

Multiple Bonds between Main-Group Elements and Transition Metals. 152.¹ Hydrolysis and Polymerization–Precipitation of Methyltrioxorhenium in Aqueous Solution

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Received February 6, 1995[⊗]

Methyltrioxorhenium, CH₃ReO₃ (**1**; MTO), hydrolyzes rapidly in basic aqueous solutions and much more slowly in acidic media. At low concentrations ($c_{\text{MTO}} < 8.0 \times 10^{-3}$ M) the formation of CH₄ gas and perrhenate was detected. The hydrolysis was followed by spectrophotometry, and the rate constants were determined as a function of temperature and pressure according to the rate law $-d[\text{MTO}]/dt = k_1[\text{OH}^-][\text{MTO}]$. The rate constant, activation enthalpy, entropy, and volume at 298.2 K are as follows: $k_1/\text{M}^{-1} \text{s}^{-1} = (8.6 \pm 0.3) \times 10^2$, $\Delta H_1^\ddagger/\text{kJ mol}^{-1} = 15.9 \pm 1$, $\Delta S_1^\ddagger/\text{J mol}^{-1} \text{K}^{-1} = -135 \pm 3$, and $\Delta V_1^\ddagger/\text{cm}^3 \text{mol}^{-1} = -2.4 \pm 0.4$. Attempts to perform the reverse reaction, the synthesis of MTO from [ReO₄]⁻ and CH₄ (200 MPa), failed: the decomposition of MTO seems to be irreversible. At higher MTO concentrations a second reaction, a faster reversible polymerization–precipitation, takes place to yield a gold solid of net formula (C_{0.92}H_{3.3}ReO_{3.0})_{*n*}. The rate of polymerization–precipitation was studied as a function of temperature in D₂O by ¹H NMR spectroscopy; it follows first-order reversible kinetics. The rate constant, activation enthalpy, and entropy of polymerization–precipitation at 298.2 K are as follows: $k_2/\text{s}^{-1} = (2.1 \pm 0.4) \times 10^{-6}$, $\Delta H_2^\ddagger/\text{kJ mol}^{-1} = 111.9 \pm 5$, $\Delta S_2^\ddagger/\text{J mol}^{-1} \text{K}^{-1} = 25 \pm 16$ (the parameters for the dissolution of the polymer are estimated data). The rate of the polymerization–precipitation is independent of the concentration of H⁺, and the reaction does not occur in the presence of [ClO₄]⁻, [NO₃]⁻, and other oxidants.

Introduction

High-oxidation-state organometallic oxides have been attracting attention *per se* and as catalysts in organic syntheses.² Methyltrioxorhenium(VII), CH₃ReO₃ (MTO) which is easily accessible,² constitutes the simplest organorhenium compound: it is air-stable and soluble in organic solvents and in water and is used as a catalyst in the epoxidation of olefins, in olefin methathesis, in Baeyer–Villiger oxidations, in aromatic oxidations,^{2,3a–f} and in the oxidation of organic sulfides.^{3g} In the present paper we describe the kinetics of the behavior of MTO in dilute aqueous solution. The

hydrolytic decomposition of MTO was investigated as a function of temperature and pressure using UV–visible spectrophotometry, and the polymerization–precipitation of MTO was studied by variable-temperature ¹H NMR spectroscopy.

Experimental Part

Materials and Preparation of Solutions. Methyltrioxorhenium(VII) was synthesized from Re₂O₇ and Sn(CH₃)₄.⁴ Aqueous MTO solutions were freshly prepared and always kept in the dark at 2–7 °C to avoid possible photochemical reaction.⁵ Double-distilled water was used in all cases. HCl (25%), HClO₄ (70%), HNO₃ (63%), and CH₃COONa were purchased from Merck, HBF₄ was obtained from Aldrich, and D₂O (99.95%) was purchased from Armar and used as received without further treatment or purification. The pH of the solutions was measured with a Metrohm 654 pH meter equipped with a Radiometer GK2322 C electrode calibrated at pH 4.000 and 6.865 with buffers KH–phthalate and K₂[HPO₄]/Na[H₂PO₄], respectively.

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⊗ Abstract published in *Advance ACS Abstracts*, December 15, 1995.

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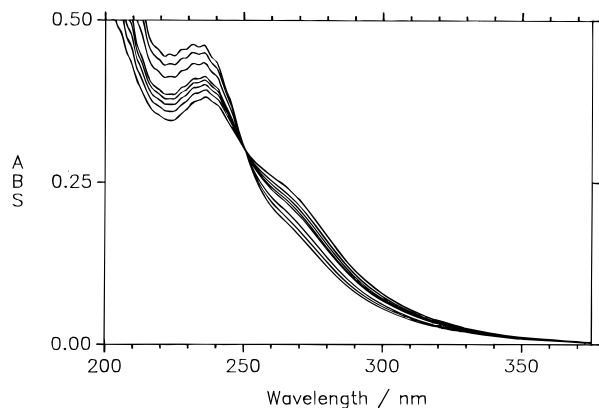


Figure 1. Absorption spectra of a 1.85×10^{-4} M solution of CH_3ReO_3 at 353.2 K ($l = 1.0$ cm) as function of time (the absorption decreases with time at $\lambda = 268.5$ nm; the time interval between each spectrum is 1800 s from run 1 to 5, and 9000 s from run 5 to 8).

Spectrophotometric Measurements. Perkin-Elmer Lambda 5 and Lambda 19 spectrophotometers were used to carry out the kinetic studies of the hydrolytic decomposition of MTO. A home-built high-pressure optical unit⁶ equipped with pillbox cells⁷ was used for the kinetic experiments. The optical pathlength at ambient pressure was 2.1 cm; the spectra were recorded between 400 and 200 nm. By pumping of a thermostated liquid through the cell, the temperature was stabilized to ± 0.2 K. The temperature range was between 283.2 and 353.2 K for the variable-temperature studies at ambient pressure and between 283.2 and 343.2 K at 195 MPa. Concentrations were expressed in molarities at 0.1 MPa.⁸

NMR Measurements. The ^1H and ^{17}O NMR spectra at variable temperature were recorded using a Bruker AC 200 spectrometer (4.7 T). The polymerization-precipitation of MTO was studied between 313.2 and 353.2 K. The temperature (± 0.2 K) was stabilized by a B-VT 2000 unit and measured by a substitution technique using a 100 Ω Pt resistor.⁹ ^1H NMR chemical shifts were measured relative to sodium 3-(trimethylsilyl)propanesulfonate as internal reference.

Results and Discussion

Methyltrioxorhenium (MTO) is water-soluble and stable toward protic acids. Its aqueous solutions decompose very slowly at room temperature but rapidly upon addition of hydroxide.^{2,10} In very dilute aqueous solution (ca. 10^{-4} M), the rate of hydrolysis of MTO increases with increasing temperature. The measured absorption spectra for MTO dissolved in water ($c_{\text{MTO}} = 1.85 \times 10^{-4}$ M) at 353.2 K are shown in Figure 1, with the time range being 10 h. The pH of the aqueous MTO solution decreases during the decomposition, while formation of the strong acid HReO_4 and evolution of CH_4 are observed.

The hydrolysis of MTO at 353.2 K was studied in dilute aqueous solution ($c_{\text{MTO}} = (1-3) \times 10^{-4}$ M) having the initial pH values equal to 2.97, 3.36, 3.67, 3.97 (adjusted with 0.01 M HClO_4), and 5.10. Each reaction was followed for 10–54 h using UV-visible spectropho-

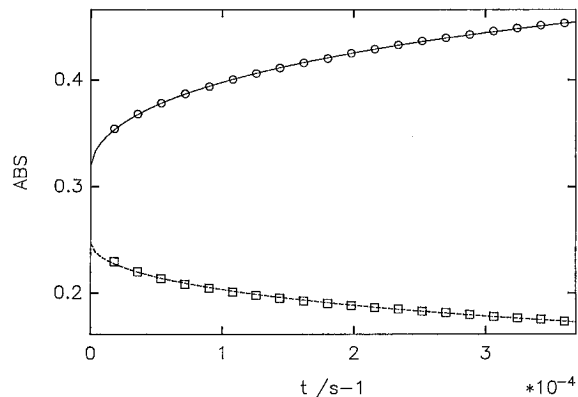


Figure 2. Measured and calculated absorbances for the CH_3ReO_3 solution (Figure 1) at $\lambda = 268.5$ (□) and 227.0 nm (○).

metry. The rate constants were calculated simultaneously from the absorbance values at two different wavelengths (268.5 and 227.0 nm), where major absorbance changes were observed:

$$A^{\lambda} = (\epsilon^{\lambda}_{\text{MTO}} c_{\text{MTO}} + \epsilon^{\lambda}_{\text{ReO}_4^-} c_{\text{ReO}_4^-}) l \quad (1)$$

where l is the optical pathlength and $c_{\text{MTO}} + c_{\text{ReO}_4^-}$ corresponds to the initial MTO concentration. The appearance of the isosbestic point (Figure 1) shows that there is no significant concentration of rhenium species other than CH_3ReO_3 and $[\text{ReO}_4]^-$. The hydrolysis



has the experimental rate law

$$-d[\text{CH}_3\text{ReO}_3]/dt = k_1[\text{OH}^-][\text{CH}_3\text{ReO}_3] \quad (3)$$

Equation 3 was integrated by using as initial conditions $[\text{ReO}_4^-]_0 = 0$ and $[\text{OH}^-]_0$ calculated from the initial pH of the MTO solution and $K_{\text{W}} = [\text{H}^+][\text{OH}^-]$. The $\text{p}K_{\text{W}}$ value is 12.62 at 353.2 K.¹¹ The absorbance values at two wavelengths were fitted with a nonlinear least-squares program¹² to calculate k_1 . The measured and calculated absorbance-time data are shown in Figure 2.

The validity of the kinetic model was checked with buffered solutions (0.01 M $\text{CH}_3\text{CO}_2\text{H}/\text{CH}_3\text{CO}_2\text{Na}$) at pH 3.78, 4.74, and 5.70 (adjusted with HClO_4). For these solutions the rate equation is

$$-d[\text{CH}_3\text{ReO}_3]/dt = k_{\text{obs}}[\text{CH}_3\text{ReO}_3] \quad (4)$$

with $k_{\text{obs}} = k_1[\text{OH}^-]_{\text{const}}$. k_1 was also calculated using the relation $k_1 = (k_{\text{obs}}K_{\text{W}})/[\text{H}^+]_{\text{const}}$. The determined average value of rate constant k_1 at 353.2 K was $(2.76 \pm 0.18) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, which agrees well with the measured k_1 at this temperature. All the measured values are shown in Figure 3.

The temperature dependence of the rate constant of the MTO hydrolysis was determined between 283.2 and 353.2 K. The corresponding Eyring plot is shown in Figure 3, and the calculated activation parameters are reported in Table 1.

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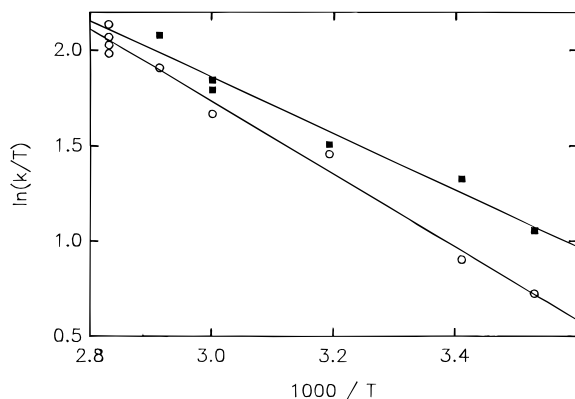


Figure 3. Eyring plots of rate constant k_1 for hydrolysis of CH_3ReO_3 at 0.1 (○) and 195 MPa (■).

Table 1. Kinetic Parameters for the Hydrolysis of MTO in Aqueous Solution ($c_{\text{MTO}} = (1-3) \times 10^{-4}$ M) and for the MTO Polymerization–Precipitation in D_2O Solution ($c_{\text{MTO}} = (1.5-7) \times 10^{-2}$ M) at 298.2 K

	P	
	0.1 MPa	195 MPa
(i) Hydrolysis of CH_3ReO_3		
$k_1/\text{M}^{-1} \text{s}^{-1}$	$(8.6 \pm 0.3) \times 10^3$	$(1.1 \pm 0.1) \times 10^3$
$\Delta H_1^\ddagger/\text{kJ mol}^{-1}$	15.9 ± 1	12.3 ± 1
$\Delta S_1^\ddagger/\text{J mol}^{-1} \text{K}^{-1}$	-135 ± 3	-145 ± 4
$\Delta V_1^\ddagger/\text{cm}^3 \text{mol}^{-1}$		-2.4 ± 0.4
(ii) Polymerization–Precipitation of CH_3ReO_3		
k_2/s^{-1}	$(2.1 \pm 0.4) \times 10^{-6}$	
$\Delta H_2^\ddagger/\text{kJ mol}^{-1}$	113 ± 5	
$\Delta S_2^\ddagger/\text{J mol}^{-1} \text{K}^{-1}$	25 ± 16	
k_2/s^{-1}^a	$\sim 8 \times 10^{-8}$	
$\Delta H_2^\ddagger/\text{kJ mol}^{-1}^a$	~ 100	
$\Delta S_2^\ddagger/\text{J mol}^{-1} \text{K}^{-1}^a$	~ 0	

^a Estimated values.

The hydrolysis of MTO has the same rate law at 195 MPa (1950 bar) as under atmospheric pressure. The kinetics of the reaction was followed at high pressure in the temperature range 283.2–343.2 K, the corresponding Eyring plot is shown in Figure 3, and the calculated activation parameters are reported in Table 1. The K_w values at 195 MPa were taken from ref 13 ($\text{p}K_w = 13.886, 13.562, 12.998, 12.510$ and 12.290 at 283.2, 293.2, 313.2, 333.2, and 343.2 K, respectively). The volume of activation was determined from the data measured at five different temperatures at ambient pressure and at 195 MPa, using the equation

$$\ln k_{195} = \ln k_1 - \Delta V^\ddagger P/RT \quad (5)$$

where $P = 195$ MPa. The calculated activation volume, ΔV^\ddagger , was $-2.4 \pm 0.4 \text{ cm}^3 \text{mol}^{-1}$. The negative value is in agreement with the negative activation entropy.

The reaction mechanism was further studied by isotopic exchange. The hydrolysis of deuterated $\text{CD}_3\text{-ReO}_3$ in $\text{OH}^-/\text{H}_2\text{O}$ gives only CD_3H and *vice versa*: $\text{CH}_3\text{-ReO}_3$ in $\text{OD}^-/\text{D}_2\text{O}$ gives only CH_3D ;¹⁴ there is no deuterium/hydrogen exchange between the CH_3 group and the solvent protons. There is a fast O exchange between CH_3ReO_3 and the solvent water: at 298 K the isotopic equilibrium in aqueous MTO solution is reached

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in 2 min either by mixing 10% ^{17}O -enriched H_2O with aqueous MTO solution or a 4.72% ^{17}O -enriched $\text{CH}_3\text{-ReO}_3$ solution with H_2O , as observed by integrating the ^{17}O NMR signals at 834 ppm (CH_3ReO_3) and 0 ppm (H_2O , reference). The CH_3ReO_3 is a weak acid in aqueous solution ($\text{p}K_a = 7.5$).^{15b,16} This means that there is a fast protonation equilibrium between $[\text{CH}_3\text{-ReO}_3(\text{H}_2\text{O})]$ and $[\text{CH}_3\text{ReO}_3(\text{OH})]^-$. The hydrolysis of MTO in D_2O (0.4 M in D^+) at 333 K is 2.2 ± 0.1 times faster than under the same conditions in H_2O .

According to these observations, it can be proposed that a rapid deprotonation equilibrium of $[\text{CH}_3\text{ReO}_3(\text{H}_2\text{O})]$ precedes the rate-determining step; *i.e.*, the simultaneous Re–C and O–H bond cleavages in $[(\text{HO})\text{O}_3\text{ReCH}_3]^-$ result in the formation of ReO_4^- and CH_4 . The observed negative value of ΔV^\ddagger (and of ΔS^\ddagger) does not necessarily indicate an associatively activated reaction pathway. Indeed, the ΔV^\ddagger value is a composite one; it includes the activation volume of the rate-determining step and the unknown reaction volume of the deprotonation preequilibrium.

The possibility of the reverse reaction



in acidic solutions of ReO_4^- with CH_4 pressurized to 200 MPa was checked. After 72–96 h of stirring, the CH_4 pressure was released and the aqueous solutions were analyzed by spectrophotometry and/or ^1H NMR (depending on the total Re concentration). Despite several attempts with different experimental conditions (concentration, pH, reaction time, temperature), no formation of MTO could be detected. This result suggests that the decomposition of MTO in aqueous solution is not a reversible reaction.

If a more concentrated solution of CH_3ReO_3 ($c_{\text{MTO}} = 2.4 \times 10^{-2}$ M) in D_2O is heated to 323.2 K, a polymerization–precipitation reaction takes place which is *faster* than MTO hydrolysis. The solution becomes blue (colloid) followed by precipitation. The precipitate was analyzed, giving the composition $\text{C}_{0.92}\text{H}_{3.3}\text{ReO}_{3.0}$,^{15–17} *i.e.* near that of $\{\text{CH}_3\text{ReO}_3\}_n$. This polymerization–precipitation was studied by ^1H NMR spectroscopy. The intensity of the CH_3 proton signal (δ 2.3 ppm) was used to determine the MTO concentration in solution: the HOD protons present in comparable and constant concentration in D_2O were used as an internal standard for integration. Figure 4 shows the decrease of the CH_3 proton signals as function of time.

This method made it possible to measure the MTO concentration in solution but could not be used to measure directly the amount of the precipitated polymer and the quantity of MTO hydrolyzed. The initial reaction rate of the hydrolysis in a 0.024 M solution of MTO was calculated to be $5 \times 10^{-8} \text{ M s}^{-1}$ at 323.2 K

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(17) We note that this "polymerization–precipitation" (polycondensation) of MTO is more complex than is suggested by this simple equation. It must particularly be taken into account that $\sim 8\%$ of the MTO loses its CH_3 groups as CH_4 upon aggregation.^{14b,16}

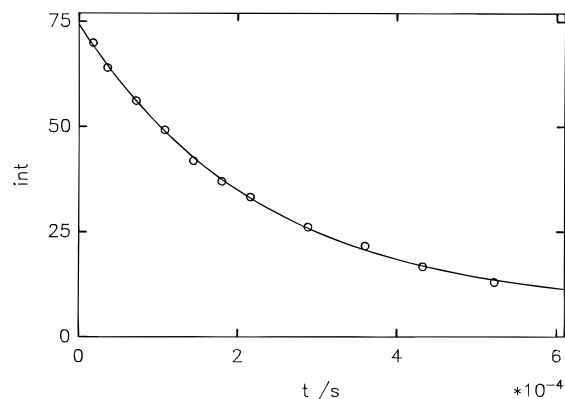


Figure 4. Measured and calculated integrals of the CH_3 protons (arbitrary units) in a 0.024 M solution of MTO in D_2O as a function of time at 323.2 K.

(the rate slows down due to the second-order kinetics and the decrease in pH during the reaction), while the first-order decrease of the methyl proton signal was measured under the same conditions to be more than 20 times faster ($1.4 \times 10^{-6} \text{ M s}^{-1}$). One can, therefore, follow the polymerization–precipitation via the decrease of the CH_3 signal.

The reaction shown in Figure 4 was stopped after 14 h. The mixture was diluted four times and stirred at 323.2 K. It was observed that all the precipitate dissolved within 3 h. The CH_3 signal was checked periodically, and its intensity increased when the dilution was taken into account. Therefore, the polymerization–precipitation reaction is reversible.

The rate of the reversible polymerization–precipitation was studied in D_2O as a function of the concentrations of MTO and H^+ , in the range of $(1.5\text{--}7.0) \times 10^{-2}$ M of MTO and from acid free solution to 1.19 M of H^+ (adjusted with HCl or HBF_4) at 323.2 K. The reaction¹⁷ $\text{CH}_3\text{ReO}_3 \rightleftharpoons (1/n)\{\text{CH}_3\text{ReO}_3\}_n$ follows first-order reversible kinetics according to the rate law

$$-d[\text{MTO}]/dt = k_2[\text{CH}_3\text{ReO}_3] - k_{-2}[\{\text{CH}_3\text{ReO}_3\}_n] \quad (7)$$

It was found that the rate constant k_2 , characterizing the decrease of MTO in solution, is independent of the concentrations of H^+ and MTO. The integral of the CH_3 signal was expressed as

$$I = I_0(k_{-2}/(k_2 + k_{-2})) + I_0(1 - k_{-2}/(k_2 + k_{-2})) \exp(-(k_{-2} + k_2)t) \quad (8)$$

where I_0 and I are the signal intensities at time zero and time t , respectively. The calculated values for k_2 and k_{-2} at 323.2 K are $(7.8 \pm 1.5) \times 10^{-4} \text{ s}^{-1}$ and $(5.3 \pm 2.8) \times 10^{-5} \text{ s}^{-1}$, respectively. While the rate constant of the polymerization–precipitation, k_2 , was determined precisely, it was found that k_{-2} , the rate constant of the dissolution of the $(\text{CH}_3\text{ReO}_3)_n$ polymer, could only be measured with a large error. The direct determination of k_{-2} was found to depend on experimental conditions: stirring, age of precipitate, size of solid particles, etc., thus reflecting the complex chemical and structural phenomena associated with this polymer.^{15b,17} Under different reaction conditions ($t_{\text{R}} = 3$ days, $t = 70\text{--}80$ °C, $0.05 \text{ M} \leq c_{\text{MTO}} \leq 0.2 \text{ M}$), the polymerization–precipitation of MTO is not reversible.^{15,16} Isolated, dry poly-MTO cannot be redissolved to monomeric MTO in any common solvent.^{15,16} The discussed reversible reac-

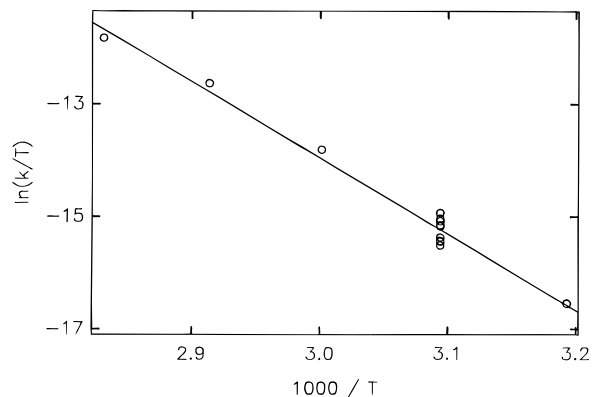


Figure 5. Eyring plot of rate constants for CH_3ReO_3 polymerization–precipitation, k_2 , at different concentrations of MTO and H^+ .

tion herein is observed in diluted freshly prepared systems after short reaction times. The activation parameters for the polymerization–precipitation were determined from measurements in the temperature range 313.2–353.2 K and are presented in Table 1. The corresponding Eyring plot is shown in Figure 5 and includes all the measurements at different concentrations and acidities.

The lowest concentration of MTO leading to polymerization–precipitation was determined by independent experiments. From spectrophotometric measurements it was found that a 8.1×10^{-3} M solution in MTO gave a precipitate after 1 day at 323.2 K, while a 7.9×10^{-3} M solution did not give a precipitate under the same conditions, even after larger periods of time.

The kinetic runs of solutions of MTO acidified with $\text{H}[\text{BF}_4]$ gave the same results as with HCl: within the concentration range used, the Cl^- ion has no effect on the reaction rate; no Cl^- adduct was observed in dilute aqueous solution, although chloride attack at the Lewis-acidic rhenium of MTO is known.^{18,19} The polymerization–precipitation also took place in diluted H_2SO_4 , but not when oxidizing acids (HClO_4 , HNO_3 , etc.) were used. Only the slow hydrolysis of MTO was observed in the latter case.

Conclusion

In dilute aqueous solutions of CH_3ReO_3 , hydrolysis of MTO is observed and proceeds via a fast deprotonation equilibrium of $[\text{CH}_3\text{ReO}_3(\text{H}_2\text{O})]$ followed by rate-determining, simultaneous Re–C and O–H bond cleavage in $[(\text{HO})\text{O}_3\text{ReCH}_3]^-$, resulting in the formation of CH_4 and ReO_4^- .

At high CH_3ReO_3 concentrations a faster aggregation process can be observed, resulting in the precipitation of a “polymeric” organometallic oxide with the average composition $\text{C}_{0.92}\text{H}_{3.3}\text{ReO}_{3.0}$. The rate of this reaction is independent of the pH.

Acknowledgment. We thank the *Swiss National Science Foundation* and the *Deutsche Forschungsgemeinschaft* for financial support. H. C. Starck GmbH (Prof. Winter) is acknowledged for a generous gift of rhenium.

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