature of the complex in solution is not known, except that it should not contain phosphane because it had been shown earlier that free phosphane is present in a dead catalysis solution. Excess of CF_3SO_3H stops the catalytic dimerization.

Conclusions as to the requirement for a ruthenium(II) complex to be catalytically active in the dimerization of MA can also be drawn from the studies on **3** and **4**. It could be shown that **3** and **4** have different redox behavior. Insertion of MA into the Ru–H bond of **3** increases the oxidation potential from 0.8 to 1.2 V versus SCE. Both are irreversible processes under our conditions. Addition of triethyloxonium tatrafluoroborate leads to the formation of ethylchloride [6], thus producing a free coordination site for MA. This complex is easily reduced (−0.13 V versus SCE) and seems to be involved in the catalytic cycle. It is interesting to note that the catalytic active species produced from **6** and **7** is reducible at an almost identical potential (−0.5 V versus SCE). The quasi-reversible oxidation potential of the active complex, however, appears at a lower potential (+1.2 V versus SCE) than that for activated **6** or **7** (+1.5 V versus SCE).

Complex **5** looses one triphenylphosphane and adds one molecule of MA in neat MA. The Ru–H bond is



Scheme 1. Formation of **10** from either **8** or **9**.

unaffected. The CV of this complex shows a reversible one-electron oxidation at +0.22 V versus SCE, a potential that is similar to that obtained for the ruthenium complex in the dead catalysis when **2** had been the starting ruthenium complex.

5. Conclusion

Besides valuable information on the species formed in activated or not-activated MA solutions of **1**–**5**, the conclusion might be that a requirement for a catalytic active ruthenium(II) complex is an easy reduction at ca. −0.1 to −0.5 V versus SCE, which is irreversible. If this reduction is not present then the complexes are catalyically inactive. This phenomenon might be used as a heuristic criterion for the screening of ruthenium complexes to be used in studies on the dimerization of MA. Studies in this direction are in progress.

References

[1] (a) G. Oehme, H. Pracejus, J. Organomet. Chem. 320 (1987) C56. (b) I. Tkatchenko, D. Neibecker, P. Grenouillet, Organometallics 3 (1984) 1130.

[2] G. Wilke, Angew. Chem. 100 (1988) 189.

[3] (a) M. Brookhart, E. Hauptmann, J. Am. Chem. Soc. 114 (1992) 4437. (b) E. Hauptmann, S. Sabo-Etienne, P.S. White, M. Brookhart, J.M. Garner, P.J. Fagan, J.C. Calabrese, J. Am. Chem. Soc. 116 (1994) 8038.

[4] M. Bruckmann, Ph.D. Thesis, Universität Essen, Essen, Germany, 1992.

[5] (a) B. Patzke, R. Sustmann, J. Organomet. Chem. 480 (1994) 65. (b) R. Sustmann, H.J. Hornung, T. Schupp, B. Patzke, J. Mol. Catal. 85 (1993) 149.

[6] Th. Schupp, Ph.D. Thesis, Universität Essen, Essen, Germany, 1994.

[7] R.J. McKinney, M.C. Colton, Organometallics 5 (1986) 1752.

[8] (a) C. Amatore, M. Azzabi, A. Jutand, J. Am. Chem. Soc. 113 (1991) 1670. (b) C. Amatore, M. Azzabi, A. Jutand, J. Am. Chem. Soc. 113 (1991) 8375. (c) C. Amatore, A. Jutand, F. Khalil, M.A. M'Barki, L. Mottier, Organometallics 12 (1993) 3168.

[9] R. Sustmann, B. Patzke, R. Boese, J. Organomet. Chem. 470 (1994) 191.

[10] C. Strehblow, R. Sustmann, C. Amatore, preceding publication.

[11] K. Hiraki, N. Ochi, Y. Sasada, H. Hayashida, Y. Fuchita, S. Yamanaka, J. Chem. Soc. Dalton Trans (1985) 873.

[12] DigiS, User guide, GfS Aachen, 1992.

[13] R.R. Gagne, C.A. Koval, G.C. Lisensky, Inorg. Chem. 19 (1980) 2854.

[14] (a) R. Holm, Inorg. Synth. 12 (1970) 238. (b) R. Young, G. Wilkinson, S. Komiya, A. Yamamoto, Inorg. Synth. 17 (1977) 75.

[15] N. Ahmed, J.J. Levison, S.D. Robinson, M.F. Uttley, Inorg. Synth. 46 (1974) 48.

[16] J.D. (a), G. Gilbert, J. Wilkinson, A Chem. Soc, 1749. (b) M.I. Bruce, C. Hameister, A.G. Swinger, R.C. Wellis, Inorg. Synth. 28 (1990) 270. (c) H. Suzuki, O.W. Lee, N. Oshima, Y. Moro-Oka, Organometallics 6 (1987) (1969) 1569.

[17] A.J. Bard, L. Faulkner, Electrochemicaal Methods, Wiley, New York, 1980.

[18] O.B. Ryan, K.-T. Smith, M. Tilset, J. Organomet. Chem. 421 (1991) 315.