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Photodisproportionation of Hg_2^{2+}

Horst Kunkely, Arnd Vogler *

Institut für Anorganische Chemie, Universität Regensburg, D-93040 Regensburg, Germany

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Abstract

The photolysis of Hg_2^{2+} in tetrahydrofuran induced by metal–metal $\sigma\sigma^*$ excitation leads to the generation of Hg^0 and Hg^{2+}. The quantum yield of this photodisproportionation is $\phi = 0.03$ at $\lambda_{irr} = 254$ nm. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

The disproportionation of metal ions is a fundamental process. In very simple systems two identical metal ions disproportionate to one unit higher and one unit lower than the original oxidation state. In principle, such a reaction should also occur photochemically. Attractive candidates are binuclear complexes which contain a covalent metal–metal bond. However, such M–M bonds are generally split homolytically by $\sigma\sigma^*$ excitation. This occurs, for example, in binuclear carbonyl complexes [1–3]:

$$(OC)_nM{-}M(CO)_n \xrightarrow{h\nu} 2{\cdot}M(CO)_n \quad (1)$$

In this case subsequent addition reactions at the photogenerated metal carbonyl radicals can induce a thermal disproportionation

$$^{\cdot}M(CO)_n + L \rightarrow {}^{\cdot}M(CO)_nL \quad (2)$$

$$^{\cdot}M(CO)_nL + {}^{\cdot}M(CO)_n \rightarrow M(CO)_nL^+ + M(CO)_n^- \quad (3)$$

This observation raises the question if a genuine disproportionation of a completely symmetric M–M bond can also occur as a primary photoprocess: $M{-}M \xrightarrow{h\nu} M^+M^-$. While this possibility has been recognized [2,3] it has apparently not yet been confirmed experimentally. In this context we wish to report our present observation of the heterolytic photocleavage of Hg_2^{2+}. This binuclear cation is an intriguing analog of H_2 since its metal–metal bond is essentially based on the overlap of Hg 6s orbitals [4,5].

2. Results

It has been previously shown that $\sigma\sigma^*$ excitation of aqueous Hg_2^{2+} leads to the homolysis of the Hg–Hg bond yielding two Hg^+ ions [5,6]. These radicals can be intercepted and oxidized by oxygen. In al-

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[*] Corresponding author. Fax: +49-941-943-4488.
E-mail address: arnd.vogler@chemie.uni-regensburg.de (A. Vogler).

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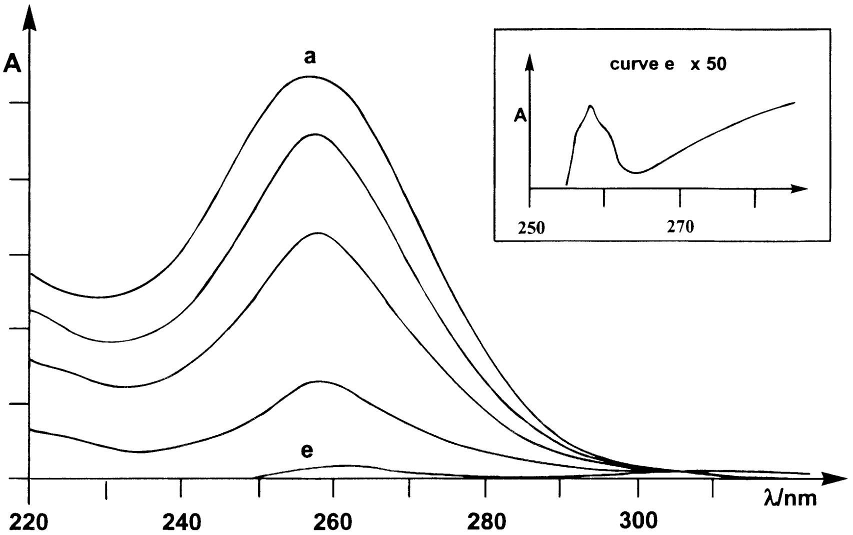

Fig. 1. Spectral changes during the photolysis of 8.87 × 10^{-5} M $Hg_2(ClO_4)_2$ in THF at room temperature after (a) 0 s, (b) 15 s, (c) 30 s, (d) 60 s, and (e) 120 s irradiation times with white light (Osram HBO 200 W/2 lamp), 1 cm cell.

coholic solution they are reduced to elemental mercury [5,7]. In tetrahydrofuran (THF) as the solvent the photolysis takes a different course. Light absorption by the spin-allowed $\sigma\sigma^*$ band [4,5] ($\lambda_{max} = 257$ nm, $\varepsilon = 24100$ dm^3 M^{-1} cm^{-1}) of Hg_2^{2+} is associated with spectral changes shown in Fig. 1. These variations are essentially based on the conversion of Hg_2^{2+} to elemental mercury which finally separates as shiny droplets. Owing to the residual solubility of atomic mercury in almost all solvents ($c \sim 10^{-7}$) the absorption of mercury atoms ($\lambda_{max} = 256$ nm) [5,7] can be recognized in the photolyzed solution (Fig. 1). Moreover, mercury atoms add also to Hg_2^{2+}. The formation of small amounts of Hg_3^{2+} are indicated by the appearance of a weak absorption at $\lambda_{max} = 315$ nm (Fig. 1) and a concomitant emission at $\lambda_{max} = 645$ nm [5,8]. After the photolysis of Hg_2^{2+} in THF was continued to completion the solution is separated from elemental mercury. This solution contains Hg^{2+} which absorbs only slightly in the UV and does not show any characteristic band. However, upon addition of dithizone, Hg^{2+} is converted to the well known complex $Hg(dithizonate)_2$ with $\lambda_{max} = 485$ nm ($\varepsilon = 70500$ dm^3 M^{-1} cm^{-1}) [9,10] which is used for the spectrophotometric identification and determination of Hg^{2+}. The analysis shows that roughly one half of the photolyzed Hg_2^{2+} is recovered as $Hg(dithizonate)_2$. It follows that the photolysis proceeds according to the equation:

$$Hg_2^{2+} \xrightarrow{h\nu} Hg^0 + Hg^{2+} \qquad (4)$$

The progress of the photoreaction is monitored by measuring the decrease of absorption at $\lambda = 257$ nm. The quantum yield for the disappearance of Hg_2^{2+} is $\phi = 0.03$ at $\lambda_{irr} = 254$ nm.

3. Discussion

The photodisproportionation of Hg_2^{2+} seems to be the first genuine case of a heterolytic photocleavage of a metal–metal bond. The existence of zwitterionic excited states of the type M^+M^- can be derived from the hydrogen molecule. Ionic excited states of H_2 had been discussed more than 60 years ago [11–13]. Quite recently, spectroscopic evidence for a zwitterionic excited state of $Mo_2Cl_4(PMe_3)_4$ has been reported [14]. Generally, the zwitterionic states occur at rather high energy but approach the singlet biradical states ${}^\cdot MM^\cdot$ if the corresponding orbitals are only weakly coupled. In the case of the hydrogen molecule or a metal–metal σ-bond this requirement is met when the H–H or M–M bond is sufficiently stretched. Even then a real disproportionation would not occur since both zwitterionic states $M_a^+M_b^- \leftrightarrow M_a^-M_b^+$ are degenerate in a symmetric system. However, when the environment of the M–M bond becomes asymmetric a real photodisproportionation may indeed take place. In organic molecules such a spontaneous formation of zwitter ions has been described as 'sudden polarization' [15,16]. In a simple molecule or ion of the type M–M an asymmetric environment for a sudden polarization could be induced by the solvent or counter ions. While it apparently occurs in the case of Hg_2^{2+} in THF the reason for this sudden polarization is yet unknown. The different behavior of Hg_2^{2+} in aqueous solution and THF could be related to the strength of the Hg–Hg bond in both solvents. According to the shift of the $\sigma\sigma^*$ absorption from 235 nm in water [6] to 257 nm in THF the metal–metal bond seems to be distinctly weaker in THF. The concomitant extension of the Hg–Hg bond might favor the photodisproportionation (see above). Although our observations are consistent with a dismutation as primary photoreaction a definitive proof for this mechanism is yet missing. However, our observations may stimulate further studies, in particular calculations and time-resolved spectroscopy, to solve this problem. Quite recently, trinuclear complexes of the type $Os_3(CO)_{10}$(α-diimine) have been shown to undergo photochemical zwitterion formation [17]. In this case, the diimine ligand which is coordinated only to one metal center certainly facilitates the generation of the zwitterion.

In the context of the present study it should be pointed out that a photodisproportionation of metal compounds can also take place by a different mechanism. In binuclear complexes both metals may be not connected only by a direct metal–metal bond but also by a suitable ligand which mediates the electronic interaction of both metals in the same oxidation state. If the metal is simultaneously reducing and oxidizing a metal-to-metal charge transfer (MMCT) absorption can be observed. The complex $[(NH_3)_5Os^{III}–CN–Os^{III}(NH_3)_5]^{5+}$ is an appropriate example [18]. MMCT excitation leads then to a disproportionation by definition

$$[(NH_3)_5Os^{III}\text{–CN–}Os^{III}(NH_3)_5]^{5+} \xrightarrow{h\nu} [(NH_3)_5Os^{IV}\text{–NC–}Os^{II}(NH_3)_5]^{5+} \quad (5)$$

However, the binuclear complex is not light sensitive since a rapid back electron transfer apparently restores the original complex. Some other complexes which contain the Fe^{III}–O–Fe^{III} moiety undergo indeed a photodisproportionation to $Fe^{IV}{=}O^{2+}$ and Fe^{2+} [19–21], but the nature of the photoactive excited state is not quite clear [21].

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