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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 Hg₂⁺ 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(0), the atomic mercury(0) produced is apparently trapped via fast electron transfer, leading to photocatalytic formation of Hg₂⁺ in excess of the initial concentration (eq 2).

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\text{Hg}_2^{2+} + 2e^- \rightarrow 2\text{Hg}(0) \tag{1}
\]

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\text{Hg}_2^{2+} + \text{Hg}(0) \rightarrow \text{Hg}_2^{2+} \tag{2}
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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 \(\Sigma_g^+ \rightarrow \Sigma_u^+(a_1^\pi \pi^*)\) transition (Figure 1). The spectrum of Hg₂⁺ in acidic water is similar with a \(\lambda_{\text{max}}\) at slightly higher energy (237 nm, 2.82 \(\times\) 10⁴ M⁻¹ cm⁻¹). The frontier orbitals of Hg₂⁺ (S=solvent) are generated by the interaction of the metal 6s orbitals, and in this transition an electron is promoted from the bonding 3σ_u MO to the antibonding 3π_u MO. The relative insensitivity of the position and intensity of this band suggests that the solvent interaction with Hg₂⁺ 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 Hg₂⁺ and H₂O₂, no net reaction was observed under argon.4,5

Upon irradiation of Hg₂⁺ in argon-flushed ethanol (\(\lambda_{\text{ip}} = 254\) 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 detectable by a semiquantitative test with Merckoquant 1001, indicating agglomeration of colloidal metal.6,10-16

The quantum yield for the disappearance of Hg₂⁺ was 0.089 \(\pm\) 0.013 in argon-flushed EtOH (4.50 \(\times\) 10⁻⁵ M Hg₂⁺).17 The photoinduced reduction of Hg₂⁺ was also operative in air-saturated EtOH, with a quantum yield of 0.027 \(\pm\) 0.004 (at 4.50 \(\times\) 10⁻⁵ M Hg₂⁺). While in the former system no peroxide was detectable by a semiquantitative test with Merckoquant 1001, the presence of oxygen a considerable increase of O₂⁻ (ca. 10⁻⁴ M, after \~100% conversion) was found. Photoreduction of Hg₂⁺ was also observed in air-saturated aqueous ethanol (20/80 v/v H₂O/EtOH) but photooxidation was seen in air-saturated 20/20 v/v H₂O/EtOH. For both systems, the absorption maximum (\(\lambda_{\text{max}} = 237\) nm) indicated that the Hg(I) was largely present as Hg₂(OH)₂⁺. These observations are suggestive of competition between EtOH and O₂ for the reactive intermediate.

The likely primary reaction of the \(\sigma^*\) excited state Hg₂⁺ is dissociation to reactive Hg⁺ radical ions, species previously

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(8) Calvert, J. G.; Pitts, J. N. Photochemistry; John Wiley: New York 1964,


(17) The incident light intensity was determined with a Polytec pyroelectric radiometer, calibrated and equipped with an RP-345 detector. Controlling measurements with ferrioxalate actinometry gave identical results.

detected in Hg$^{2+}$ pulse radiolysis studies.\textsuperscript{19,20} Formation of this intermediate was also assumed in the photolysis of aqueous Hg$^{2+}$; however, in the absence of O$_2$, recombination was suggested to occur.\textsuperscript{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 radicals and finally contributing to the peroxide formation.

A possible but unlikely mechanism\textsuperscript{22} for Hg(0) formation would be a photoinduced disproportionation of Hg$^{2+}$ to Hg(0) and Hg$^{+}$. As a control experiment, the photolysis (254 nm) of Hg$^{2+}$ (1.85 $\times$ 10$^{-5}$ M) in air-saturated aqueous ethanol (20/80 v/v) was carried out in the presence of excess Hg$^{2+}$ (4.9 $\times$ 10$^{-5}$ M), under which conditions the absorbance by Hg$^{2+}$ is negligible. Remarkably, the result was not quenching or suppression of Hg$^{2+}$ photoreactivity; instead an entirely new photoprocess was observed, namely the rapid increase in the concentration of Hg$^{2+}$ 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 [Hg$^{2+}$] = 4 $\times$ 10$^{-5}$ M and [Hg$^{2+}$] = 8 $\times$ 10$^{-5}$ M in deaerated 20/80 (v/v) H$_2$O/ EtOH indicated a quantum yield of $\sim$0.1 for Hg$^{2+}$ formation. Photolysis of an analogous solution without added Hg$^{2+}$ gave a comparable quantum yield for Hg$^{2+}$ photoreduction, suggesting that the same primary photochemical step is operative. In the absence of other trapping agents, the atomic Hg(0) formed via photoreduction of Hg$^{2+}$ 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$^{8}$ M$^{-1}$ s$^{-1}$). The net result with excess Hg$^{2+}$ present is that 2 mol of Hg$^{2+}$ 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$^{2+}$ are in progress in our laboratory, with special emphasis on the catalytic and medium effects.

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