

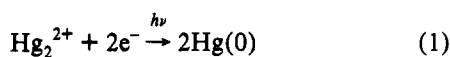
Photocatalytic Self-Generation. Mercury(II) Reduction via Photochemical Reactions of the Dimercury(I) Cation, Hg_2^{2+}

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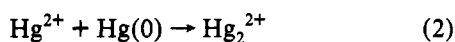
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Received December 23, 1992

Typically irradiation of a photoactive chromophore serves to deplete that material, although cyclic processes in some cases lead to its regeneration. Thus, it is rare for an absorbing substrate to increase in concentration as the result of direct photolysis. In this context, we report an example of "photocatalytic self-generation", a process by which photolysis leads to increased concentrations of the original chromophore, in this case the dimercury(I) cation in aqueous ethanol solution. This effect is achieved via the previously unreported photoreduction of Hg_2^{2+} under these conditions (eq 1, where the reducing equivalents



originate in the organic component of the medium). When this photoprocess is accomplished in the presence of added mercury(II), the atomic mercury(0) produced is apparently trapped via fast electron transfer, leading to photocatalytic formation of Hg_2^{2+} in excess of the initial concentration (eq 2).



The dimercury(I) cation in room-temperature ethanol has an ultraviolet spectrum dominated by an intense broad band centered at 248 nm ($\epsilon_{\text{max}} = (2.82 \pm 0.06) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) which can be assigned to the $^1\Sigma_g^+ \rightarrow \Sigma_u^+(a^1\Sigma_u^+)$ transition³ (Figure 1). The spectrum of Hg_2^{2+} in acidic water is similar with a λ_{max} at slightly higher energy (237 nm, $2.82 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). The frontier orbitals of $\text{Hg}_2(\text{S})_2^{2+}$ (S = solvent) are generated by the interaction of the metal 6s orbitals, and in this transition an electron is promoted from the bonding $3\sigma_g^+$ MO to the antibonding $3\sigma_u^+$ MO. The relative insensitivity of the position and intensity of this band suggests that the solvent interaction with Hg_2^{2+} only moderately affects the metal–metal bond.

So far, scant attention has been paid to light-induced reactions of inorganic Hg(I) compounds. Although UV excitation of the dimercury(I) cation in aerated, aqueous solutions resulted in the formation of Hg_2^{2+} and H_2O_2 , no net reaction was observed under argon.^{4,5}

Upon irradiation of Hg_2^{2+} in argon-flushed ethanol ($\lambda_{\text{ir}} = 254 \text{ nm}$), a monotonic decrease in the absorption band was observed in the 200–280-nm range (Figure 1). An isosbestic point was seen at 280 nm. At higher conversion, a small band became observable (curve e), with maxima at $\lambda = 253$ and 257 nm (Figure 1, inset). This band is assigned to the $^1S_0 \rightarrow ^3S_{1p}$ transition of solvated atomic mercury.^{6–9} As a consequence of its very low

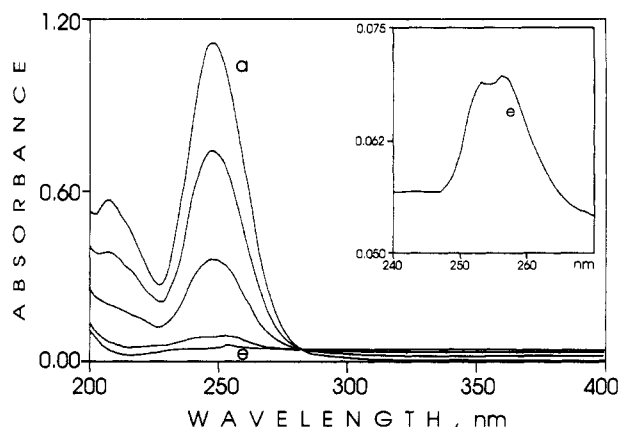


Figure 1. Temporal spectral changes during the photolysis of $4.50 \times 10^{-5} \text{ M Hg}_2(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ in argon-saturated EtOH. Curves a and e are for 0, and 10-min irradiation time ($\lambda_{\text{ir}} = 254 \text{ nm}$). Inset: curve e at higher resolution.

solubility of ($\sim 10^{-7} \text{ M}$),⁷ colloidal mercury forms during the photolysis, as can be recognized by the gradual increase of apparent absorption at longer wavelengths, due to the light scattering by the colloid. The isosbestic point at 280 nm suggests that the particle size does not significantly change. For higher initial $[\text{Hg}_2^{2+}]$ (e.g. $8 \times 10^{-5} \text{ M}$), there is an overall decrease in the absorbance at longer wavelength at later photolysis stages, indicating agglomeration of colloidal metal.^{10–16}

The quantum yield for the disappearance of Hg_2^{2+} was 0.089 ± 0.013 in argon-flushed EtOH ($4.50 \times 10^{-5} \text{ M Hg}_2^{2+}$).¹⁷ The photoinduced reduction of Hg_2^{2+} was also operative in air-saturated EtOH, with a quantum yield of 0.027 ± 0.004 (at $4.50 \times 10^{-5} \text{ M Hg}_2^{2+}$). While in the former system no peroxide was detectable by a semiquantitative test with Merckoquant 10011, in the presence of oxygen a considerable amount of O_2^{2-} (ca. 10^{-4} M , after $\sim 100\%$ conversion) was found. Photoreduction of Hg_2^{2+} was also observed in air-saturated aqueous ethanol (20/80 v/v $\text{H}_2\text{O}/\text{EtOH}$) but photooxidation was seen in air-saturated 80/20 v/v $\text{H}_2\text{O}/\text{EtOH}$. For both systems, the absorption maximum ($\lambda_{\text{max}} = 237 \text{ nm}$) indicated that the Hg(I) was largely present as $\text{Hg}_2(\text{H}_2\text{O})_2^{2+}$. These observations are suggestive of competition between EtOH and O_2 for the reactive intermediate.

The likely primary reaction of the $\sigma\sigma^*$ excited state Hg_2^{2+} is dissociation to reactive Hg^+ radical ions, species previously

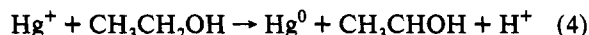
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detected in Hg_2^{2+} pulse radiolysis studies.^{19,20} Formation of this



intermediate was also assumed in the photolysis of aqueous Hg_2^{2+} ; however, in the absence of O_2 , recombination was suggested to occur.⁴ In contrast, the Hg^+ cations can react with ethanol to give atomic mercury (eq 4). While generation of Hg^0 as one end



product is unambiguous on the basis of the spectral changes, the further reactions of the organic radicals in this system are yet unclear. In air-saturated solutions, oxygen can also react with the latter species, giving peroxy radicals²¹ and finally contributing to the peroxide formation.

A possible but unlikely mechanism²² for $\text{Hg}(0)$ formation would be a photoinduced disproportionation of Hg_2^{2+} to $\text{Hg}(0)$ and Hg^{2+} . As a control experiment, the photolysis (254 nm) of Hg_2^{2+} (1.85×10^{-5} M) in air-saturated aqueous ethanol (20/80 v/v) was carried out in the presence of excess Hg^{2+} (4.9×10^{-5} M), under which conditions the absorbance by Hg_2^{2+} is negligible. Remarkably, the result was not quenching or suppression of Hg_2^{2+} photoreactivity; instead an entirely new photoprocess was observed, namely the rapid increase in the concentration of Hg_2^{2+} as the result of irradiating this chromophore (Figure 2). This photocatalytic self-generation proceeded as long as mercury(II) persisted in solution. There was no formation of metallic mercury. A preliminary study with $[\text{Hg}_2^{2+}] = 4 \times 10^{-5}$ M and $[\text{Hg}^{2+}] = 8 \times 10^{-5}$ M in deaerated 20/80 (v/v) $\text{H}_2\text{O}/\text{EtOH}$ indicated a quantum yield of ~ 0.1 for Hg_2^{2+} formation. Photolysis of an analogous solution without added Hg^{2+} gave a comparable quantum yield for Hg_2^{2+} photoreduction, suggesting that the same

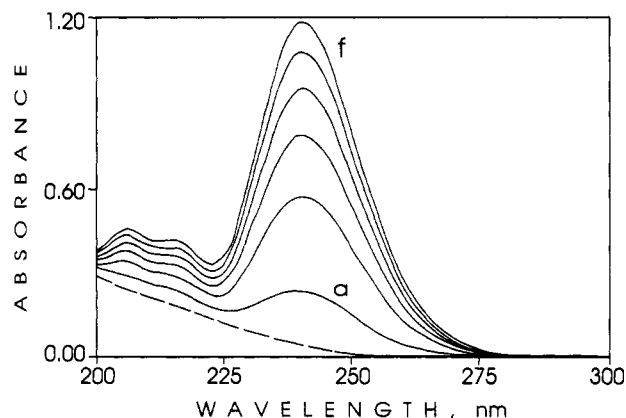


Figure 2. Temporal spectral changes during the photolysis of 1.85×10^{-5} M $\text{Hg}_2(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ and 4.9×10^{-5} M $\text{Hg}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ in air-saturated ethanolic solution containing 20% (by volume) H_2O and 0.01 M HClO_4 . Curves a and f are for 0 and 28-min irradiation time ($\lambda_{\text{ir}} = 254$ nm). The dashed line represents the absorption of the Hg_2^{2+} compound alone.

primary photochemical step is operative. In the absence of other trapping agents, the atomic $\text{Hg}(0)$ formed via photoreduction of Hg_2^{2+} would aggregate to give colloidal particles, but apparently it can also be trapped by a more rapid redox reaction with Hg^{2+} (eq 2, $k \sim 6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ²⁰). The net result with excess Hg^{2+} present is that 2 mol of Hg_2^{2+} will be generated for each mole of this chromophore fragmented and reduced.

The efficiency of the photocatalytic self-generation may prove to be a complex function of reagent concentrations, irradiation intensity, and medium conditions. Further quantitative studies on the versatile photochemistry of Hg_2^{2+} are in progress in our laboratory, with special emphasis on the catalytic and medium effects.

Acknowledgment. Support of this work by BMFT and the Fonds der Chemischen Industrie is gratefully acknowledged. O.H. and P.C.F. thank the Alexander von Humboldt Foundation for fellowship support.

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