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Photooxidation of the Diaquodimercury(I) Cation

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The cation Hg_2^{2+} may be regarded as the simplest binuclear complex that contains a metal–metal single bond. This bond consists of an electron pair in a σ-bonding MO which is formed by the interaction of the 6s orbitals of both mercury ions [1]. While in numerous studies it has been shown that metal–metal single bonds of binuclear transition metal complexes can be split homolytically by $\sigma\sigma^*$ excitation [2, 3], the photochemistry of Hg_2^{2+} is virtually unexplored to our knowledge. We present here the first results on the photoreactivitiy of Hg_2^{2+}. Our study was stimulated partially by Mason [1], who assigned electronic transitions to absorption bands in the spectrum of $[Hg_2(H_2O)_2]^{2+}$ and raised the question of whether the $\sigma\sigma^*$ state of the Hg_2^{2+} moiety is an unbound state which may lead to a dissociation.

The electronic absorption spectrum of $[Hg_2(H_2O)_2]^{2+}$ [1] in diluted $HClO_4$ (0.01 M) is dominated by a very broad and intense band in the UV (Fig. 1) at $\lambda_{max} = 237$ nm ($\epsilon = 27600$). The complex did not show any luminescence ($\lambda_{exc} = 250$ nm) in deaerated aqueous solutions at room temperature or in ethanol glasses at 77 K. Light absorption by aqueous $[Hg_2(H_2O)_2]^{2+}$ was not associated with a permanent chemical change if the solution was saturated with argon. However, in air-saturated solutions a rather efficient photolysis was observed, as indicated by the spectral changes which accompanied the irradiation (Fig. 1). The UV band of $[Hg_2(H_2O)_2]^{2+}$ disappeared; Hg(I) was apparently photooxidized to Hg(II). The spectrum of the photolyzed solution was very similar to that of $Hg(ClO_4)_2$ in diluted $HClO_4$ (~0.01 M). The formation of Hg(II) was confirmed by a qualitative analysis. While the addition of iodide to aqueous $[Hg_2(H_2O)_2]^{2+}$ (~10^{-4} M) was accompanied by the precipitation of greenish yellow Hg_2I_2, the photolyzed solution yielded a red precipitate of HgI_2. The irradiation led also to an increase in the pH. In addition, H_2O_2 was formed as a photoproduct. It was detected by a qualitative test for peroxide (Merckoquant 10011). The progress of the photolysis was monitored by measuring the extinction at the band maximum at 237 nm where the absorption of the photoproduct is negligible. The quantum yield for the disappearance of $[Hg_2(H_2O)_2]^{2+}$ was $\phi = 0.05$ at $\lambda_{irr} = 254$ nm.

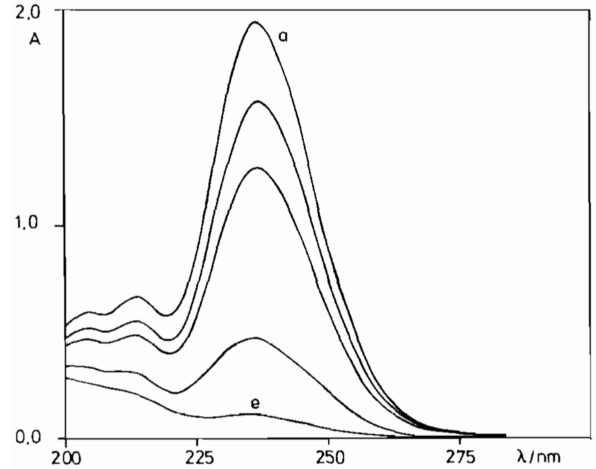

Fig. 1. Spectral changes during the photolysis of 7.03×10^{-5} M $Hg_2(ClO_4)_2 \cdot 4H_2O$ in 0.01 M $HClO_4$ at (a) 0, 1, 2, 5, and (e) 10 min irradiation time, with white-light irradiation (Osram HBO 100 W/2 lamp) and a 1-cm cell.

The frontier orbitals of $[Hg_2(H_2O)_2]^{2+}$ are generated by the σ interaction of the 6s orbitals of mercury [1]. The metal–metal bond of Hg_2^{2+} is formed by the occupation of the bonding $3\sigma_g^+$ orbital. The $3\sigma_u^+$ orbital is the corresponding antibonding combination. The intense absorption band of $[Hg_2(H_2O)]^{2+}$ at $\lambda_{max} = 237$ nm is then assigned to the ${}^1\Sigma_g^+ \rightarrow \Sigma_u^+(a^1\Sigma_u^+)$ transition which involves the promotion of an electron from the $3\sigma_g^+$ to the $3\sigma_u^+$ orbital [1]. On the basis of our observations, we suggest that the $\sigma\sigma^*$ state of $[Hg_2(H_2O)_2]^{2+}$ is indeed dissociative:

$$Hg_2^{2+} \xrightarrow{h\nu} 2Hg^+$$

In the absence of oxygen, the Hg^+ radical ions regenerate Hg_2^{2+}. In air-saturated solutions, Hg^+ is intercepted by oxygen

$$2Hg^+ + O_2 + 2H^+ \longrightarrow 2Hg^{2+} + H_2O_2$$

As an alternative our results can be also explained by another mechanism which in our opinion is less likely to be operative. Electronically excited (*) $[Hg_2(H_2O)_2]^{2+}$ may be oxidized directly by oxygen

$$Hg_2^{2+*} + O_2 + 2H^+ \longrightarrow 2Hg^{2+} + H_2O_2$$

However, the absence of any luminescence of $[Hg_2(H_2O)_2]^{2+}$ [4]† supports the suggestion that the primary photochemical step involves a homolytic cleavage of the metal–metal bond [5]. More experi-

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†Some Hg(I) halides such as Hg_2Cl_2 show a strong orange or green luminescence [4]. However, this emission is apparently a solid-state effect and not a molecular property.

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mental work, especially the detection of Hg^+ as intermediate, is required to distinguish between both mechanisms. Further studies of this subject are in progress.

Acknowledgements

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