Inorganica Chimica Acta, *221* (1994) 79–84

Photoredox chemistry of iodomercurate(II) complexes in acetonitrile

Ottó Horváth*

Department of General and Inorganic Chemistry, University of Veszprém, POB 158, H-8201 Veszprém (Hungary)

Arnd Vogler*

Institut für Anorganische Chemie, Universität Regensburg, Universitätsstrasse 31, 93053 Regensburg (Germany)

(Received October 20, 1993; revised February 3, 1994)

Abstract

The stepwise formation constants of the kinetically labile iodomercurates(II) in acetonitrile are relatively high; even for the tetraiodo complex a value of 1220 was determined. Ligand-to-metal charge transfer transitions of different energies and intensities feature the ultraviolet spectra of these compounds. Photolysis of their CH_3CN solution results in the formation of Hg(I) and $I^{\bullet}$ or I_2^- as primary products. The quantum yields of this reaction are 0.8 and 0.41 for HgI_3^- and HgI_4^{2-}, respectively, at 355 nm excitation in a deaerated system. Due to the very efficient back reaction HgI_2 does not undergo permanent photoredox change, while irradiation of tri- and tetraiodomercurate(II) complexes leads to the accumulation of I_2 and I_3^-. The efficiencies of these overall reactions are rather low (0.07 and 0.02 at 333 nm), compared to the primary quantum yields, because of the fast reconversion.

Key words: Photochemistry; Redox reactions; Mercury complexes; Iodo complexes

Introduction

Mercury(II) cation possesses filled d and empty s and p subshells, thus its chemical features are similar to both transition and main-group metal ions. Formation of kinetically labile complexes with halo and pseudohalo ligands in water and different non-aqueous solvents is characteristic for Hg^{2+}, like other metal ions with $(n-1)d^{10}ns^0$ electronic configuration [1, 2]. Ligand-to-metal charge transfer transitions determine the spectral features of the halomercurate(II) complexes. The corresponding bands in their absorption spectra significantly depend on the coordination number [3]. The individual photochemical activities of the different $HgX_n^{(n-2)-}$ complexes can also be strongly affected by n.

Inorganic mercury(II) complexes were photochemically studied many years ago [4], but their further investigation in this respect has been rather recently started [5]. In all cases studied so far, the LMCT reaction was the primary photochemical step, resulting in the reduction of the Hg(II) center [6, 7]. Similarly, photoinduced reduction of mercury(II) was observed in the metal-to-metal charge transfer excitation of the $[(NC)_2Hg^{II}NCFe(CN)_5]^{4-}$ and $[Hg^{II}Co_2^{I}(CN)_{10}]^{6-}$ complexes [8]. In flash photolyses investigation of HgX_2 and HgX_4^{2-} (X = Cl, Br, I) in aqueous solutions formation of X_2^- radical ions was detected [9], but no quantum yield determination by either flash or CW irradiation was carried out.

Since aprotic solvents cannot strongly coordinate to mercury(II), the stability of the halomercurate(II) complexes in them are much higher than in protic media [1, 3]. Thus, a relatively small change in the ligand concentration can significantly influence the complex equilibria of halomercurates(II) in solvents such as acetonitrile. The aim of our work was to study the light induced reactions of $HgI_n^{(n-2)-}$ complexes, in order to determine the role of the coordination number in the photoactivity and the elementary steps of the reaction mechanism.

Experimental

Dry spectrograde acetonitrile was applied as solvent. Stock solutions of reagent grade and properly dried HgI_2 and Et_4NI were used to prepare the solutions of desired metal and ligand concentrations for spectral

---

*Authors to whom correspondence should be addressed.

0020-1693/94/$07.00
SSDI 0020-1693(94)03950-S

and photochemical measurements. Similarly pure iodine served for calibration.

An Uvikon 860 double-beam spectrophotometer was utilized for taking absorption spectra in 1 cm and 1 mm quartz cuvettes. Typically 2.5 cm^3 solutions were irradiated in 1 cm cells at room temperature. Deaerated samples were prepared by purging with CH_3CN-saturated Ar for at least 1 h before the photolysis. The light source was a Hanovia Xe/Hg 977 B-1 (1000 W) lamp equipped with a Schoeffel GM 250-1 monochromator. A Polytec pyroelectric radiometer calibrated and equipped with an RkP-345 detector was applied for determination of the incident light intensity. Samples used for quantum yield measurements absorbed nearly 100% at the excitation wavelengths.

Laser flash photolysis experiments were carried out with a system described elsewhere [10]. For excitation 266 and 355 nm pulses of *c*. 15 ns duration were utilized in these measurements. Aberchrome-540 was employed as an actinometer at 355 nm [11]. A constant absorbance of 0.4 was adjusted in the samples for actinometry at this wavelength.

Results

Spectroscopy and equilibria

The UV absorption spectrum of HgI_2 in CH_3CN displays a relatively broad band at 265–267 nm and a more intense peak at 211 nm (Fig. 1, curve a). The spectrum does not obey Beer's law as was earlier experienced [12]. Addition of iodide ion (in 10^{-5} M increments) to a 10^{-4} M solution of HgI_2 gives rise to new absorption bands at 217, 256 and 301 nm, and a shoulder at 340 nm. The absorbance increases at these wavelengths are proportional to the amount of added I^- ions (up to about 60% of the HgI_2 concentration) (Fig. 1). The iodide ions added are quantitatively coordinated by the diiodo species, because the stepwise formation constant of HgI_3^-, K_3, in CH_3CN is rather high (*c*. 10^8 M^{-1}) [13]. Thus, using pure CH_3CN as reference solution, the molar absorbance of the triiodo complex can be directly determined from the slope of the A_{301} versus C_I(added) plot (not shown), which is the difference between the extinction coefficients of HgI_3^- and HgI_2 at 301 nm. A similar relationship is valid for the other band maximum (256 nm). The extinction coefficients of the different iodomercurate(II) complexes in acetonitrile at the absorption maxima are summarized in Table 1.

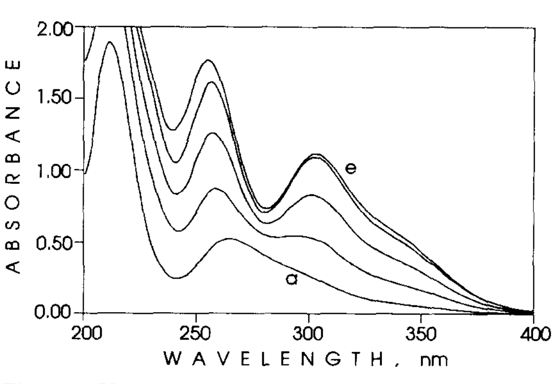

Fig. 1. UV absorption spectra changes (a→e) obtained upon addition of iodide (in 2×10^{-5} M increments) to HgI_2 (10^{-4} M) in acetonitrile at room temperature, $l=1$ cm, reference solution = pure CH_3CN.

Upon increasing the amount of added iodide (C_I(added) > C_{HgI_2}), new bands arise at 273 and 329 nm, while the peak at 301 nm disappears, resulting in two isosbestic points (Fig. 2). This is a clear indication that mercury(II) is distributed between two complexes, i.e. HgI_3^- and HgI_4^{2-}, in equilibrium. The spectra shown in Fig. 2 were measured against reference solutions which contained the same amount of added iodide as the samples. Thus, due to the absorbance of I^-, the shape of the spectra involves the effect of the iodide imbalance (as a consequence of the coordination in the samples, decreasing [I^-]) at wavelengths below 280 nm. This effect was taken into account at the determination of the molar absorbance for HgI_4^{2-} at 273 nm. At high concentrations of excess iodide, its very strong absorbance hampers the measurement of

TABLE 1. Band maxima and molar absorbances of iodomercurate(II) complexes in acetonitrile

Complex	λ_{max} (nm) (ϵ (M^{-1} cm^{-1}))	
HgI_2	211 (1.9×10^4)	265–267 (5.2×10^3)^a
HgI_3^-	217 (3.5×10^4)	256 (2.28×10^4)
	301 (1.61×10^4)	340 (8.0×10^3)^b
HgI_4^{2-}	273 (3.79×10^4)	329 (2.24×10^4)

^{a}Molar absorbances for HgI_2 are estimated in the 0.5–4×10^{-4} M range, because no satisfactory Beer's law plot was obtained for them. ^{b}Shoulder.

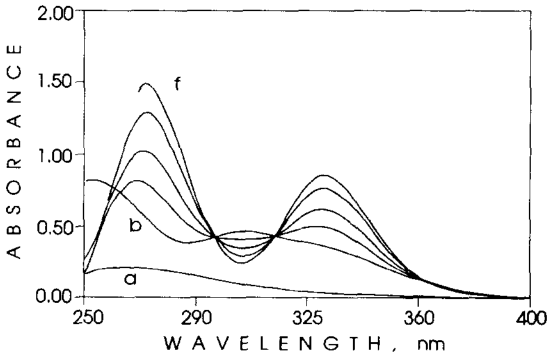

Fig. 2. UV spectra changes obtained upon addition of (a) 0, (b) 2.14×10^{-4}, 4.09×10^{-4}, 1.46×10^{-3}, 3.76×10^{-3} and (f) 4.81×10^{-2} M iodide to HgI_2 (4×10^{-4} M) in acetonitrile at room temperature, $l=0.1$ cm. The same amounts of iodide were added to the reference solution.

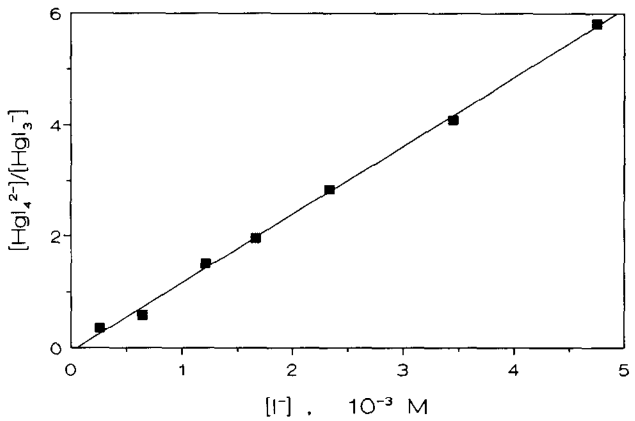

Fig. 3. Concentration ratio of tetra- and triiodomercurate(II) vs. free-ligand concentration in acetonitrile at room temperature ($C_{Hg(II)}=4\times10^{-4}$ M).

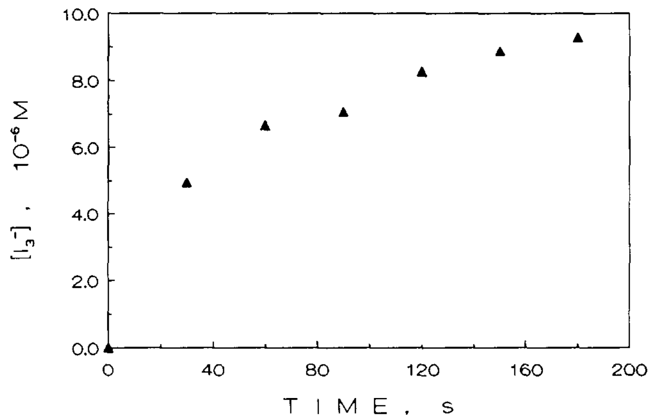

Fig. 4. Accumulation of I_3^- during the photolysis of 4×10^{-4} M HgI_4^{2-} in argon-saturated CH_3CN at 333 nm irradiation wavelength ($[I^-]=4\times10^{-2}$ M).

the spectra below 268 nm (Fig. 2, curve f). Nearly 100% conversion to tetraiodo complex can be achieved by addition of 0.02 M excess I^-. Taking the molar absorbance of this system at 329 nm as that of HgI_4^{2-} and knowing the extinction coefficient of HgI_3^- at the same wavelength, the stepwise formation constant of the former species can be determined, using the absorbances at different $[I^-]$ values. On the basis of the equation of the complex formation constant (eqn. (1)) the concentration ratio of HgI_4^{2-} and HgI_3^- ($R=[HgI_4^{2-}]/[HgI_3^-]$) linearly depends on $[I^-]$.

$$K_4=[HgI_4^{2-}]/([HgI_3^-][I^-]) \qquad (1)$$

After calculation of the actual concentrations of tri- and tetraiodo species at various values of $[I^-]$, the slope of the R versus $[I^-]$ plot (Fig. 3) gives K_4 (1220 ± 80 M^{-1}, at 0.5–5 × 10^{-3} M ionic strength). This is somewhat higher than the value determined by Coetzee *et al.* with polarography (631 M^{-1}) [13], but differs significantly from the earlier results obtained by solubility (75 M^{-1}) [14] and conductometry (40 M^{-1}) [15]. A similar tendency was experienced in the case of $HgCl_4^{2-}$ [16], indicating that formation constants determined on the basis of different physicochemical properties can strongly deviate from each other in these systems.

Continuous photolysis

Irradiation of HgI_2 in argon-saturated CH_3CN (4×10^{-4} M) did not cause any permanent chemical change either at 254 or 313 nm excitation wavelength. A similar experience was found with an aerated solution.

Addition of iodide to the system to give 60% HgI_3^- and 40% HgI_2 ($C_{Hg(II)}=4\times10^{-4}$ M) led to a significant change in the photochemical behavior; formation of I_2 was detected upon irradiation in the 313–333 nm range. The concentration of the iodine produced was spectrophotometrically monitored at 400 nm, where the absorbance of the Hg(II) complexes is negligible. The rate of the iodine production slowed down relatively fast as can be seen in Fig. 4. This phenomenon indicates a rather efficient back reaction, which is confirmed by the fact that reconversion of the irradiated solution containing *c.* 2×10^{-5} M I_2 reached more than 50% overnight. Thus, the quantum yield for the iodine production was determined from the initial slope of the $[I_2]$ versus irradiation time plot. In argon-saturated solution a value of 0.065 was obtained. Presence of air caused a decrease in the quantum yield ($\Phi=0.035$) at 333 nm.

In solution containing 4×10^{-2} M Et_4NI and 4×10^{-4} M HgI_2 mercury(II) exists as HgI_4^{2-}. Photolysis of such a solution resulted in the formation of I_3^-. Its photoproduction also slowed down rather rapidly. The quantum yields determined from the initial slopes were found to be significantly lower than for the photolysis of the HgI_3^-/HgI_2 system (0.02 in argon-saturated and 0.015 in aerated solution at 333 nm). Addition of EtOH did not affect the photochemical behavior of the iodomercurate(II) complexes in acetonitrile.

Flash photolysis

A solution of HgI_4^{2-} ($C_{Hg(II)}=4.5\times10^{-5}$ M, $[I^-]=4\times10^{-2}$ M) was also excited by 15 ns laser pulses at 355 nm. Two intermediates were detected; a short-lived one, which appeared right after the pulse, and a longer-lived one, which was apparently formed via decay of the former species. The spectrum of the shorter-lived intermediate was taken 1 μs after the pulse and displays an intense band at 390 nm (Fig. 5). This is in good accordance with the spectrum of I_2^- in aqueous solution [17]. Analysis of this transient at 390 nm, taking the residual absorbance (after 200 μs) into consideration, shows that it obeys a second order kinetics (Fig. 6) with the k/ϵ value of 3.0×10^5 cm s^{-1}. Taking 9400

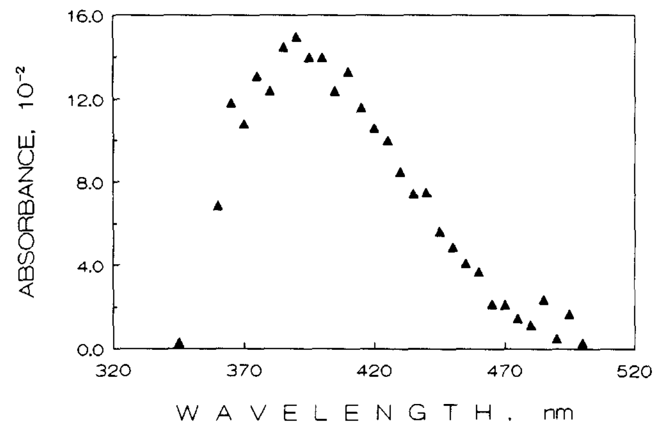

Fig. 5. Transient absorption spectrum recorded 1 μs after a 355 nm laser pulse in acetonitrile solution of HgI_4^{2-} ($C_{Hg(II)} = 4.5 \times 10^{-5}$ M, $[I^-] = 4 \times 10^{-2}$ M, $l = 1$ cm).

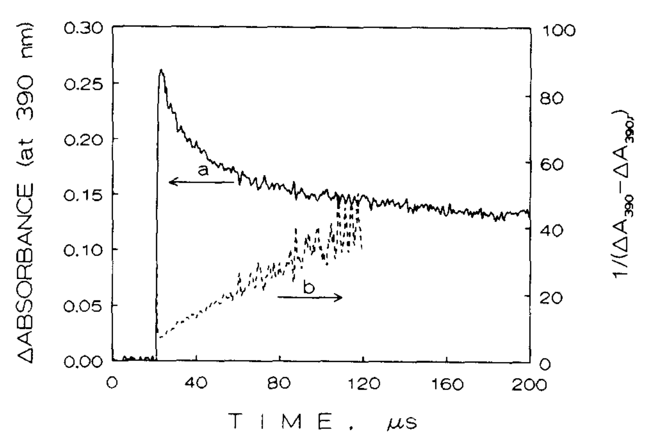

Fig. 6. Transient absorption at 390 nm (conditions as in Fig. 5).

M^{-1} cm^{-1} as the molar absorbance of I_2^- at 390 nm [17], although it was measured in aqueous solution, the rate constant of the decay is 2.8×10^9 M^{-1} s^{-1}. This high value indicates a diffusion controlled reaction and agrees fairly well with the observation in the aqueous system [9].

The spectrum of the longer-lived intermediate (not shown) proved to be equal to that of I_3^-, having a maximum at 360 nm. This transient also obeys a second order kinetics with a rate constant of 2.6×10^8 M^{-1} s^{-1}. Flash photolysis experiments ($\lambda_{ir} = 355$ nm) with solutions containing 60% HgI_3^- and 40% HgI_2 gave similar results, but the intensity of the transients was much lower as a consequence of the most negligible free iodide concentration. It is worth mentioning at this point that molar absorbances of I_3^- in the 300–400 nm range are about eight times higher than those of I_2. The quantum yield for the formation of diiodide in the photoreaction of HgI_4^{2-} was determined from the peak value of the transient at 390 nm ($\Phi = 0.41$, using 9400 M^{-1} cm^{-1} as the molar absorbance of I_2^-). On the basis of the residual absorbance at this wavelength after 200 μs, about 75% of I_2^- formed in the photoinduced reaction was converted to I_3^-. Quantum yield calculated in a similar way for the HgI_2/HgI_3^- system would not be correct because the molar absorbance used for the previous case (with significant excess of I^-) is not appropriate here. Thus, a reasonable estimation can be made for Φ from the residual absorbance (after 200 μs) representing I_2 formed from the primary product. Provided the conversion of the primary products (probably a mixture of I_2^- and $I^{\bullet}$) is also about 75%, the quantum yield for the shorter-lived intermediate is *c.* 0.8.

Flash irradiation of HgI_2 at 355 nm results in no detectable transient, due to the very low absorbance. Excitation at 266 nm, however, led to the appearance of a weak unidentified transient, the spectrum of which is rather featureless with an uncertain maximum in the 300–320 nm range. Its decay obeys a mixed (first and second) order kinetics, and no second step was experienced in the transient at 310 nm. No residual absorbance was observed either.

The presence of air or EtOH did not cause any effect in these flash photolysis experiments.

Discussion

Spectroscopy and equilibria

Although the absorption spectra of the individual iodomercurate(II) complexes are rather different, the characteristic bands in all the three cases are attributed to LMCT transitions. The significant deviations in the molecular structures, bond strengths, orbital symmetries and energies, however, can result in different spectral properties. The linear HgI_2 complex displays a rather sharp band at 211 nm and a weaker one at 265–267 nm (Fig. 1). The latter band is assigned as a π-LMCT transition, which can be either ${}^1\Sigma_g^+ \rightarrow {}^1\Pi_u$ involving the ligand p_π orbitals (as $1\pi_u$ MO) and the metal 6s orbital (as $3\sigma_g^+$ MO), or ${}^1\Sigma_g^+ \rightarrow {}^1\Sigma_u^+$ involving the ligand p_π orbitals (as $1\pi_g$ MO) and the metal 6p orbital (as $2\pi_u$ MO) [12, 18]. The higher energy band is attributed to a combination of d→p and σ-LMCT transitions (${}^1\Sigma_g^+ \rightarrow \Pi_u$). In the latter one an electron is promoted from the halogen's p_σ orbital (as $1\sigma_g^+$ MO) to the $2\pi_u$ MO.

The pyramidal [19] HgI_3^- ion exhibits three bands at 220, 256 and 301 nm, and a shoulder at 343 nm (Fig. 1). The 256 and 301 nm bands are attributed to ${}^1A_1 \rightarrow {}^1E$ transitions from the ligand p orbitals (as 3e and 4e MOs) to the metal 6s orbital (as $4a_1$ MO) [20]. The appearance of the shoulder at 340 nm can be explained by the mixing of ${}^1E$ and ${}^3E$ states (via spin–orbit coupling), which makes the corresponding spin-forbidden transition, ${}^1A_1 \rightarrow {}^3E$, partially allowed

[19, 21]. The highest energy band can also be assigned as a $^1A_1 \rightarrow {}^1E$ transition in which an electron is excited from the 3a$_1$ MO consisting mainly of the halogen's p orbital to the 4a$_1$ MO.

The HgI_4^{2-} ion has a tetrahedral symmetry and displays two intense bands at 273 and 329 nm. The stronger one (273 nm) is assigned as a $^1A_1 \rightarrow {}^1T_2$ transition from the t$_2$ MO mainly composed of the iodide's p_π orbital to the a$_1$ MO consisting basically of the Hg's 6s orbital [22, 23]. The lower energy band is attributed to the originally spin-forbidden $^1A_1 \rightarrow {}^3T_2$ transition (involving the same orbitals), which, via spin–orbit coupling resulting in the mixing of the $^3T_2$ and $^1T_2$ states, becomes partially allowed. The filled d orbitals of Hg are non-bonding in all cases, thus in these complexes mercury behaves like main-group metals.

The stability constant of HgI_2 in acetonitrile is about 10^{38} M^{-1} [13]. In aqueous systems β_2 is significantly lower (c. 10^{24} M^{-1}) [1], but high enough so that the dissociation of diiodomercurate(II) (at $C > 10^{-5}$ M) is negligible (<1%) even in protic solvents. For the triido species, HgI_3^-, however, the stepwise formation constant, K_3, in protic systems is less than 10^4 M^{-1} [13]. Thus, the quantitative formation of triidomercurate(II) requires a considerable ligand excess. In the weakly coordinating CH_3CN, however, the rather high value of K_3 (10^8 M^{-1}) [13] makes it possible for the iodide ions added to HgI_2 (up to about 60% of C_{HgI_2}) to be totally taken up via formation of triido species. Such a difference between the equilibrium constants in CH_3CN compared to protic solvents can also be experienced in the case of HgI_4^{2-} ($K_4 = 10^2$–10^3 M^{-1} in CH_3CN and 0.4 M^{-1} in MeOH [3]). Similar tendencies can be observed for other halomercurates. It is worth mentioning that the order of the formation constants for the trihalomercurates is I>Br>Cl, while for the tetrahalo species it is the reverse, independent of the solvent. This phenomenon demonstrates how the change in the structure of these complexes affects their stability as a function of the ligand.

Photochemistry

The results of both the continuous and the flash photolysis experiments indicate that the primary photochemical reaction of iodomercurate(II) complexes in acetonitrile, similarly to the corresponding chloromercurates [16], is an LMCT process with a formation of Hg(I) species and I$^\bullet$.

$$HgI_n^{(n-2)-} \xrightarrow{h\nu} HgI_{n-1}^{(n-2)-} + I^\bullet \qquad (2)$$

The primary products undergo different parallel or consecutive thermal reactions. In the case of HgI_2 the direct back reaction (eqn. (3)) is the most probable way because no permanent chemical change was experienced in continuous photolysis and the transient observed in the flash photolysis experiments decays in one step without residual absorbance.

$$HgI_{n-1}^{(n-2)-} + I^\bullet \longrightarrow HgI_n^{(n-2)-} \qquad (3)$$

When iodide ions of suitable concentration were present in the solutions, formation of I_2^- could be detected, due to reaction (4).

$$I^\bullet + I^- \longrightarrow I_2^- \qquad (4)$$

This intermediate can undergo recombination (eqn. (5)) or back reaction (reconversion) with Hg(I) species (eqn. (6)).

$$I_2^- + I_2^- \xrightarrow{k_5} I_3^- + I^- \qquad (5)$$

$$I_2^- + HgI_{n-1}^{(n-2)-} \xrightarrow{k_6} HgI_n^{(n-2)-} + I^- \qquad (6)$$

In this competition the recombination process is predominant as indicated by the flash photolysis experiments, due to the higher rate constant ($k_5 = 2.8 \times 10^9$ M^{-1} s^{-1}).

The Hg(I) monomer formed in the primary reaction (eqn. (2)) can recombine to give Hg_2I_2. The appearance of such a species could not be noticed in this system because of the very low conversion rate and a probable oversaturation.

Although the triiodide ion is a stable species in pure I^- solution, the photochemically produced ones in this system disappear in a second order process, which can be a reconversion with Hg(I) species formed (eqn. (7)).

$$I_3^- + HgI_{n-1}^{(n-2)-} \xrightarrow{k_7} HgI_n^{(n-2)-} + I_2^- \qquad (7)$$

The quantum yield for the primary reaction (eqn. (2)) is rather high for both HgI_3^- (c. 0.8) and HgI_4^{2-} (0.41) complexes, while the corresponding overall quantum yields for I_2 or I_3^- production (accumulation) are about one order of magnitude lower (0.065 and 0.02). This confirms that back reactions and reconversions are predominant in these systems and efficiently hinder the accumulation of the final products. That is why the apparent rate of the I_2 or I_3^- generation rapidly decreases and a reconversion of the irradiated system can be observed in the dark.

The individual quantum yields of the triiodo complex are significantly higher than those of the tetraiodo species for both the primary and the overall processes. A similar tendency was experienced for the photoactivity of the corresponding chloromercurates(II) [16]. In the case of the primary photoreaction this phenomenon may be interpreted by the relation of the corresponding molar absorbances. The lifetime of an excited state is inversely proportional to the oscillator strength, and, thus, to the molar absorbances. Since in the case of the iodomercurate(II) complexes in the vicinity of the excitation wavelength (333 nm) the extinction coefficients of the band maxima increase upon coordination of more ligands, shorter excited-state lifetimes result and, thus, a lower probability for the LMCT reaction. Unfortunately, in the case of HgI_2 no quantum yield could be determined for the primary reaction, while, due to the very fast back reaction (eqn. (2)), no overall net reaction could be observed. However, this cannot exclude the fact that the efficiency of the primary reaction in this case is even higher than those for the other two iodo complexes. Elucidation of this problem requires further kinetic studies.

Acknowledgements

This work was supported by BMFT and the Fonds der Chemischen Industrie. O.H. is especially grateful to the Alexander von Humboldt Foundation for the fellowship making his research possible at Regensburg University. We thank Dr Horst Kunkely for the competent technical assistance.

References

1 (a) A.E. Martell and L.G. Sillén, *Stability Constants of Metal-Ion Complexes,* Special Publication No. 17, The Chemical Society, London, 1964; (b) A.E. Martell and L.G. Sillén, *Stability Constants of Metal-Ion Complexes,* Special Publication No. 25, The Chemical Society, London, 1971; (c) E. Högfeldt, *Stability Constants for Metal-Ion Complexes, Part A: Inorganic Ligands,* Pergamon, Oxford, 1982.
2 F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry,* Wiley-Interscience, New York, 1988.
3 T.R. Griffiths and R.A. Anderson, *Can. J. Chem., 69* (1990) 451.
4 V. Balzani and V. Carassiti, *Photochemistry of Coordination Compounds,* Academic Press, New York, 1970, pp. 277–281.
5 O. Horváth and K.L. Stevenson, *Charge Transfer Photochemistry of Coordination Compounds,* VCH, New York, 1993, pp. 76–79.
6 H. Kunkely and A. Vogler, *Polyhedron, 8* (1989) 2731.
7 D. Rehorek and E.G. Janzen, *Z. Chem., 25* (1985) 69.
8 H. Kunkely, G. Stochel and A. Vogler, *Z. Naturforsch., Teil B, 44* (1989) 145.
9 M.E. Langmuir and E. Hayon, *J. Phys. Chem., 71* (1967) 3808.
10 K.L. Stevenson, R.M. Berger, M.M. Grush, J.C. Stayanoff, A. Horváth and O. Horváth, *J. Photochem. Photobiol., A, 60* (1991) 215.
11 V. Wintgens, L.J. Johnston and J.C. Scaiano, *J. Am. Chem. Soc., 110* (1988) 511.
12 M.E. Koutek and W.R. Mason, *Inorg. Chem., 19* (1980) 648.
13 J.F. Coetzee, J.J. Campion and D.R. Liberman, *Anal. Chem., 45* (1973) 343.
14 A. Garrett, *J. Am. Chem. Soc., 61* (1939) 2744.
15 G. Ellendt and K. Cruse, *Z. Phys. Chem., 201* (1952) 130.
16 O. Horváth and A. Vogler, *Inorg. Chem., 32* (1993) 5485.
17 G.L. Hug, *Optical Spectra of Nonmetallic Inorganic Transient Species in Aqueous Solution,* National Bureau of Standards, Washington, DC, 1981, pp. 54–55.
18 M.M. Savas and W.R. Mason, *Inorg. Chem., 26* (1987) 301.
19 T.R. Griffiths and R.A. Anderson, *Inorg. Chem., 30* (1991) 1912.
20 A.D. Walsh, *J. Chem. Soc.,* (1953) 2301.
21 T.R. Griffiths and R.A. Anderson, *J. Chem. Soc., Faraday Trans., 86* (1990) 1425.
22 P. Day and R.H. Seal, *J. Chem. Soc., Dalton Trans.,* (1972) 2054.
23 S. Sakaki, N. Hagiwara, N. Iwasaki and A. Ohyoshi, *Bull. Chem. Soc. Jpn., 50* (1977) 14.