The Oxidation of Mercury(I) by Ozone in Acidic Aqueous Solutions

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The oxidation of mercury(I) (Hg_2^{2+}) by ozone (O_3) in acidic aqueous solutions has been investigated using stopped-flow techniques. The reaction is essentially second order, and the rate was found to be independent of pH and temperature for the conditions employed (pH 1–3, $T = 283$–293 K) with a rate coefficient $k(Hg_2^{2+} + O_3) = (9.2 \pm 0.9) \times 10^6$ M^{-1} s^{-1}. A small first-order component is attributed to the dissociation of Hg_2^{2+}, with $k(Hg_2^{2+} \rightarrow Hg^0 + Hg^{2+}) = 4.5 \pm 3.5$ s^{-1} (pH 1, $T = 293$ K). Elemental mercury is subsequently oxidised by ozone at a rate which appears to approach the diffusion-controlled limit.

Monovalent mercury (Hg_2^{2+}) is stable in acidic solutions and in the absence of ligands which form complexes with divalent mercury. Disproportionation will occur to some extent through equilibrium reaction (1). Values of

$$Hg_2^{2+} \rightleftharpoons Hg^{2+} + Hg^0 \quad (1)$$

2.9×10^{-9} M at 293 K and $(5.2$–$5.3) \times 10^{-9}$ M at 298 K have been reported for the equilibrium constant K_1.[1,2]

Very few measurements have been made of the rates of decomposition and formation of monovalent mercury. Sanemasa[3,4] has measured the rate of decomposition in alkaline solutions, and in acidic solutions containing cyanide. Mechanisms (2)–(4) have been suggested. The

$$Hg_2OH^+ \rightarrow Hg^0 + HgOH^+ \qquad k = 9\ s^{-1} \quad (2)$$

$$Hg_2OH^+ + OH^- \rightarrow Hg^0 + Hg(OH)_2 \qquad k = (2.8 \pm 0.1) \times 10^2\ M^{-1}\ s^{-1} \quad (3)$$

$$Hg_2CN^+ \rightarrow Hg^0 + HgCN^+ \qquad k = 2.2 \times 10^3\ s^{-1} \quad (4)$$

rate of formation of the mercury(I) ion from elemental and divalent mercury is very rapid. A rate constant with a value of $k_{1r} = 5.9 \times 10^8$ M^{-1} s^{-1} has been measured in pulse-radiolysis experiments.[5] The rate of dissociation of the mercury(I) ion in the absence of ligands such as OH^- or CN^- can be calculated from the values of the rate constant of the reverse reaction and the equilibrium constant. Values of 1.7 and 3.1 s^{-1} are obtained using the reported values of K_1 at 293 and 298 K, respectively, which are comparable to the value obtained by Sanemasa[3] in alkaline solutions. In the presence of CN^- the formation of the complex Hg_2CN^+ appears to reduce the stability of the mercury(I) ion.

Oxidation of monovalent mercury may proceed by two different mechanisms. These have been discussed in studies of the oxidation of Hg_2^{2+} by thallium(III)[6] as well as by $Fe(phen)_3^{3+}$, $Ru(bipy)_3^{3+}$ and BrO_3^-.[7] Davies *et al.*[7] observed that one-equivalent oxidants [e.g. $Fe(phen)_3^{3+}$] react directly with Hg_2^{2+} to form Hg^+, which is rapidly oxidised to Hg^{2+}, whereas two-equivalent oxidants (e.g. BrO_3^-) react with Hg^0. The oxidation of elemental mercury was found to be the rate-determining step when two-equivalent oxidants were used.

The present work was initiated with the intention of obtaining information about the reaction between ozone and monovalent mercury and also to estimate the rate of the reaction between ozone and elemental mercury, which is believed to be of importance in the atmospheric cycling of mercury. This latter reaction is known to be rapid[8] but has not been studied in detail.

Experimental

A schematic diagram of the stopped-flow spectrometer is presented in Fig. 1. A quartz stopped-flow reaction cell (Hellma GmbH), comprising a small mixing chamber and an observation tube, with internal dimensions $2 \times 2 \times 10$ mm, was mounted in an aluminium block. Both the block and the tubes transporting the reactant solutions from the driving syringes to the stopped-flow cell were maintained at a constant temperature using a water circulator (Tecam C-400) and a heat exchanger (Tecam 1000). The monitoring light source was a point deuterium lamp (Cathodeon Ltd.), which produces broad-band radiation in the wavelength range 200–350 nm. Ultraviolet light was focussed on the entrance slits of a monochromator (Applied Photophysics Ltd., slit width 1.25 mm, band pass 1 nm) before passing

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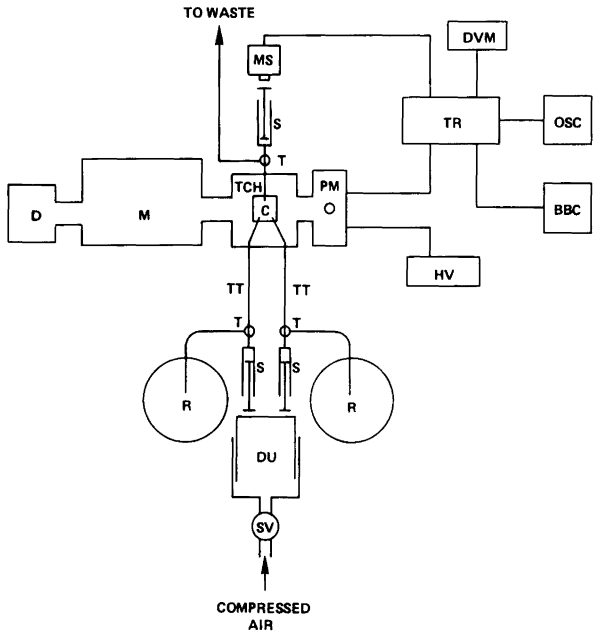

Fig. 1. Schematic diagram of the stopped-flow spectrometer. BBC, BBC microcomputer; C, reaction cell; D, deuterium lamp; DU, syringe drive unit; DVM, digital voltmeter; HV, photomultiplier high-voltage supply; M, monochromator; MS, microswitch; OSC, oscilloscope; PM, photomultiplier tube; R, solution reservoir; S, glass syringe; SV, solenoid valve; T, three-way valve; TCH, thermostatted cell holder; TT, thermostatted PTFE tubing; TR, transient recorder.

through the observation cell (optical pathlength 10 mm) on to the photomultiplier tube (RCA IP28, S-5 response). The output of the photomultiplier tube was developed across a 10 kΩ resistor before being monitored by a fast transient digitizer (Datalab DL905). The system is capable of monitoring reactions with half-lives greater than 5 ms.

Experimental data were transformed to a BBC Master Series microcomputer for subsequent analysis. A suite of BASIC programs has been written to handle kinetic information obtained for any reaction of the general type $aA + bB \rightarrow cC + dD$, where *a, b, c* and *d* are the stoicheiometric coefficients. When more sophisticated data analysis was required, optical density data were transferred to a mainframe computer on which curve-fitting could be carried out using the FACSIMILE chemical modelling package.[9]

Chemicals used were mercury(I) nitrate, >98 %, and perchloric acid, 60 %, both of AnalaR grade (BDH). Ozone was produced by passing oxygen through a silent electrical discharge (Wallace & Tiernan Ltd.) and absorbing the ozone in an aqueous solution. The concentration was calculated from the measured absorbance at 260 nm. Stock solutions of monovalent mercury were prepared by weighing a small amount of mercury(I) nitrate (~10 mg) which was dissolved in 250 ml perchloric acid of desired concentration (0.1–0.001 M). This stock solution was found to be stable for several weeks, but fresh solutions were generally prepared every week. Working solutions were made by diluting aliquots from the stock solution with perchloric acid of appropriate concentration. These solutions were prepared daily. The concentration of the mercury(I) ion was checked by measurement of the optical density at 236 nm.

The extinction coefficient for monovalent mercury was determined by preparing solutions of different concentrations and measuring the optical densities at 236 nm. The value obtained (ε = 26850 M^{-1} cm^{-1}) agrees reasonably well with values reported by other authors (Onat,[10] ε = 28000 M^{-1} cm^{-1}, Fujita *et al.*,[5] ε = 24000 M^{-1} cm^{-1} and Davies *et al.*,[7] ε = 27700 M^{-1} cm^{-1}). The reproducibility between weighing of solid mercury(I) nitrate and measurements of the optical densities (using the extinction coefficient determined in this work) was generally better than ±2 %.

Results and discussion

The reaction between Hg_2^{2+} and O_3 was monitored at 236 nm, where mercury(I) absorbs strongly (ε = 26850 M^{-1} cm^{-1}), or at 260 nm, the wavelength of maximum absorption of ozone (ε = 3292 M^{-1} cm^{-1}).[11] Hg^{2+} is a weak absorber at these wavelengths ($\varepsilon_{260} \approx 0$, $\varepsilon_{236} \approx 40$ M^{-1} cm^{-1}). Concentrations of both reactants were in the range 1×10^{-4} to 1×10^{-5} M. The most satisfactory signals were obtained at concentrations around 3×10^{-5} M. At higher concentrations the decay was too fast to be measured accurately using the present experimental set-up, as significant depletion of the reactants (>90 %) occurred during mixing. This also made it difficult to study the reaction under pseudo-first-order conditions. Lowering the reactant concentrations in an attempt to reduce the reaction rate resulted in an unacceptable degradation of the signal-to-noise ratio. The concentration of divalent mercury after mixing was calculated by comparing the optical density observed on the spectrometer for the original Hg_2^{2+} solution with that obtained after mixing, assuming Hg^{2+} to be the reaction product.

Signals obtained from measurements of the absorption of the mercury(I) ion at 236 nm were of much higher quality than those of ozone at 260 nm. The former were used to obtain estimates of the rate constants using conventional first- and second-order least-squares analyses, as well as from more detailed analysis using the FACSIMILE curve-fitting procedure.

The overall stoicheiometry of the reaction was studied by comparing the relative changes in optical density at 236 and 260 nm when the reaction had gone to completion in the presence of an excess of Hg_2^{2+} and O_3, respectively (pH 1, T = 293 K). In all cases it was clear that the reaction proceeds with a 1:1 stochiometry. This eliminates the involvement of a free-radical chain mechanism due to electron transfer between Hg_2^{2+} and O_3.

A large number of experiments (>500) were performed under varying conditions in an attempt to elucidate the

mechanism of the oxidation of Hg_2^{2+} by O_3. The pH was varied between 1 and 3 by the addition of perchloric acid (0.1–0.001 M). Temperature was varied in the range 283–293 K. Experimental transmittance data were converted into concentration data using a BASIC program based on the Beer–Lambert law and the measured stoicheiometry. Analysis of these concentration data over a wide range of initial reactant concentrations demonstrated that the reaction was essentially second order, with a rate constant of 1×10^7 M^{-1} s^{-1}, which was independent of pH and temperature for the conditions employed. In some studies, notably those where the initial Hg_2^{2+} and O_3 concentrations were similar (i.e. within 10 %), the results obtained when processing the experimental data indicated the presence of an additional reaction mechanism in which the first-order dissociation of Hg_2^{2+} was the rate-determining step. Two possible explanations could account for this behaviour. Either a real first-order component exists, or errors in the measurements of the initial reactant concentrations resulted in the apparent deviation from the second-order kinetics. Assuming the first-order component to be genuine, the following mechanism was postulated to account for the observed oxidation of monovalent mercury by ozone.

$$Hg_2^{2+} \rightleftharpoons Hg^0 + Hg^{2+} \quad (1)$$

$$Hg_2^{2+} + O_3 \rightarrow Hg^{2+} + HgO + O_2 \quad (5)$$

$$Hg^0 + O_3 \rightarrow HgO + O_2 \quad (6)$$

$$HgO + 2H^+ \rightarrow Hg^{2+} + H_2O \quad (7)$$

The relevant rate expression derived for this model is given by eqn. (I). The product in reactions (5) and (6) is assumed

$$-(d[Hg_2^{2+}]/dt) = k_{1f}[Hg_2^{2+}] - k_{1r}[Hg^0][Hg^{2+}] + k_5[Hg_2^{2+}][O_3] \quad (I)$$

to be HgO. This species is not known in solutions and, if formed, can be assumed to hydrolyse according to reaction (7), particularly in the presence of an excess of H^+, so that formation of Hg^{2+} is expected to be rapid.

As a significant fraction of the monovalent mercury was oxidised during mixing (19–65 %), the concentration of Hg^{2+} should have been similar or higher than the concentration of Hg_2^{2+} immediately after mixing. This increase in concentration of Hg^{2+} should have produced a significant decrease in the concentration of elemental mercury by shifting equilibrium (1) to the left. Typical concentrations of Hg^0, calculated from K_1, and the concentrations of monovalent and mercuric mercury were in the range $(1–3)\times10^{-9}$ M.

In the present study it is apparent that reaction (5) is the dominant process. Reaction (1) can only contribute at most a few percent of the total decay of the mercury(I) ion. Consequently the rate constant for reaction (6) cannot be directly determined in this case, although this reaction must be very rapid, approaching the diffusion-controlled limit, if the first-order component due to reaction (1) is to be observed at all. This is consistent with the previous observations of Iverfeldt and Lindqvist.[8]

Table 1. Fitted rate constants for the oxidation of Hg(I) by O_3. $T = 293$ K, pH 1. S.d. is the standard deviation as a ratio, given for each individual curve fit.

Expt. No.	$k_5/10^6$ M^{-1} s^{-1}	S.d.	k_{1f}/s^{-1}	S.d.
930	10.0	0.007	3.30	0.12
931	8.95	0.010	7.33	0.08
932	8.76	0.011	6.41	0.10
936	9.94	0.005	2.66	0.01
937	8.89	0.006	2.75	0.01
943	9.99	0.011	1.85	0.02
977	7.44	0.011	15.2	0.10
979	8.51	0.012	3.30	0.55
983	8.50	0.004	1.31	0.03
984	8.85	0.003	1.93	0.01
985	8.71	0.005	7.93	0.01
986	8.81	0.004	5.26	0.01
989	8.82	0.004	1.25	0.01
990	10.6	0.007	3.68	0.01
991	10.9	0.008	3.10	0.01

To establish the source of the first-order component in the observed decays, a series of experiments was performed, taking extreme care to establish accurate values for initial concentrations of the reacting species. Data sets were analysed using the FACSIMILE software package to establish the most consistent reaction mechanism for the oxidation of monovalent mercury by ozone. The experimental transmittance data were converted into optical densities, and these served as input to the curve-fitting procedure. The starting concentrations were calculated from the optical density measured after mixing (i.e. the first value of the input optical densities) and the concentrations of the reactants in the original solutions. The quality of the fits was assessed by inspecting plots of the predicted optical densities superimposed on the experimental data, as well as the statistical output provided by the FACSIMILE program itself. For almost all the experiments the best fits were obtained when only two reactions were included in the model: reaction (1) in the forward direction and reaction (5).

Table 2. Summary of fitted rate constants for the oxidation of Hg(I) by O_3 at different temperatures and pH values.

T/K	pH	$k_5 \pm \sigma/10^6$ M^{-1} s^{-1}	$k_{1f} \pm \sigma/s^{-1}$	n[a]
293	1	9.2±0.9	4.5±3.5	15
288	1	10.0±2.6	35.7±18.1	4
283	1	9.7±0.6	5.1±3.0	5
293	2	9.6±0.4	3.3±0.04	7
293	3	9.7±3.8	37.4±37.5	5

[a]Number of experiments.

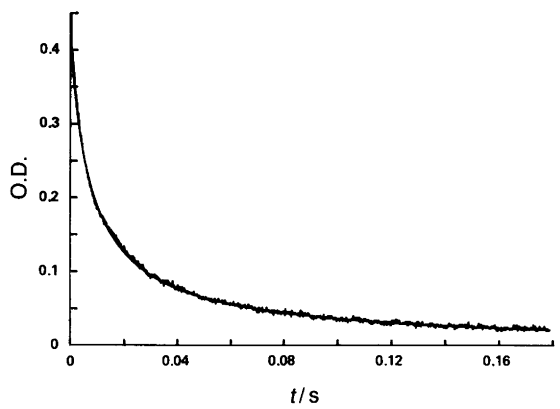

Fig. 2. Predicted and observed optical densities versus time for experiment 984. $[Hg_2^{2+}]_0 = 2.59\times10^{-5}$ M, $[O_3]_0 = 2.48\times10^{-5}$ M, pH 1, $T = 293$ K.

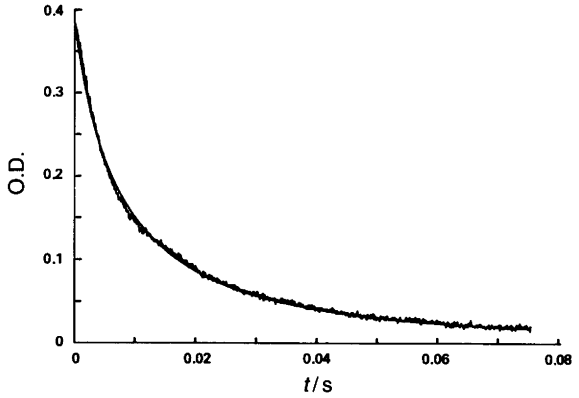

Fig. 3. Predicted and observed optical densities versus time for experiment 959. $[Hg_2^{2+}]_0 = 2.59\times10^{-5}$ M, $[O_3]_0 = 2.84\times10^{-5}$ M, pH 1, $T = 283$ K.

The most consistent set of rate coefficients was obtained from a series of 15 experiments carried out at $T = 293$ K and pH 1. The fitted rate constants k_{1f} and k_5 are presented in Table 1. k_5 showed relatively little variation, with an average value of $(9.2\pm0.9)\times10^6$ M^{-1} s^{-1}. The scatter in k_{1f} reflects the relatively small contribution of the first-order component to the overall decay. The mean value (k_{1f} = 4.5 ± 3.5 s^{-1}) is comparable to that of 1.7 s^{-1} calculated from the literature values for K_1 and k_{1r}. Table 2 summarises the average values obtained for the various experimental conditions. Figs. 2 and 3 show typical predicted fits to the experimental data.

The results presented in Table 2 suggest that the second-order rate coefficient, k_5, shows little variation with pH or temperature for the range of conditions employed. The value of the first-order rate constant, k_{1f}, measured at $T = 288$ K is considerably higher than those measured at 283 and 293 K, which may be due to experimental errors. The second-order rate constant, k_5, is among the highest reported using stopped-flow techniques, which accounts for the experimental difficulties encountered in obtaining reproducible signals.

It is clear from the previous discussion that errors in calculating reactant concentrations immediately after mixing could have a significant influence on the ability of FACSIMILE to fit the experimental data. The largest uncertainty is associated with the extinction coefficient of O_3 at 260 nm, which could be in error by ±4 %. When the starting O_3 concentration was varied to take account of this uncertainty, no systematic trend could be observed. The same results were obtained when varying the input concentrations of the other reactants (i.e. Hg_2^{2+}, Hg^{2+} and Hg^0). It must therefore be concluded that the first-order component is genuine.

The absence of any requirement for the reverse step in the Hg_2^{2+} dissociation equilibrium was unexpected, as the rate constant is known to be large ($k_{1r} = 5.9\times10^8$ M^{-1} s^{-1}).[5] Production of Hg^{2+} via reactions (5) and (7) should retard the production of Hg^0 as the oxidation of Hg_2^{2+} proceeds. The results suggest that reaction (5) proceeds via a relatively long-lived intermediate complex which decomposes slowly to release Hg^{2+}. In this way Hg^{2+} is unable to retard the dissociation of Hg_2^{2+} significantly. For similar reasons it would seem that Hg^0 is rapidly removed by reaction with O_3.

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