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Kinetics of the homogeneous reaction between cerium(IV) and mercury(I) ions in aqueous perchloric acid

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Abstract

The reaction between Ce(IV) and Hg_2^{2+} in 1 M (M = mol dm^{-3}) $HClO_4$ at 25 °C has been shown to be catalysed by light, glass and metallic mercury. The kinetics were therefore studied in Teflon vessels in the dark. The addition of Hg^{2+} ions to mercury(I) stock solutions avoided the formation of colloidal mercury through the disproportionation of Hg_2^{2+}. When these precautions were taken, the reaction was found to be much slower than reported by previous workers. The rate was first order in Ce(IV) but zero order in Hg(I), and the activation energy was 125 kJ mol^{-1}.

Introduction

Despite the fact that aqueous Ce(IV) is an extremely strong oxidising agent [1], its reaction with Hg(I)

$$\mathrm{Ce(IV)} + \frac{1}{2}\mathrm{Hg_2}^{2+} \longrightarrow \mathrm{Ce}^{3+} + \mathrm{Hg}^{2+} \qquad (1)$$

is known to be very slow. This is related to the strong tendency for Ce(IV) to form hydroxy complexes even in concentrated acid solutions [2, 3]; the reactant has therefore been written as Ce(IV). There have been three previous studies of the kinetics of reaction (1) in perchloric acid media. Two groups [4, 5] followed the reaction by titrating the unreacted Ce(IV) with Fe(II), the third [6] measured the Ce(IV) optical absorbance at 360 nm. McCurdy and Guilbault's initial rates [4] were fitted to the equation

$$v = -(\mathrm{d[Ce(IV)]/d}t)_0 = k'[\mathrm{Ce(IV)}][\mathrm{Hg_2}^{2+}][\mathrm{H}^+] \qquad (2)$$

with $k' = 3.8$ l^2 mol^{-2} min^{-1} at 50 °C. From the rates in 2 M $HClO_4$ at 50, 60 and 70 °C they obtained an activation energy of 60.2 kJ mol^{-1}. Combination of these data gives predicted second order rate constants in 1 M $HClO_4$ of 0.87 and 0.58 l mol^{-1} min^{-1} at 30 and 25 °C, respectively, and twice these values in 2 M $HClO_4$.

Casado *et al.* [6] tabulated first order rate constants which were some 40 times greater with 4×10^{-2} M Hg(I) than with 4×10^{-4} M Hg(I). These figures lead to second order rate constants of 0.31 and 0.77 l mol^{-1} min^{-1}, respectively, in 1 M $HClO_4$ at 25 °C, comparable with the extrapolated value from ref. 4. The activation energies were 54.8 and 64.4 kJ mol^{-1} for these two series of runs.

Quite different and variable results are given by El-Tantawy *et al.* [5] for 2 M $HClO_4$ solutions at 30 °C. When the pseudo-first order rate constants in their Table 1 are divided by the concentration of $Hg_2(NO_3)_2$ used, one obtains a second order rate constant of 0.034 l mol^{-1} min^{-1}. For the same conditions, their Table 2 presents a set of second order rate constants k_{II} which average 0.19(5) l mol^{-1} min^{-1} while in their Table 4 this k_{II} is quoted as 7.38 l mol^{-1} min^{-1}. A still different k_{II} value for these conditions, *c.* 0.45 l mol^{-1} min^{-1}, has been plotted in their Arrhenius diagram. However, their activation energy of 65.0 kJ mol^{-1} is comparable with the values of the other two groups.

The homogeneous kinetics of reaction (1) have now been reinvestigated as part of a study into its heterogeneous catalysis by metallic platinum [7]. Several new and important aspects of the reaction were thereby discovered and are presented in the present paper.

Experimental

All solutions were prepared in de-ionised Milli-Q (Millipore) water and were stored in the dark. Stock solutions of 1 M $HClO_4$ made up from BDH 71% AnalaR were employed as solvent for the

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reactants to prevent hydrolysis. All the salts used were of BDH AnalaR grade. Solutions of Ce(IV) were prepared from solid $(NH_4)_2Ce(NO_3)_6$ dried at 80 °C for 4–6 h [8]. Hg(I) solutions were made by dissolving $Hg_2(NO_3)_2 \cdot 2H_2O$ (recrystallised from dilute nitric acid) in perchloric acid containing $Hg(NO_3)_2 \cdot H_2O$ to prevent the disproportionation reaction

$$Hg_2^{2+} \rightleftharpoons Hg(0) + Hg^{2+} \qquad (3)$$

The concentrations of Hg(I) were determined by titration against standard Fe(III) solutions [9]. The Ce(IV) and Hg(I) + Hg(II) solutions were prepared and used on the same day, and stored in the dark until required.

The kinetic experiments were carried out in a thermostat bath controlled to ±0.1 °C, usually at 25.0 °C. Solutions of the reactants and of perchloric acid were thermally equilibrated before mixing in the glass or Teflon conical reaction flask which was kept stoppered. Reactions were followed for at least 8 h. Samples were removed at specific times with a Pasteur pipette and analysed in a Unicam SP 1800 spectrophotometer at 356 nm against a reference cell. Only Ce(IV) absorbed at this wavelength. Calibration experiments showed that solutions of Ce(IV) in 1 M $HClO_4$ obeyed the Beer–Lambert law with small intercepts of less than 0.01 in absorbance. The extinction coefficient of 507 $l\ mol^{-1}\ cm^{-1}$ for solutions of the cerium salt alone increased on the addition of $NaNO_3$, rising to 589 $l\ mol^{-1}\ cm^{-1}$ for a total nitrate concentration of 28 mM. The extinction coefficient employed for any given run depended on the concentration of nitrate ions introduced by the mercury salts into the reaction mixture.

Results and discussion

Representation of results

The experiments were carried out under pseudo-first order conditions with $[Hg_2^{2+}]_0 \gg [Ce(IV)]_0$. Since the Beer–Lambert law was followed, values of ln A (A = absorbance at 356 nm) were plotted against time to obtain the first order rate constant. The data were fitted to straight line plots whose slopes were calculated by a least-squares computer programme. Although runs were often followed for 2 or even 3 days, the rate constants quoted refer to the first day only. The uncertainty limits given are average deviations from the mean for a set of replicate runs.

Effect of light

An early run performed in a clear glass flask over 47 h gave much higher rates during the daytime, in a laboratory illuminated by north-facing windows and fluorescent lights, than during periods of darkness. Figure 1 shows the marked differences in behaviour which were observed. Several other experiments confirmed this effect. Thus higher rates were obtained if samples were returned to the reaction flask after being exposed to the spectrophotometer beam. As Table 1 shows, a set of runs carried out in glass vessels in diffuse daylight gave a first order rate constant of $6.9(\pm 0.7) \times 10^{-4}$ min^{-1} compared with an average of $2.3(\pm 0.6) \times 10^{-4}$ min^{-1} when similar runs were carried out in the dark with the glass vessels painted with black paint (and also in the presence of 0.6 mM Hg(II); see below). In view of this striking evidence of photocatalysis, all subsequent experiments were conducted in blackened reaction vessels with the laboratory lights switched off. It is surprising that the effect of light has not been mentioned by any previous workers. It might well be responsible for some of the marked variations in rate constant reported by the Egyptian group [5].

Effect of glass and atmospheric gases

Six runs were carried out in darkened glass vessels to test the reproducibility of the rates. With solutions containing 0.5 mM Ce(IV), 5.0 mM Hg_2^{2+}, 0.6 mM Hg^{2+} and 1 M $HClO_4$ at 25 °C, the rate constants ranged from 1.2×10^{-4} to 4.2×10^{-4} min^{-1} with a mean and average deviation of $2.3(\pm 0.6) \times 10^{-4}$ min^{-1}. Stirring had no effect on the result nor, as Table 1 shows, did the use of a nitrogen or an oxygen atmosphere. However, the addition of 11.6 g of powdered glass to 80 cm^3 reaction mixture raised k to 10.9×10^{-4} min^{-1}. Although previous investigators of reaction (1) had not noticed this catalytic effect, Grant [10] reported that in concentrated sulfuric acid between 40 and 100 °C the reaction

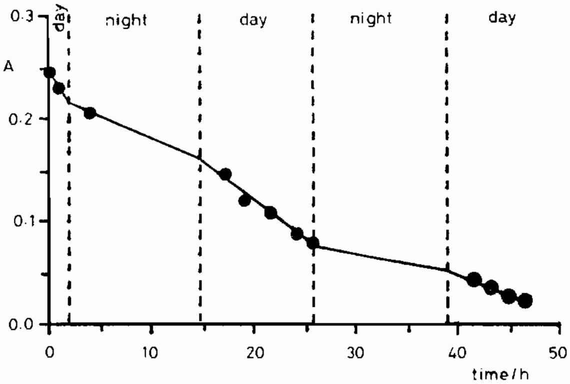

Fig. 1. Absorbance–time profile for a reaction mixture containing 0.4 mM Ce(IV), 5.0 mM Hg_2^{2+} and 1 M $HClO_4$ at 25 °C.

TABLE 1. First order rate constants for the reaction between Ce(IV) and Hg(I) in 1 M $HClO_4$ at 25 °C in the dark, except where stated otherwise

[Ce(IV)] (mM)	[Hg_2^{2+}] (mM)	[Hg^{2+}] (mM)	Vessel	k^a (10^{-4} min^{-1})	Comments
0.4	5.0		glass	6.9(±0.7)	in diffuse daylight
0.4	5.0		glass	5.7, 6.1	samples returned to the flask
0.2	6.2		glass	9.0	samples returned to flask after 5 min exposure to UV
0.5	5.0	0.6	glass	2.3(±0.6)	
0.5	5.0	0.6	glass	2.1, 3.3	solution stirred
0.5	5.0	0.6	glass	2.1(±0.5)	under N_2
0.5	5.0	0.6	glass	1.8	under O_2
0.5	5.0	0.6	glass	10.9	with powdered glass
0.5	2.5	0.24	Teflon	1.8	
1.0	2.4	0.25	Teflon	1.65, 1.80	doubled Ce(IV)
2.0	2.5	0.23	Teflon	1.80	quadrupled Ce(IV)
1.0	1.26	0.26	Teflon	1.8	halved Hg(I)
1.0	5.0	0.27	Teflon	1.55, 1.82	doubled Hg(I)
1.0	2.5	0.25	Teflon	1.6, 1.9	22 mM NH_4NO_3 added
1.0	2.7	0.50	Teflon	1.65	doubled Hg(II)
1.0	2.3		Teflon	2.8	no Hg(II)
1.0	2.5	0.25	Teflon	43	drop of Hg(0) added
1.0	2.6	0.28	Teflon	19.4	at 40 °C

[a] When at least 3 replicate runs were carried out under the same conditions, the mean value of the rate constant and the average deviation from the mean are stated.

$$Ce(IV) + \frac{1}{2}H_2O \longrightarrow Ce^{3+} + H^+ + \frac{1}{2}O_2 \qquad (4)$$

took place on the walls of a glass vessel. Glass is also known to catalyse a number of isotopic exchange reactions in solution [11].

Following the above discovery, all subsequent experiments with reaction (1) were performed in 125 cm^3 Teflon (Nalgene) conical flasks (CP Instrument Co.) wrapped in black PVC tape in the dark.

Effect of concentration variation and temperature

A set of 10 runs, with 0.5–2.0 mM Ce(IV), 1.3–5.0 mM Hg_2^{2+} and 0.23–0.50 mM Hg^{2+} in 1 M $HClO_4$ at 25 °C in Teflon flasks in the dark, yielded first order rate constants ranging from 1.55×10^{-4} to 1.9×10^{-4} min^{-1}, with a mean of $1.74(\pm0.19)\times10^{-4}$ min^{-1}. Variations in the concentrations of Ce(IV) or of Hg(I) by a factor of four, or of Hg(II) by a factor of two, did not alter k significantly. Nor did the presence of 22 mM NH_4NO_3, added in order to test whether the larger concentrations of these ions introduced as part of the reactant salts had any bearing on the rate. The reaction is therefore first order in Ce(IV) and zero order in Hg(I). The latter finding is contrary to the earlier reports summarised in the 'Introduction'. Because adventitious catalytic effects were excluded, our rate constant is also much smaller than the literature values. The comparable figure from the work of McCurdy and Guilbault [4] and Casado *et al.* [6] for a solution containing 5 mM Hg_2^{2+} is *c.* 3×10^{-3} min^{-1}, some 17 times larger than our value.

At 40 °C the rate constant rose to 19.4×10^{-4} min^{-1}, leading to an activation energy of 125 kJ mol^{-1}. This is twice as large as the activation energies reported by all previous workers who had not excluded the catalytic effects of light, glass and colloidal mercury.

Stoichiometry

The finding that the rate of decrease of the Ce(IV) concentration was independent of the concentration of Hg(I) raised the question as to whether the reaction being followed was really the redox reaction (1) between Ce(IV) and Hg(I) or the Ce(IV) oxidation of water as in eqn. (4). The matter was resolved by measuring the loss of Hg_2^{2+} as well as the loss of Ce(IV). Since the standard methods of analysing for Hg(I) were not suitable for the reaction mixtures, a new method was developed based on the gravimetric determination of Hg_2Cl_2 after excess of Ce(IV) had been removed by the addition of Fe(II) [12]. In a run at 25 °C with 1 mM Ce(IV), 2.5 mM Hg_2^{2+}, 0.25 mM Hg^{2+} and 1 M $HClO_4$ in a Teflon flask in the dark, the loss of Ce(IV) after 8 h was found to be 0.09(4) mM and the loss of Hg_2^{2+} 0.05(1) mM. Thus 2 mol of Ce(IV) had reacted with 1 mol of Hg_2^{2+}, as required by eqn. (1).

A series of 4 blank runs was also carried out at 25 °C with 1 mM Ce(IV) and 1 M $HClO_4$, but with no mercury salts, in Teflon flasks in the dark. The Ce(IV) concentration decreased slowly with time to give a first order rate constant of $1.15(\pm 0.11)\times 10^{-4}$ min^{-1} over the first 8 h. The rate constant then decreased by a factor of more than two over the next 24 h. These results are not inconsistent with Casado *et al.*'s rate constant of 5.92×10^{-5} min^{-1} [6] for a 0.4 mM Ce(IV) solution in 1 M $HClO_4$ at 25 °C followed over 3 days. In these experiments the oxidation of water by Ce(IV) was made possible by the fact that the formal potential of the Ce(IV)/Ce(III) couple in 1 M $HClO_4$ is 1.70 V [1], much higher than that of the O_2/H_2O couple (1.23 V). The fall in the equilibrium potential of the cerium couple as Ce^{3+} forms helps to explain the decrease in the rate constant with time. However, in the Ce(IV) and Hg(I) reaction mixtures the mixture potential was only 1.0–1.1 V [7] which is not high enough to oxidise water. Equation (1) therefore represents the stoichiometry of the reaction studied.

Effect of mercury

When one of the above experiments in a Teflon vessel in the dark at 25 °C was carried out in the absence of added Hg(II), the rate constant rose to 2.8×10^{-4} min^{-1}. This increase was attributed to the formation of finely divided mercury produced by the disproportionation reaction (3). Its equilibrium constant

$$K=[Hg^{2+}]/[Hg_2{}^{2+}] \qquad (5)$$

can be calculated from thermodynamic data [1] to be 1.14×10^{-2} at 25 °C. Addition of sufficient Hg(II) to raise the ratio $[Hg^{2+}]/[Hg_2{}^{2+}]$ to *c.* 0.1 in non-complexing solutions should therefore prevent the formation of Hg(0). This procedure was adopted in the present paper.

In another experiment, a drop of metallic mercury (2.165 g) was deliberately added to a magnetically stirred reaction mixture of 105 cm^3 containing 1.0 mM Ce(IV), 2.5 mM $Hg_2{}^{2+}$ and 0.25 mM Hg^{2+} in 1 M $HClO_4$ at 25 °C. This increased the rate constant to 4×10^{-3} min^{-1}. Strong catalysis by an electron-conducting metallic phase was to be expected for a redox reaction like eqn. (1), and is in line with its marked heterogeneous catalysis by a platinum disc covered with a surface layer of mercury [7]. Furthermore, the liquid mercury itself will have been oxidized by Ce(IV) and thereby caused a decrease in the Ce(IV) concentration.

Initial drop in optical absorbance

Throughout this work, a rapid decrease in optical absorbance of *c.* 10% was observed immediately after mixing the reactants provided $[Ce(IV)]_0 < [Hg(I)]_0$. This rapid loss of Ce(IV) occurred independently of the order of mixing the reactants, the shaking or stirring of the reaction mixture, variations in temperature from 17 to 40 °C, the presence or absence of illumination, whether the reaction vessel was glass or Teflon, or whether the Hg(I) nitrate salt was used as supplied or after recrystallisation. Three possible explanations can be given for this phenomenon: (i) the presence in the cerium solutions of a small concentration of a highly reactive species which reacts rapidly with $Hg_2{}^{2+}$ ions; (ii) the presence in the Hg(I) solutions of a small concentration of a reducing impurity which is rapidly oxidised by Ce(IV); (iii) the formation of a complex between Ce(IV) and Hg(I) which absorbs less light at 356 nm than Ce(IV) itself.

Similar initial decreases in Ce(IV) concentration have been reported by other workers. El-Tantawy *et al.* [5] found a consistent drop of about 12% in the Ce(IV) concentration immediately after mixing the Ce(IV) and Hg(I) reactants in perchloric acid. Since they determined the Ce(IV) concentrations by titration with Fe(II), this finding cannot be attributed to spectral changes. An initial drop in the Ce(IV) absorbance, much greater than any expected experimental error, was also observed by El-Tantawy and Rechnitz [13] in a study of the Ce(IV)–oxalic acid reaction in sulfuric acid media. There was evidence here of the formation of an unstable intermediate of Ce(IV) and oxalate. The rapid formation of a complex between the reactants was also postulated by Amjad and McAuley [14] to account for initial absorbance changes in their stopped flow study of the reaction between Ce(IV) and malic acid in perchlorate media. More recently, Thompson [15] reported an initial rapid but not instantaneous consumption of Ce(IV) after it was mixed with an excess of peroxozirconium(IV) complex(es) in perchloric acid. The mean absorbance drops ranged from 12% at 25 °C to 29% at 10 °C. The phenomenon has also been noted in heterogeneously catalysed reactions of cerium(IV). Mills *et al.* [16], studying the oxidation of water by Ce(IV) ions catalysed by thermally activated ruthenium dioxide hydrate, observed an initial reduction step which was ascribed to the charging up of the catalyst particles. An initial drop of about 7% in the Ce(IV) absorbance was also found by the present authors in the catalysis of reaction (1) by platinum [7] and 12% in the catalysis by mercury.

Reaction mechanism

Since reaction (1) has been shown to be first order in Ce(IV) and zero order in Hg(I), the mechanism is likely to involve three steps and a cerium intermediate **I**.

$$\mathrm{Ce(IV)} \xrightarrow{\text{r.d.s.}} \mathbf{I} \qquad (6)$$

$$\mathbf{I} + \mathrm{Hg_2}^{2+} \xrightarrow{\text{fast}} \mathrm{Ce}^{3+} + \mathrm{Hg}^{+} + \mathrm{Hg}^{2+} \qquad (7)$$

$$\mathrm{Ce(IV)\ (or\ \mathbf{I})} + \mathrm{Hg}^{+} \longrightarrow \mathrm{Ce}^{3+} + \mathrm{Hg}^{2+} \qquad (8)$$

Steps (7) and (8) are those postulated by Davies *et al.* [17] for a reaction between Hg_2^{2+} ions and one-equivalent oxidants. A pathway via Hg(0), as suggested by them for two-equivalent oxidants, is less likely in solutions such as ours which contain added Hg^{2+} ions to hinder reaction (3).

The identity of the intermediate **I** is unknown as there is still profound disagreement in the literature as to the type and proportion of Ce(IV) species present in perchloric acid solutions. Thus values for the hydrolysis constant of the reaction

$$\mathrm{Ce}^{4+} + \mathrm{H_2O} \rightleftharpoons \mathrm{CeOH}^{3+} + \mathrm{H}^{+} \qquad (9)$$

vary from 5.2 [18] to 0.2 mol l^{-1} [3] at 25 °C. The percentage of $CeOH^{3+}$ in a 1 mM Ce(IV) solution in 1 M $HClO_4$ could therefore range from 84 to 17% according to different authors. Controversy exists, too, about the presence of $Ce(OH)_2^{2+}$ ions [19] and especially about the existence of Ce(IV) dimers with a Ce–O–Ce skeleton. While some workers have published evidence in their favour [18, 19], others believed their concentrations to be negligible [3, 14]. The intermediate **I** could then be one of the species in dispute or else a complex between Ce(IV) and Hg(I), and it may also be responsible for the rapid initial drop in the cerium absorbance.

In view of Grant's suggestion [10] that the glass catalysis of reaction (4) proceeds by a radical chain mechanism, an attempt was made to detect the presence of paramagnetic species by electron spin resonance using a Varian E-9 spectrometer at 9.518 MHz. However, both a 5 mM Ce^{3+} solution in 1 M $HClO_4$ and an 8-h-old reaction mixture (containing 1 mM Ce(IV), 2.58 mM Hg_2^{2+} and 0.37 mM Hg^{2+} in 1 M $HClO_4$) gave first-derivative spectra closely similar to that of a cell filled with water. In fact, few Ce^{3+} ion spectra have been recorded [20], all of them at temperatures between 4 and 20 K. The reason these ions cannot be detected at 25 °C lies in the strong spin–orbit coupling typically observed in the electronic structure of rare earth ions at room temperature [20]. Thus the failure to observe cerium paramagnetic species by ESR at 25 °C does not rule out the formation of cerium radicals in the reaction mixture.

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