JOURNAL OF APPLIED ELECTROCHEMISTRY 25 (1995) 846–851

Electrochemical mediators for total oxidation of chlorinated hydrocarbons: formation kinetics of Ag(II), Co(III), and Ce(IV)

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Received 25 November 1994; revised 12 January 1995

Mediated electrochemical oxidation (MEO) with Ag(II) and Co(III) in 7 M HNO_3 and 3.5 M H_2SO_4 has been studied. High degradation rates were found for superchlorinated organic substances such as pentachlorophenol (PCP), Lindane and polychlorinated biphenyls (PCBs) using Ag(II) in HNO_3 as mediator. An investigation on the formation kinetics of Ag(II), Co(III), and Ce(IV) by means of a rotating disc electrode (RDE) led to a quantitative determination of limiting currents at various mediator concentrations. Reaction rate constants of water oxidation by Ag(II) were determined at various temperatures and compared to reaction rates of Co(III).

1. Introduction

The incineration of superchlorinated organic substances is problematic; on the one hand, due to the high chlorine load and, on the other hand, because toxic compounds; e.g., furans or polychlorinated dibenzo-(*p*)-dioxins, may be produced [1–3]. One alternative to incinerating chlorinated hydrocarbons is provided by mediated electrochemical oxidation (MEO) [4–16]. In this process metal ions in aqueous acid solutions are oxidized anodically from a stable oxidation state to reactive species (Equation 1), which, in turn, are capable of oxidizing organic substances dispersed in the solution to CO_2 (Equation 2):

$$xM^{n+} \longrightarrow xM^{(n+1)+} + xe^- \qquad (1)$$

$$xM^{(n+1)+} + \text{reacting agent} \longrightarrow xM^{n+} + yCO_2 \qquad (2)$$

Subsequently, the mediator is regenerated at the anode (Equation 1) so that the cycle is closed. Redox pairs with a high oxidation potential, e.g. Ag(II)/Ag(I) ($E_0 = 1.98\,V$), Co(III)/Co(II) ($E_0 = 1.83–1.92\,V$), and Ce(IV)/Ce(III) ($E_0 = 1.72\,V$) are suitable for total oxidations [17]. The mediators indicated are compared in this paper as regards their capability of oxidizing superchlorinated organic substances. Considering the positive results obtained in these tentative experiments, the formation kinetics of Ag(II), Co(III), and Ce(IV) was investigated using a rotating disk electrode (RDE). By means of the potential–current density plots obtained in the latter experiments limiting current densities have been determined for Ag(II) and Ce(IV) generation. As Ag(II) ions in aqueous, low-complexing media do not only oxidize organic substances, but also water, experiments were performed on the determination of reaction rate constants applicable to the oxidation of water at various temperatures.

2. Experimental details

2.1. *Chemicals*

All solutions used were prepared with triply distilled water and with nitric acid (65%) and sulfuric acid (98%), respectively (E. Merck). Likewise, the a.p. inorganic mediators $AgNO_3$, Ag_2SO_4, $Co(NO_3)_2$, $CoSO_4$, and $Ce(NO_3)_3$ were Merck products. The organic reference substances used in the total oxidation experiments, pentachlorophenol (PCP) and γ-hexachlorocyclohexane (Lindane), were at least 99% pure (Fluka Chemie, Switzerland). Another organic reference substance was 'Chlophen', a transformer oil consisting of trichlorobenzene, tetrachlorobenzene and polychlorinated biphenyls (PCBs).

2.2. *Electrochemical cells and equipment*

The total oxidation experiments were performed in a purpose designed cell. This consisted of a thermostated vessel of about 800 ml volume, divided by a Nafion® 450 membrane (DuPont). To avoid the formation of elemental silver at the cathode ($Ag^+ + e^- \longrightarrow Ag$, $E_0 = 0.7996\,V$), the nitric acid concentration must be at least 7 M. Instead of reducing Ag(I) to elemental silver, nitric acid is reduced under these conditions according to the Vetter mechanism [18]:

$$HNO_3 + 2H^+ + 2e^- \longrightarrow HNO_2 + H_2O$$

$$(E_0 = 0.934\,V)$$

The electrodes were made from platinum sheets ($A = 60\,cm^2$). Platinum exhibits high overvoltage with respect to anodic oxygen evolution. The initial concentration of the inorganic mediators was 100 or 500 mM in all total oxidation experiments; the temperature was 70 or 90 °C. 200 mg of each of the organic substance to be examined were weighed into the batch cell and then a current of 6 A, corresponding to an anodic current density of 100 mA cm^{-2}, was applied to the electrodes. The electrolytic cell described is shown in Fig. 1. This equipment was also used to perform experiments for determination of Ag(II) destruction by reaction with water. For this, a current of 1.5 A (corresponding to 25 mA cm^{-2} anodically) was applied to the electrodes for generation of Ag(II). After the current had been switched off, samples (1000 μl) were taken at specified times and analysed immediately. These experiments were performed in 7 M HNO_3 at temperatures of 30, 40, 50 and 70 °C.

The experiments with the RDE to allow steady-state current density–potential curves to be plotted were performed in a similar, although smaller, cell with 500 ml electrolyte volume. The platinum sheet anode was replaced by a rotating platinum disc electrode (3 mm dia.) supplied by Metrohm, Switzerland. In front of the RDE, at 2*d* distance from it, a Haber–Luggin capillary (where *d* is the outside diameter of the capillary tip) was provided with a Ag/AgCl reference electrode ($E_0 = 0.222$ V). The potential was controlled by an electronic potentiostat (Wenking HP 72) coupled to a voltage scan generator (Wenking VSG 72) and a X–Y plotter (Linseis L800). In all experiments with the RDE the temperature was 20 °C, the nitric acid concentration 7 M. The concentrations of the inorganic mediators ($AgNO_3$, $Co(NO_3)$, $Ce(NO_3)_3$) were varied between 20 and 500 mM.

2.3. *Analytical procedure*

The rates of destruction of the organic reference substances were determined by measurement of the CO_2 and CO contents in the carrier gas stream (200 ml min^{-1} of N_2). For this purpose, two infrared flow spectrometers URAS 10E (Hartmann & Braun),

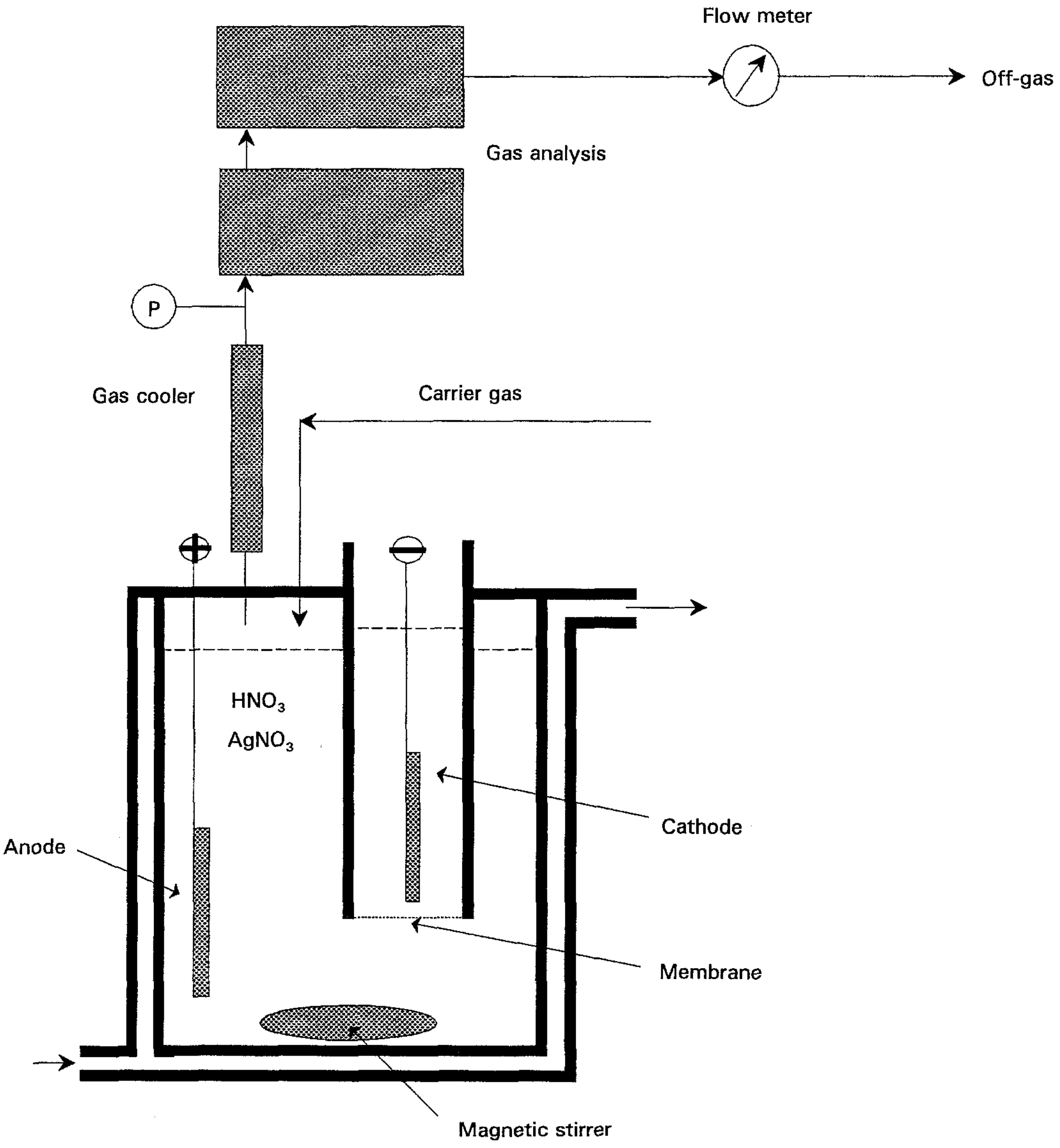

Fig. 1. Batch cell for total oxidation of organic substances.

coupled with a computer for online data processing, were connected to the off-gas stream. By integration of the plots of the CO_2 and CO content versus time, the carbon recovery rate was directly determined for known overall gas flows.

The Ag(II) concentrations in the water oxidation experiments were determined indirectly. 1000 μl of the solution to be examined for its Ag(II) content were mixed in a cuvette with 2000 μl of a 500 mM $Co(NO_3)_2$/3.5 M HNO_3 solution and absorption at 606 nm was immediately measured. The method relies on the fact that Ag(II) reacts quickly with Co(II) to Ag(I) and Co(III). Co(III) has an absorption shoulder at 606 nm which enables an indirect quantitative analysis to be made of the Ag(II) content. The assumption can be made that Co(II) enters into a quantitative reaction with Ag(II) because (i) the reaction Co(II) + Ag(II) $\xrightarrow{k_{\mathrm{II}}}$ Co(III) + Ag(I) takes place quickly: $k_{\mathrm{II}} = 2.4 \times 10^3$ [19] and $k_{\mathrm{II}} = 1.8 \times 10^3$ [20] ($dm^3\,mol^{-1}\,s^{-1}$), respectively; and (ii) the equilibrium of the reaction occurs far to the right: $K = 43.2$ [21].

3. Results

3.1. *Oxidation experiments with organic reference substances*

Studies by Leffrang [4], who performed oxidation experiments with Co(III)/3 M H_2SO_4 solution, showed that superchlorinated organic substances, e.g. PCP and PCBs, are destroyed but not completely. To be able to compare the destruction of PCP through Co(III) and Ag(II), experiments were performed at 70 °C and initial mediator concentrations of 100 mM. In the anode compartment the electrolyte was either 7 M HNO_3 or 3.5 M H_2SO_4. The destruction of 'Chlophen' was studied in 500 mM $AgNO_3$/7 M HNO_3 solution and compared with the results obtained by Leffrang [4]. It appeared that Ag(II) ions do not only destroy tri- and tetrachlorobenzenes, but also the PCBs. Using Co(III) ions, only the tri- and tetrachlorobenzenes could be oxidized completely. As 'Chlophen' is a mixture of substances which has not been clearly defined, the analysis according to [4] was made in such a manner that at the end of the experiment 100 ml of the reaction solution were extracted with 10 ml benzene and a gas chromatographic examination was made to detect tri-/tetrachlorobenzenes and PCBs. The destruction experiments with Lindane were performed only in a 500 mM $AgNO_3$/7 M HNO_3 solution. In all experiments involving silver as the mediator it was observed that AgCl which was initially precipitated from the reaction solution was redissolved so that at the end of the experiment the solution obtained was clear.

3.2. *Formation kinetics*

The current density–potential plots of anodic Ag(II) generation in 7 M HNO_3 are characterized by a rise beginning at approx. 1.87 V (NHE) which is indicative of the onset of Ag(II) generation. A marked dependency on rotation speed of the RDE could be observed. With further rise in potential the curves end in a plateau. The current density value corresponding to this plateau is assumed to be the limiting current, j_{lim}. In the limiting current zone mass transport determines the limiting current density [22]:

$$j_{\mathrm{lim}} = 0.62nFD^{2/3}\nu^{-1/6}\omega^{1/2}c_0 \qquad (3)$$

If the anodic potential is increased further, the current density experiences a new steep rise because anodic oxidation of water ($H_2O \longrightarrow 2H^+ + 2e^- + 1/2O_2$) starts in parallel to Ag(II) generation. Figure 2 shows the course of the current density–potential curves for a Ag(II) initial concentration of 20 mM in 7 M HNO_3 and for various rotation speeds n of the RDE. The current density–potential curve of pure 7 M HNO_3 is shown for comparison.

In Ag(II) generation a plateau can no longer be observed, beginning at an Ag(II) concentration of 200 mM. By contrast, the current density–potential curves of Ce(IV) generation in 7 M HNO_3 are characterized by the formation of plateau up to a Ce(III) initial concentration of 500 mM.

Several current density–potential curves were plotted for a 100 mM $Co(NO_3)_2$/7 M HNO_3 solution which, however, coincide with the current density–potential curve of pure 7 M HNO_3. Experiments performed with a 100 mM $CoSO_4$/3.5 M H_2SO_4 solution exhibited the same behaviour when compared to

Table 1. Destruction rates of PCP, Lindane and Chlophen

Substance	*Anodic medium*	*T*/°C	*Degradation rate*/%
PCP	0.1 M $CoSO_4$/3.5 M H_2SO_4*	70	30
PCP	0.1 M $Co(NO_3)_2$/7 M HNO_3*	70	63
PCP	0.05 M Ag_2SO_4/3.5 M H_2SO_4†	70	62
PCP	0.1 M $AgNO_3$/7 M HNO_3†	70	93
PCP	0.5 M $AgNO_3$/7 M HNO_3‡	90	96
Lindane	0.5 M $AgNO_3$/7 M HNO_3‡	70	96
Chlophen	0.5 M $AgNO_3$/7 M HNO_3‡	90	total destruction

* The cathodic solution consisted of 0.1 M $Co(NO_3)_2$/7 M HNO_3.
† The cathodic solution consisted of 0.1 M $AgNO_3$/7 M HNO_3.
‡ The cathodic solution consisted of 0.5 M $AgNO_3$/7 M HNO_3.

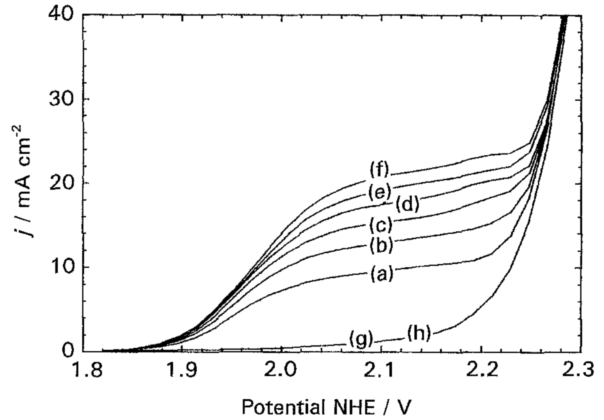

Fig. 2. Current density–potential curves in 7 M HNO_3 ($T = 20\,°C$). Key for rotation speed and concentration (n/min^{-1}, $c_0(AgNO_3)$/ mM): (a) 500, 20; (b) 1000, 20; (c) 1500, 20; (d) 2000, 20; (e) 2500, 20; (f) 3000, 20; (g) 500, 0; (h) 3000, 0.

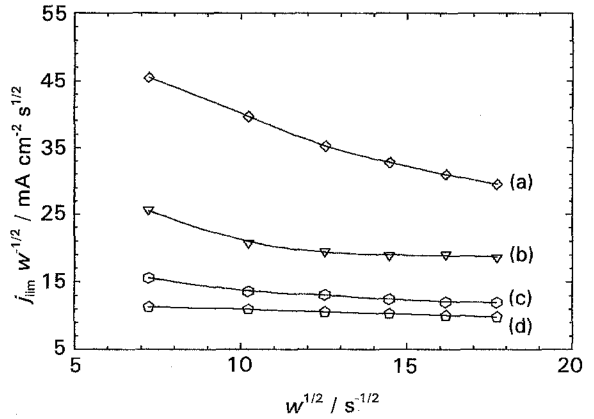

Fig. 4. Levich/Koutecky plot for c_0 ($AgNO_3$) at (a) 500, (b) 300 and (c) 200 mM and c_0 ($Ce(NO_3)_3$) at (d) 500 mM.

pure 3.5 M H_2SO_4. The anodic potentials of Co(III) generation and anodic water oxidation were probably close to each other. In any case, Co(III) is produced under these conditions with current yields up to 70% [4].

In Fig. 3 the limiting current densities j_{lim} are plotted against the initial concentrations c_0 of $AgNO_3$ (20, 100, 200, 300 and 500 mM) and $Ce(NO_3)_3$ (20, 100, 250 and 500 mM). The plots show that, for silver, very high limiting currents in excess of 500 mA cm^{-2} are attained at rotation speeds above 2000 min^{-1}. Anodic oxygen production contributes only about 0.5% to the total current production. The limiting current densities for cerium are clearly lower under comparable conditions.

A Levich/Koutecky plot (Fig. 4) for Ag(I) initial concentrations of 200, 300 and 500 mM is an indication of an electrochemical or a chemical-kinetic inhibition of Ag(II) formation [23]. In case of pure mass transport control the product $j_{lim}\omega^{-1/2}$ is independent of $\omega^{1/2}$. However, it should be noted that at Ag(I) initial concentrations of more than 100 mM noticeable amounts of gaseous oxygen were produced nearly to the surface of the disc as a result of the reaction of Ag(II) with water. Gas bubbles adherent to the surface of the RDE disturbed the potential measurements. This does not allow a definite interpretation of the Levich/Koutecky plot.

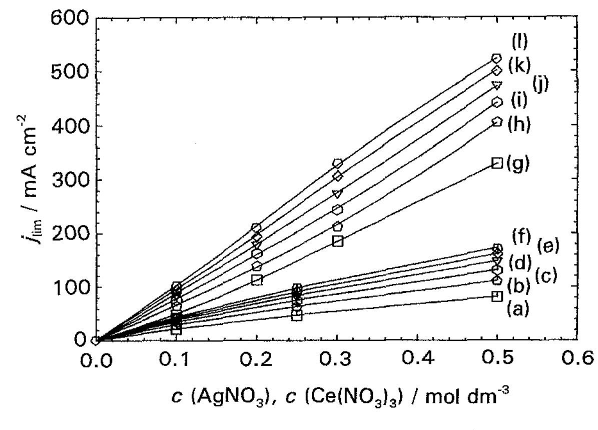

Fig. 3. Limiting current densities of Ag(II) and Ce(IV) generation as a function of the initial concentrations c_0 ($AgNO_3$) and c_0 ($Ce(NO_3)_3$) ($T = 20\,°C$). Rotation speed for Ce (at $E(j_{lim}) =$ 2.16 V vs NHE): (a) 500, (b) 1000, (c) 1500, (d) 2000, (e) 2500 and (f) 3000 min^{-1}; rotation speed for Ag (at $E(j_{lim}) = 2.12$ V vs NHE): (g) 500, (h) 1000 (i) 1500, (j) 2000, (k) 2500 and (l) 3000 min^{-1}.

3.3. *Oxidation of water by Ag(II)*

The reaction of Ag(II) with H_2O for Ag(II) concentrations greater than 10^{-1} mM is described by the following reaction scheme [24]:

$$2Ag^{2+} \rightleftharpoons Ag^+ + Ag^{3+} \tag{4}$$

$$Ag^{3+} + H_2O \rightleftharpoons AgO^+ + 2H^+ \tag{5}$$

$$AgO^+ + H_2O \rightarrow Ag^+ + H_2O_2 \tag{6}$$

$$Ag^{2+} + H_2O_2 \rightarrow Ag^+ + H^+ + \cdot O_2H \tag{7}$$

$$Ag^{2+} + \cdot O_2H \rightarrow Ag^+ + H^+ + O_2 \tag{8}$$

$$4Ag^{2+} + 2H_2O \xrightarrow{k_{II}} 4Ag^+ + 4H^+ + O_2 \tag{9}$$

A second order law was found for overall Reaction 9 [24]:

$$-\frac{d[Ag^{2+}]}{dt} = k_{II}[Ag^{2+}]^2 \tag{10}$$

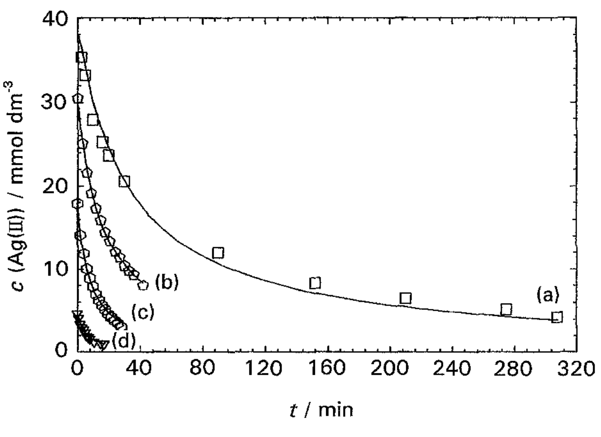

Fig. 5. c (Ag(II)) against time plot for different temperatures, T: (a) 30, (b) 40, (c) 50 and (d) 70 °C.

Table 2. Reaction rate constants k_{II} of water oxidation by Ag(II) in 7 M HNO$_3$

T/°C	$k_{\mathrm{II}}/\mathrm{dm^3\,mol^{-1}\,min^{-1}}$
29.3	0.76
29.5	0.74
39.4	2.06
48.9	6.92
50.6	7.70
69.6	52.32
70.0	47.60

Figure 5 shows a plot of the measured Ag(II) concentrations versus time at various temperatures. The curves were fitted to the measured points using the integral form of Equation 10.

Plotting $-\ln(k_{\mathrm{II}}/k^+)$ against T^{-1} (Fig. 6) produces a straight line from which, according to

$$k_{\mathrm{II}} = A\exp(-E_{\mathrm{a}}(RT)^{-1}) \qquad (11)$$

an activation energy E_{a} of 91 kJ mol^{-1} is obtained (the literature is 99 kJ mol^{-1} [24]).

Leffrang [4] studied the oxidation of water by Co(III) in 3 M H$_2$SO$_4$. The data obtained at 30, 40, 50 and 70 °C are represented in Fig. 7. The curves (solid lines) of Ag(II) destruction in 7 M HNO$_3$ have been traced for comparison. According to

$$c(\mathrm{Ag(II)}) = \frac{1}{(1/c_0^*) + k_{\mathrm{II}}t} \qquad (12)$$

these curves have been constructed using the mean rate constants of Ag(II) destruction determined from Fig. 6. The initial concentrations c_0^* of Ag(II) have the same value as the initial concentrations in the experiments involving Co(III).

4. Discussion of the results

4.1. *Ag(II)*

The total oxidation experiments with Ag(II) show that this mediator is capable of destroying even superchlorinated hydrocarbons, e.g. PCP, PCBs and Lindane, by oxidation. With Co(III) as the mediator, the measured oxidation is incomplete. AgCl precipitated from the solution during chlorinated hydrocarbon destruction with Ag(II) is redissolved, as already mentioned. The following overall reaction takes place:

$$\mathrm{AgCl} + 8\mathrm{Ag}^{2+} + 4\mathrm{H_2O} \longrightarrow 9\mathrm{Ag}^+ + 8\mathrm{H}^+ + \mathrm{ClO_4^-}$$

Perchlorate was found in the electrolyte after the reaction. Leffrang [4] also demonstrated that organic chlorine is oxidized by Co(III) to perchlorate.

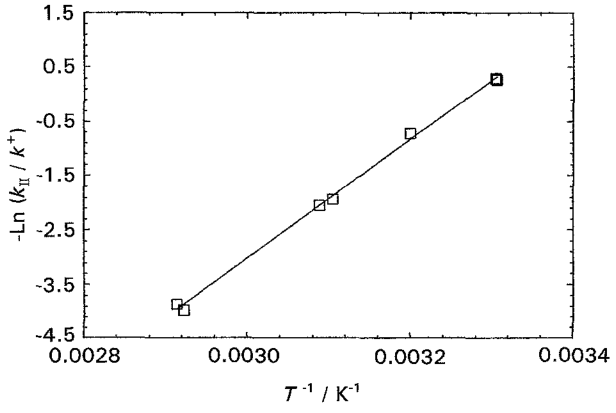

Fig. 6. $-\ln(k_{\mathrm{II}}/k^+)$ plotted against T^{-1} for the determination of E_{a}.

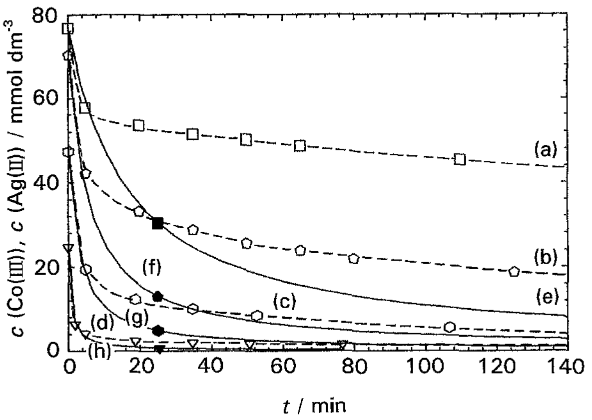

Fig. 7. Destruction rates at different temperatures, T. Key for Co(III): (a) 30, (b) 40, (c) 50 and (d) 70 °C; for Ag(II): (e) 30, (f) 40, (g) 50 and (h) 70 °C.

The experiments with the RDE show that under favourable flow conditions very high current densities of more than 500 mA cm^{-2} are attained in the electrochemical reactor. If on the assumption of a merely transport controlled reaction Equation 3 is simplified to read $j_{\mathrm{lim}} = nF\beta\omega^{1/2}c_0$, an averaged value of 0.488 cm s$^{-1/2}$ is obtained for β. However, to generate Ag(II), a divided cell would have to be used, in contrast to Co(III) generation, which complicates the cell design. If the anodic potential is carefully controlled, anodic water oxidation can be suppressed so that current yields of more than 99% for Ag(II) generation can be achieved. However, current yields are lowered due to the parallel reaction of Ag(II) with water, depending on the reaction rate of the substance to be destroyed. Comparing the rates of destruction of water oxidation by Ag(II) in 7 M HNO$_3$ and Co(III) in 3 M H$_2$SO$_4$ shows that Ag(II) is less stable in aqueous media than is Co(III). This result was expected from the thermodynamic point of view because the oxidation potential of Ag(II) exceeds that of Co(III) by 60 to 150 mV.

4.2. *Co(III)*

Leffrang [4] succeeded in demonstrating that Co(III) is a suitable mediator for total oxidation up to a certain chlorination grade, e.g. tetrachlorinated benzene derivates. Smaller limiting current densities have been achieved than in Ag(II) generation with a maximum current yield of 75%. Studies made on Co(III) generation with the RDE showed that anodic oxidation of water and Co(III) generation are probably simultaneous reactions.

4.3. *Ce(IV)*

Ce(IV) is not suited for total oxidation of superchlorinated organics because the low oxidation potential of Ce(IV)/Ce(III). However, it should be noted in this context that Ce(IV) can be used for selective partial oxidation of organic substances [25–27].

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