208. The Electrochemical Measurement of Rate Constants for the Catalyzed Oxidation and Reduction of Water in Microheterogeneous Systems

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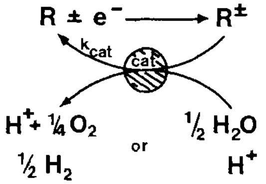
Summary

The appearent first-order rate constants for the oxidation of water by iron tris(bipyridyl)(Fe(bpy)$_3^{3+}$), and reduction of water by methylviologen (MV^+) catalyzed by a stabilized RuO_2 or Pt-sol, respectively, were measured. Rate constants for water oxidation at pH 7 of 0.4 s^{-1} and water reduction at pH 4.7 and pH 1 of up to 460 s^{-1} for different sols were found.

Introduction. - The oxidation and reduction of water to oxygen and hydrogen, respectively, by chemical species (relays, R) of appropriate redox potentials in solution has been shown to be efficiently catalyzed by suspensions of finely devided metallic particles [1]. Pt- and RuO_2-sols have been investigated extensively as catalysts in photochemical water-splitting [2]. These colloidal species of metallic character can be treated as catalytic microelectrodes for the respective processes. A strong dependence of appearent rate constants on catalyst concentration (total surface area/weight) has been observed. Mixing of the electroactive species, being capable to oxidize or reduce water, with a catalyst sol and observing the time-dependent disappearance of the former should lead to the corresponding rate constants. Stopped-flow experiments of this type have been performed by *Pramauro et al.* [3]. An easy way of mixing would be the *in situ* generation of the electrochemically active relay species. This can be done by electrochemical oxidation or reduction of the relay on a macroelectrode. The oxidized (or reduced) relay is then restored *via* the reaction with the catalyst.

Scheme



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When the potential is scanned, the value of the time-(potential-)dependent current can be used to calculate the catalytic rate constant. This catalytic case has been solved by *Saveant & Vianello* [4] and *Nicholson & Shain* [5]. In the presence of catalyst the maximal current, i_{cat}, is bigger than the peak current, i_{peak}, observed in the voltammogramm without catalyst. From the ratio of kinetic peak current to the diffusion-controlled peak current, k_{cat}, can be obtained from a working curve [5]. When this ratio exceeds ~1.5 the curve is linear and k_{cat} for a one-electron redox process (for the relay) at room temperature is expressed by

$$k_{cat}/s^{-1} = 3.316\,(i_{cat}/i_{peak})^2 \times \text{scan rate}/(V.s^{-1}) \qquad (1)$$

From the difference between the potential at half peak height and the half-wave potential k_{cat} can also be derived, using a table or working curve [5] which expresses k_{cat}/a as a function of $(E_{p/2}-E_{1/2})$ where $a = 16.67 \times$ scan rate, $E_{p/2}$ is the potential at which the current is half the maximal current in the voltammogramm, and $E_{1/2}$ is the half-wave potential. Examples for systems where substances being present in great excess and reacting irreversibly with the oxidized (or reduced) relay to restore it have been given in the literature [6]. We here apply the treatment of the catalytic case for the first time to measure the kinetic parameters for the catalyzed reaction of a relay with a substrate, in our case water, employing catalysts of high activity and very low particle concentration[1]).

Experimental Part. - Iron (II) tris(bipyridyl) perchlorate was synthesized according to a literature procedure [7], methylviologen. $MV^{2+}(Cl^-)_2$ was obtained from *BDH Chemical Ltd.* A colloidal RuO_2-catalyst was prepared from K_2RuO_4 and protected with SDS (sodium dodecyl sulfate) according to [8]. A completely transparent solution was obtained. Pt-catalysts, also being transparent were prepared according to [9] (*Carbowax*-protected Pt). All other chemicals were reagent grade. Triply distilled water was used throughout. Solutions were purged with N_2 and kept at 25°. A *Tacussel PRT 30-0.1* potentiostat in connection with a *PRG4* command unit was used for cyclic voltammetry. Pt- or C-paste (0.01 cm^2, *Metrohm*) served as an electrode in water oxidation experiments and a hanging drop Hg electrode (*Metrohm*) of 0.0138 cm^2 or a gold electrode was used for reduction experiments at pH 1 and pH 4.7, respectively. All potentials are given *vs.* NHE. (normal hydrogen electrode). Cyclic voltammogramms at scan rates $\geq 1\ V \cdot s^{-1}$ were recorded on a *Tektronix* storage oscilloscope.

Results and Discussion. - The oxidation of water on an electrode (macro or micro) is a process that occurs at low overvoltages only on certain catalytic materials. Amongst them RuO_2 has turned out to be a very good choice [10] being applied in water electrolysis [11], photoelectrochemical cells [12] and microheterogenous systems [2]. To test the ability of a RuO_2-sol to catalyze water oxidation, cyclic voltammogramms of mmolar solutions of $Fe(bpy)_3^{2+}$ in 0.05 M phosphate buffer, 0.5 M Na_2SO_4 were recorded on Pt- or C-paste electrodes. When the catalyst was added, the current increased and at sufficiently low scan rates ($<50\ mV \cdot s^{-1}$) a plateau was observed. From the ratio of maximal catalytic current to peak current in the absence of catalyst the appearent first-order rate con-

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[1]) During preparation of this work *G. McLendon* sent us a manuscript reporting similar experiments done with a polyvinyl alcohol-stabilized Pt-catalyst.

stant, k_{cat}, was computed to be 0.4 s^{-1}. Using the other method (see Introduction) a value of k_{cat} close to this value was calculated from $(E_{p/2} - E_{1/2})$.

For water reduction at pH 4.7 a gold electrode was employed. mmolar solutions of MV^{2+} in 0.05 M phosphate buffer, 0.5 M Na_2SO_4 in the presence and absence of a Pt-sol (<20 mg Pt/l, protected with *Carbowax* 20 M [9]) were also investigated by cyclic voltammetry. From i_{cat}/i_{peak} a first-order rate constant of $\sim 1\ s^{-1}$ was calculated. Experiments at pH 1 (in HCl/0.1 M KCl) were carried out at a Hg electrode which provides high enough an overpotential for H_2-formation. A different Pt-sol (80 mg/l) was used in this case (*Fig. 1*). The following observations have been made that substantiate the very high activity observed for this catalyst: When the potential was held fixed beyond the peak as well as upon slow-enough scans, instead of the blue cloud, visible on the electrode when no catalyst is present, the platinum-catalyzed formation of H_2-bubbles can be observed. Due to increasing coverage of the electrode with bubbles the current (which did not decrease in the beginning when the potential is held beyond the peak as it is the case in catalyst-free systems where the current decreases with $t^{-1/2}$) falls off after some time until the contact to the solution is interrupted. Thus slow scan rates have to be avoided in the case of very active catalysts. Catalytic currents were also observed (bubbles of H_2 formed) when no MV^{2+} was present. They are independent of scan rate from 2 mV · s^{-1} to 100 mV · s^{-1}. The onset of the catalytic wave occurs about 200 mV more negative than the thermodynamic hydrogen potential at the respective pH. Without catalyst H_2 is formed only at very high overpotentials on Hg. Generally the catalytic currents in the presence of the catalyst alone should be a measure for its activity if adsorption is absent. In such case at least relative activities could be determined. With respect to the size of the electroactive species this would represent a situation in between a catalytic slurry electrode and catalytic case for a molecular species as described above. Slurry electrodes have been described in the literature [13]. For the *Carbowax*-protected catalyst k_{cat} was calculated in the same way and found to be 463 s^{-1} at pH 1.

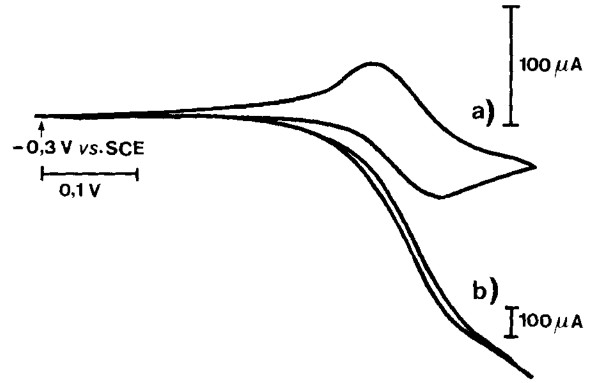

Fig. 1. *Voltammogramm of methylviologen* (10^{-2} M) *at pH 1, 0.1 M KCl, on mercury (0.0138 cm^2);* a) Without catalyst, b) With catalyst 80 mg Pt/l, 125 mg *Carbowax*/l.

The dependence of rate constant on catalyst concentration was not linear, the above mentioned value was only obtained for the undiluted catalyst (all rate constants are normalized to the undiluted catalyst). The reason might be the precipitation of the Pt-sol by MV^+ which becomes an important process at low particle concentrations and high MV^{2+}-concentrations. Therefore the real rate constant is presumably even higher. Visible precipitation could indeed be observed in some experiments. Using a aggregation number of 1200 for the Pt-sol [9] a bimolecular rate constant of $1.35 \times 10^9 \text{M}^{-1} \text{s}^{-1}$ can be calculated for the particles. This is near the diffusion controlled limit ($k_{\text{diff}} \approx 1.2 \times 10^{10} \text{M}^{-1} \text{s}^{-1}$, calculated for 32 Å particles from *Smoluchowski*'s equation) as one would expect under the given circumstances: The inverted cathodic branch of the i-E curve for the H^+/H_2 reaction intersects the i-E curve for MV^{2+}/MV^+ at the diffusion limited plateau for MV^+ oxidation *(Fig. 2)*.

Adsorption of MV^+ has been observed in some experiments. To study this effect we also tried to use other electrode materials. Experiments on gold have already been described above. Adsorption seems to be absent in that case but gold can not be used at low pH (the overpotential for H_2-evolution is not big enough). C-paste gave to high background currents in the electrolyte used (HCl/KCl, pH 1). Pb was found to be a good material for MV^+ synthesis but is not suitable for analytical applications. Adsorption of MV^+ on Hg is indicated by the appearance

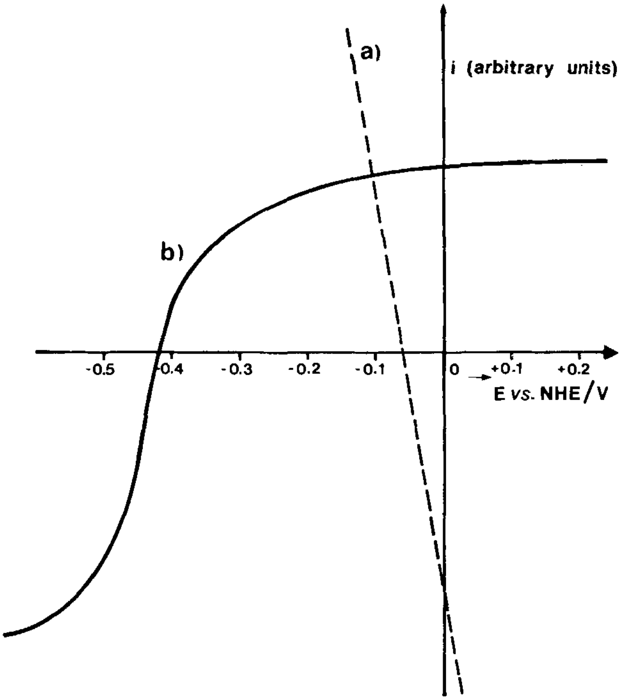

Fig. 2. *Current-potential curves on a Pt microelectrode at pH 1* (schematic). a) For H^+/H_2 (inverted with respect to current), upper part shows H^+ reduction, b) For MV^{2+}/MV^+, upper part shows MV^+ oxidation.

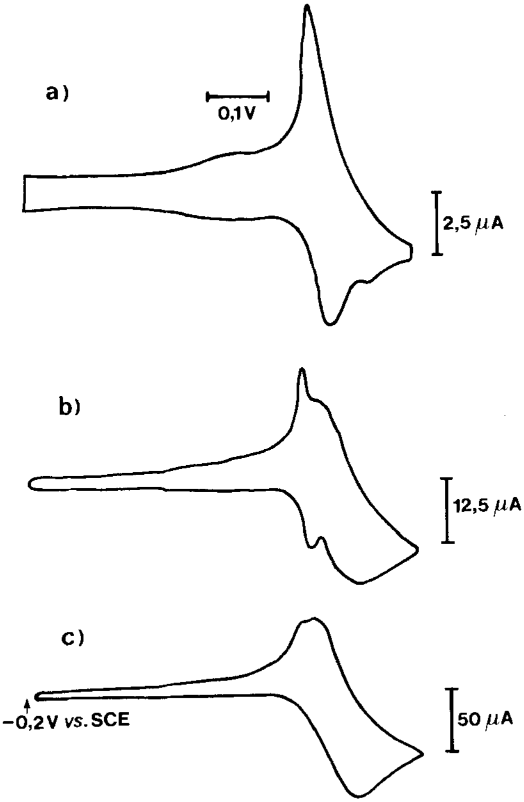

Fig. 3. *Oscillographic traces of cyclic voltammogramms of methylviologen on mercury* (hanging drop of 0.0138 cm^2), *0.1* M *KCl, pH 1(HCl), scan rate 1 V · s^{-1}.*). a) 4× 10^{-4}M, b) 2× 10^{-3}M, c) 1× 10^{-2}M.

of prepeaks in the cyclic voltammogramms. The behaviour of these prepeaks follows the theoretical description given by *Whopshall & Shain* [14]. Their relative size is increased with decreasing MV^{2+} concentration and increasing scan rate. Cyclic voltammogramms at 1 V · s^{-1} are shown in *Figure 3* for 4× 10^{-4}M, 2× 10^{-3}M and 10^{-2}M MV^{2+}. At the highest concentrations used, the shape of the voltammogramms approach the behaviour of a quasi-reversible system on which the calculations can be made only. High methylviologen concentrations were used accordingly.

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