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Photoredox Chemistry of Chloromercurate(II) Complexes in Acetonitrile

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The kinetically labile chloromercurates(II) have rather high stepwise formation constants in acetonitrile; even for $HgCl_4^{2-}$ a value of 1.07×10^4 M^{-1} was determined. The ultraviolet spectra of these complexes are characterized by ligand-to-metal charge-transfer transitions of different energies and intensities. Their photolysis leads to the formation of Hg(I) and $Cl^\bullet$ in the primary photochemical reaction. The mercury(I) monomers recombine to give Hg_2Cl_2, while chlorine radicals are reconverted to Cl^-, increasing the Cl^-/Hg(II) ratio in the solution. In considerable excess of Cl^- ($[Cl^-] = 5 \times 10^{-3}$ M at 4.5×10^{-5} M $HgCl_4^{2-}$) mercury(I) species undergo disproportionation giving Hg^0 as end product. The higher the ligand number of the complex, the lower is the quantum yield for the overall reaction: 5.3 10^{-2}, 1.35×10^{-2}, and 9.5×10^{-3} for $HgCl_2$, $HgCl_3^-$, and $HgCl_4^{2-}$, respectively, in deaerated solution at $\lambda_{ir} = 254$ nm. In the presence of air quantum yields are lower and the main product is Hg_2Cl_2 in all cases. Ethanol enhances the efficiency of the photoreduction but only in argon-saturated systems, indicating competitive reactions of the Hg(I) monomers formed in the primary step and a considerable oxygen sensitivity of Hg^0 as well.

Introduction

As well-known, mercury displays chemical similarities to both transition and main-group metals. Thus, Hg^{2+} having filled d and empty s and p subshells readily forms kinetically labile complexes with halo and pseudohalo ligands in various solvents as do numerous other metal ions of $(n-1)d^{10}ns^0$ configuration.[2,3] If the metal center of such a complex is in a higher oxidation state, its electronic absorption spectrum is featured by LMCT transitions. The energies and intensities of the corresponding bands strongly depend on the coordination number as in the case of the halomercurate(II) complexes, $HgX_n^{(n-2)-}$ (X = Cl, Br, I; n = 2–4).[4] Hence, their photoactivities can also be significantly influenced by n.

Although the light sensitivity of inorganic mercury(II) complexes has been known for many decades,[5] a more intense photochemical investigation of these compounds started only in the past few years.[6] Irrespectively of the ligands, the primary photoreaction of the Hg(II) complexes studied so far (e.g. $Hg(N_3)_3^-$, $Hg(CN)_2$) was the reduction of the metal center, due to LMCT excitations.[7,8] Also in the photoinduced metal to metal charge-transfer reactions in $[(NC)_2Hg^{II}NCFe(CN)_5]^{4-}$ and $[Hg^{II}Co_2^{I}(CN)_{10}]^{6-}$ complexes, mercury(II) played the role of the electron acceptor.[9] A flash photolysis study by Langmuir and Hayon proved the formation of the X_2^- radical ion in aqueous solutions of halomercurates(II),[10] but no quantum yield determination was done. Besides, aprotic solvents which are rather weakly coordinated to Hg^{2+} can be more favorable to investigate the role of the complex equilibria in the photochemistry of these compounds. In this work we studied the photoredox behavior of chloromercurate(II) complexes in acetonitrile in order to elucidate how the number of the coordinated ligands affects the photoactivity and what kind of reaction mechanism is operative in this system.

Experimental Section

All solutions were prepared to the desired concentration from stock solutions of reagent grade and suitably dried $HgCl_2$, LiCl, and Et_4NCl. Dry spectrograde CH_3CN was used as solvent. Ethanol of the same quality was applied as a reductive agent for mechanistic experiments.

Absorption spectra were taken on an Uvikon 860 double-beam spectrophotometer, using 1-cm and 1-mm quartz cuvettes. Typically the photolyses were carried out with 2.5-mL solutions in 1-cm cells at room temperature. Oxygen-free samples were prepared by purging with CH_3CN-saturated argon for at least 1 h before the irradiation. A Hanovia Xe/Hg 977 B-1 (1000 W) lamp equipped with a Schoeffel GM 250–1 monochromator served as the light source. Incident light intensity (I_0 = 7.0×10^{-6} mol photon dm^{-3} s^{-1} at 254 nm) was determined by a Polytec pyroelectric radiometer calibrated and equipped with an RkP-345 detector. Experiments for quantum yield determination were carried out with samples of nearly 100% light absorption.

Time-resolved absorption measurements were obtained in Veszprém University's laser photolysis system described elsewhere.[11] Pulse energies of 10–20 mJ at 266 nm with a width of about 15 ns were used in these experiments.

Results

Spectroscopy and Equilibria. The UV absorption spectrum of $HgCl_2$ in acetonitrile is rather featureless; it displays a very broad and moderately large band with a maximum close to 200 nm (Figure 1, curve a). Gradual addition of chloride (in 4×10^{-5} M increments) to the solution of 4.5×10^{-4} M $HgCl_2$ gives rise to the formation of a new band at 240 nm. The increase of its absorbance is proportional to the amount of chloride added until it reaches about 50% of the $HgCl_2$ concentration (Figure 1). Since the stepwise formation constant of $HgCl_3^-$, K_3, in acetonitrile is *ca.* 10^6 M^{-1}, the added chloride ions are quantitatively coordinated to the Hg^{2+} center. Thus, the molar absorptivity of

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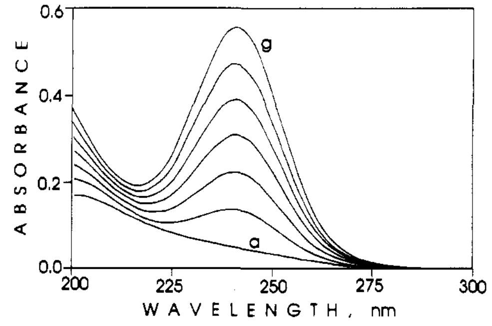

Figure 1. Ultraviolet absorption spectra changes (a → g) obtained upon addition of chloride (in 4 × 10^{-5} M increments) to $HgCl_2$ (4.5 × 10^{-4} M) in acetonitrile at room temperature. l = 0.1 cm.

Table I. Molar Absorptivities of Chloromercurate(II) Complexes in Acetonitrile

	ϵ_i, M^{-1} cm^{-1}		
λ, nm	$HgCl_2$	$HgCl_3^-$	$HgCl_4^{2-}$
234	690	18 100	41 800
240	510	21 200	35 800
254	145	10 800	5 640

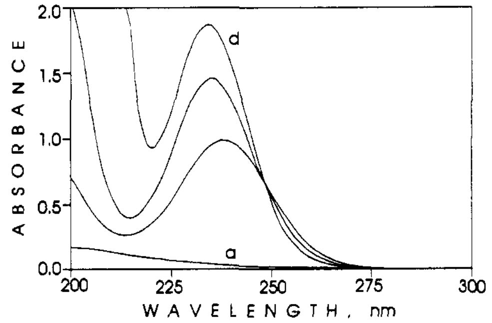

Figure 2. Ultraviolet spectra changes obtained upon addition of (a) 0, (b) 8 × 10^{-4}, (c) 2.8 × 10^{-3}, and (d) 9.4 × 10^{-3} M chloride to $HgCl_2$ (4.5 × 10^{-4} M) in acetonitrile at room temperature. l = 0.1 cm.

$HgCl_3^-$ can be directly determined in this way. The slope of the A_{240} vs C_{Cl}(added) plot (not shown) is $\epsilon_3^{240} - \epsilon_2^{240}$, where ϵ_3^{240} and ϵ_2^{240} are the absorption coefficients of $HgCl_3^-$ and $HgCl_2$, respectively, at 240 nm. Table I summarizes the molar absorbances determined at different wavelengths for $HgCl_n^{(n-2)-}$ (n = 2–4) complexes in CH_3CN.

Addition of more chloride to this system (C_{Cl}(added) > C_{HgCl_2}) results in a slight blue shift of the absorption band, while its intensity increases monotonically further (Figure 2). However, at longer wavelengths a continuous decrease can be observed, giving rise to an isosbestic point at 248 nm. This clearly indicates that basically two species exist in the system at this stage, $HgCl_3^-$ and $HgCl_4^{2-}$. About 5.9 × 10^{-3} M chloride added to 4.5 × 10^{-4} $HgCl_2$ (i.e. $[Cl^-]$ = 5 × 10^{-4} M) is necessary for the 100% conversion to the tetrachloro complex. This is in accordance with the previous experiences by Day and Seal.[12] $HgCl_4^{2-}$ shows an absorption band at 234 nm with the extinction coefficient of 4.18 × 10^4 M^{-1} cm^{-1}. This is also in good agreement with the data published earlier.[12] Knowing the molar absorbances of both $HgCl_3^-$ and $HgCl_4^{2-}$ at 234 and 240 nm, the stepwise formation constant of the latter species can be determined using the absorptions measured at different $[Cl^-]$ values. The concentration ratio of the two chloro complexes in equilibrium ($R = [HgCl_4^{2-}]/[HgCl_3^-]$) can be calculated with a simple linear equation: $R\epsilon_4 + (1 - R)\epsilon_3 = A/C_{HgCl_2}$. Then the R values obtained are plotted as a function of free-ligand concentration ($[Cl^-] = C_{Cl}(\text{added}) - [HgCl_3^-] - 2[HgCl_4^{2-}]$). The equation on the formation constant,

$$K_4 = [HgCl_4^{2-}]/([HgCl_3^-][Cl^-]) \qquad (1)$$

predicts a linear relationship with an intercept at the origin. Our results fulfill this expectation (Figure 3), and the slope of the plot gives the value of (1.07 ± 0.10) × 10^4 M^{-1} for K_4. This is in accordance with the data measured by Coetzee *et al.* with polarography (1.58 × 10^4 M^{-1}).[13] However, an earlier result by Ellendt *et al.* (170 M^{-1})[14] is more than 1 order of magnitude lower, indicating that conductometry, which they applied, was not a reliable method for this system. Experiments for spectral studies were carried out with both LiCl and Et_4NCl. No cation size effect was observed, probably due to the relatively low concentrations (C_{Cl}(added) < 10^{-2} M). Thus, in the photochemical experiments LiCl was exclusively applied as a source of added chloride.

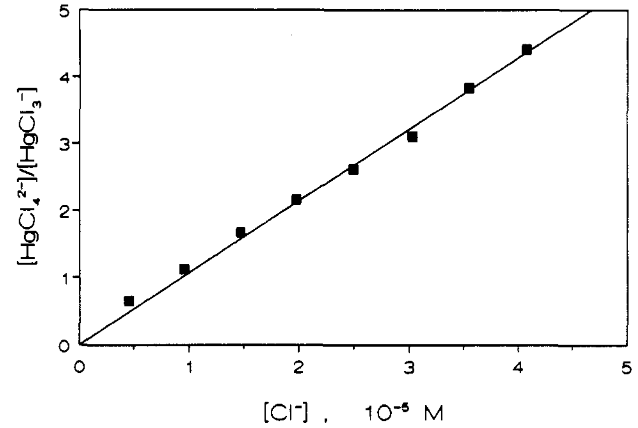

Figure 3. Concentration ratio of tetra- and trichloromercurate(II) *vs* free-ligand concentration in acetonitrile at room temperature ($C_{Hg(II)}$ = 4.5 × 10^{-4} M).

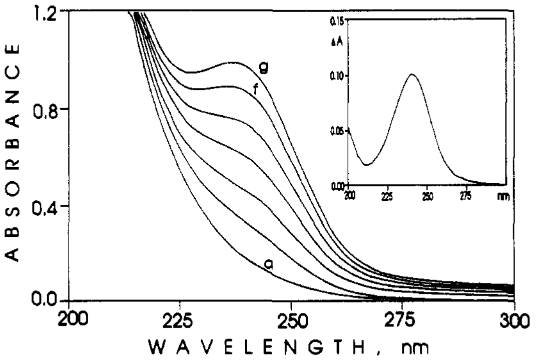

Figure 4. Temporal spectral changes during the photolysis of 5 × 10^{-3} M $HgCl_2$ in argon-saturated CH_3CN at (a) 0-, (b) 5-, (c) 10-, (d) 15-, (e) 20-, (f) 25-, and (g) 30-min irradiation times (λ_{ir} = 254 nm). l = 0.1 cm. Inset: difference spectrum (g – f).

Continuous Photolysis. Upon irradiation (λ_{ir} = 254 nm) of $HgCl_2$ in argon-saturated CH_3CN (5 × 10^{-3} M) a monotonic increase of absorption can be observed in the 220–270-nm range (Figure 4). This, on the basis of the difference spectrum (see inset in Figure 4), can be attributed to the formation of $HgCl_3^-$. Besides, a gradual increase in the baseline absorbance indicates the production of some colloid, namely the practically insoluble Hg_2Cl_2.

The formation of trichloromercurate(II) is the consequence of the change in the Cl^-/Hg(II) ratio in solution, which increases in this case, due to the Hg_2Cl_2 production. This explanation assumes that chloride ions do not take part in any other net

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reactions changing their concentration. The primary photoreaction, on the basis of earlier observations in aqueous systems[10] and evidence presented here later, is a LMCT process generating Hg(I) and Cl·. While mercury(I) forms Hg_2Cl_2, chlorine radical is reconverted to Cl^- in a thermal redox reaction with the solvent. A similar phenomenon was observed in the photoreduction of chlorocuprate(II) complexes in acetonitrile.[15,16] Hence, the quantum yield for the overall photoreaction can be determined from the absorbance change (ΔA_{240}) due to the $HgCl_3^-$ formation. Division of ΔA_{240} by $\Delta\epsilon = \epsilon_3^{240} - 2\epsilon_2^{240}$ gives the actual concentration of the trichloromercurate(II) photoproduced because formation of one trichloromercurate(II) complex is accompanied by consumption of two $HgCl_2$ species (converted to $^1/_2Hg_2Cl_2$ and $HgCl_3^-$). In order to determine the quantum yield for photoreaction of $HgCl_2$ the initial slope of the $[HgCl_3^-]$ vs time plot must be taken because of the big difference (about 2 orders of magnitude) between the molar absorbances of $HgCl_2$ and $HgCl_3^-$. Otherwise the inner filter effect by the trichloro species would diminish the estimated quantum yield. On the other hand, in this case the absorbance of Hg_2Cl_2 should also be taken into consideration, because at the very beginning of the reaction it is comparable with that of $HgCl_3^-$ (2.3×10^4 M^{-1} cm^{-1} at 235 nm[17]). At a later stage of the reaction, it contributes much less to the absorption increase, in a form of colloid, due to its very poor solubility.

The quantum yield for the photoreaction of trichloromercurate(II), Φ_3, can also be directly measured if photolysis of a solution containing 40% $HgCl_3^-$ and 60% $HgCl_2$ is carried out. In this case 99% of the light is absorbed by the trichloro species. Thus, at low conversion a linear ΔA_{240} vs time plot is obtained, the slope of which corresponds to Φ_3.

At an appropriate excess of Cl^- ($\geq 5 \times 10^{-3}$ M), mercury(II) exists in this system exclusively as $HgCl_4^{2-}$. Irradiation of such an argon-saturated solution results in a decrease in the absorbance at 234 nm, due to the reduction of tetrachloromercurate(II) (Figure 5a). In this case no change occurs in the complex equilibrium; therefore the absorbance, A_{234}, corrected by the slight increase of the baseline, gives the actual concentration of $HgCl_4^{2-}$. The difference spectrum (Figure 5a, inset) clearly shows the formation of atomic mercury,[18,19a,20] while in the presence of air Hg_2Cl_2 is the main product giving rise to an isosbestic point at 222 nm (Figure 5b). As shown, the quantum yields for the photoreactions of each chloromercurate(II) complex in this system can be separately estimated. Table II summarizes the values obtained for both deaerated and air-saturated conditions.

The relatively low quantum yields suggest that an effective back-reaction may be operative between the primary photoproducts, i.e. $HgCl_{n-1}^{(n-2)-}$ and Cl·. Application of some reductive agent which can react with one or both of these species may efficiently hinder the recombination and thus enhance the overall quantum yield. Addition of ethanol (in the concentration range 0–0.15 M) dramatically increased Φ for the photoreduction of $HgCl_4^{2-}$ in argon-saturated solutions. The formation of atomic mercury became more pronounced in this case, due to the higher oversaturation as a consequence of the faster reaction. The quantum yield as a function of C_{EtOH} added shows a monotonic increase in the 0–0.15 M region, reaching a more than 5-fold enhancement compared to the initial value (Figure 6). In the presence of air, however, alcohol shows no effect on the photoreaction, which is, similarly to the cases without EtOH, accompanied by Hg_2Cl_2 production.

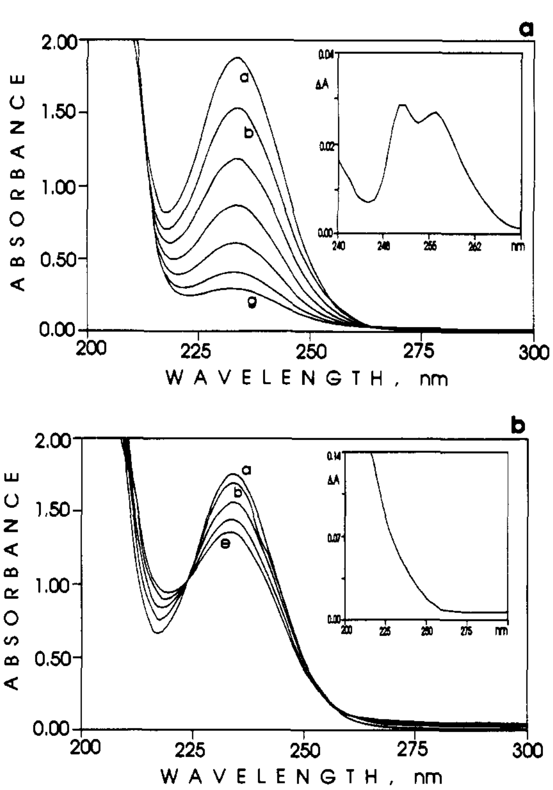

Figure 5. (a) Temporal spectral changes during the photolysis of 4.5×10^{-5} M $HgCl_4^{2-}$ ($[Cl^-] = 5 \times 10^{-3}$ M) in argon-saturated CH_3CN at (a) 0-, (b) 2-, (c) 4-, (d) 6-, (e) 8-, (f) 10-, and (g) 12-min irradiation times (λ_{ir} = 254 nm). l = 1 cm. Inset: difference spectrum (b – 0.8a). (b) Temporal spectral changes during the photolysis of 4.2×10^{-5} M $HgCl_4^{2-}$ ($[Cl^-] = 5 \times 10^{-3}$ M) in aerated CH_3CN at (a) 0-, (b) 5-, (c) 10-, (d) 15-, and (e) 20-min irradiation times (λ_{ir} = 254 nm). l = 1 cm. Inset: difference spectrum (b – 0.94a).

Table II. Individual Quantum Yields for Photoreduction of Chloromercurate(II) Complexes in Acetonitrile (λ_{ir} = 254 nm)

	$10^2\Phi_i$[a]		
condition	$HgCl_2$	$HgCl_3^-$	$HgCl_4^{2-}$
Ar	5.3	1.35	0.95
air	3.1	0.56	0.21

[a] Uncertainty: ±20% for Φ_2, ±10% for Φ_3 and Φ_4.

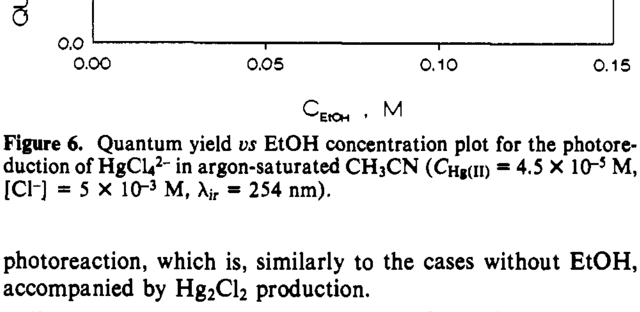

Figure 6. Quantum yield *vs* EtOH concentration plot for the photoreduction of $HgCl_4^{2-}$ in argon-saturated CH_3CN ($C_{Hg(II)} = 4.5 \times 10^{-5}$ M, $[Cl^-] = 5 \times 10^{-3}$ M, λ_{ir} = 254 nm).

Flash Photolysis. A solution of $HgCl_4^{2-}$ (10^{-3} M) was also irradiated by 15-ns laser pulses at 266 nm. A long-lived intermediate was detected, the absorption spectrum of which

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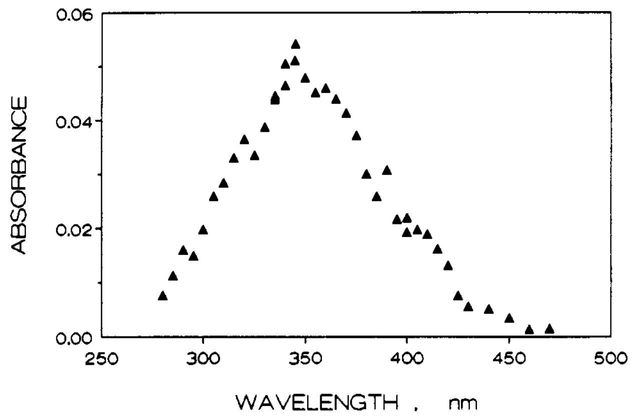

Figure 7. Transient absorption spectrum recorded 5 μs after a 266-nm laser pulse in acetonitrile solution of $HgCl_4^{2-}$ ($C_{Hg(II)} = 10^{-3}$ M, [Cl⁻] = 5 × 10^{-3} M. l = 1 cm).

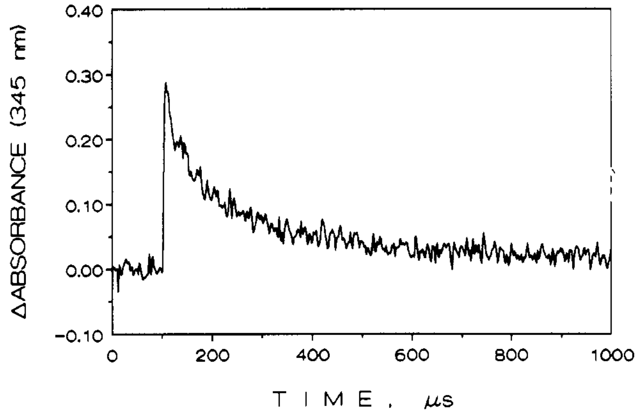

Figure 8. Transient absorption at 345 nm. (Conditions are as in Figure 7.)

displays an intense band at 345 nm (Figure 7). This fairly well agrees with the spectrum of the Cl_2^- radical ion in both acetonitrile[21] and aqueous solutions.[22] The decay of this species obeys a first-order kinetics with a lifetime of 200 ± 20 μs (Figure 8). This value of τ was obtained under both deaerated and air-saturated conditions. Addition of EtOH (in the same concentration range as applied for continuous irradiations) hardly affects the decay of this intermediate.

Discussion

Spectroscopy and Equilibria. Although the UV absorption spectrum of $HgCl_2$ in CH_3CN is significantly different from those of the tri- and tetrachloro species in the respect of both the energy and the intensity of the main band, in all the three cases the most intense electronic transitions are of LMCT type. The deviating molecular structures, bond strengths, orbital symmetries, and energies can cause essential changes in the spectral properties. In the linear $HgCl_2$ complex the only allowed transition is $^1\Sigma_g^+ \rightarrow {}^1\Pi_u$, in which one electron is promoted from the π_u MO mainly composed of the halogen's p_π orbital to the σ_g^+ MO, the main component of which is the Hg's 6s orbital.[23] The $HgCl_3^-$ ion is trigonal planar, and its allowed lowest energy transition is $A_1' \rightarrow E'$, in which an electron is excited from the e′ MO consisting mainly of the halogen's nonbonding p orbital to the a_1' MO composed of the 6s orbital of mercury.[24] Finally, $HgCl_4^{2-}$ has a tetrahedral symmetry, and its intense band is considered as an $^1A_1 - {}^1T_2$ transition from the t_2 MO mainly composed of the chloride's p_π orbital to the a_1 MO composed basically of the Hg's 6s orbital.[12,25] In all cases the filled d orbitals are of nonbonding type, and from the Hg atom essentially the 6s and 6p orbitals contribute to the Hg–Cl bond.

According to the data in the literature, the stability constant of $HgCl_2$ in acetonitrile is *ca.* 10^{35} M⁻¹,[13] while in aqueous systems it is about 10^{13} M⁻¹.[2] This means that dichloromercurate(II) ($C > 10^{-5}$ M) does not dissociate to an appreciable extent (<1%) even in protic solvents. In the case of $HgCl_3^-$, however, the stepwise formation constant, K_3, in a protic solvent like MeOH falls below 10^2 M⁻¹. Hence, a considerable excess of ligand is necessary for quantitative formation of trichloromercurate(II). On the contrary, in CH_3CN, which is very weakly coordinated to Hg^{2+}, the relatively high value of K_3 (10^6 M⁻¹)[13] results in that chloride ions added to $HgCl_2$ (up to 50%) will be entirely taken up by the dichloro complexes. This significant difference between the equilibrium constants in acetonitrile compared to protic solvents remains in the case of $HgCl_4^{2-}$ too. It is demonstrated by the values of 1.07 × 10^4 M⁻¹ for K_4 in CH_3CN against e.g. 5.7 M⁻¹ determined in MeOH.[4] Similar tendencies are effective for other halomercurates(II).

Photochemistry. The results of the continuous and flash photolyses unambiguously proved that the primary photoreaction of chloromercurate(II) complexes in CH_3CN like in water[10] is an LMCT process, producing Hg(I) species and $Cl^\bullet$,

$$\mathrm{HgCl}_n^{(n-2)-} \xrightarrow{h\nu} \mathrm{HgCl}_{n-1}^{(n-2)-} + \mathrm{Cl}^\bullet \qquad (2)$$

These primary products can undergo a thermal back-reaction (eq 3) or react further in different ways (eqs 4–9), where D

$$\mathrm{HgCl}_{n-1}^{(n-2)-} + \mathrm{Cl}^\bullet \rightarrow \mathrm{HgCl}_n^{(n-2)-} \qquad (3)$$

$$\mathrm{Cl}^\bullet + \mathrm{Cl}^- \rightarrow \mathrm{Cl}_2^- \qquad (4)$$

$$2\mathrm{Cl}_2^- \rightarrow \mathrm{Cl}_2 + 2\mathrm{Cl}^- \qquad (5)$$

$$\mathrm{Cl}_2^- + \mathrm{Hg(I)} \rightarrow \mathrm{Hg(II)} + 2\mathrm{Cl}^- \qquad (6)$$

$$\mathrm{Cl}^\bullet \text{ or } \mathrm{Cl}_2^- + \mathrm{D} \rightarrow 2\mathrm{Cl}^- + \mathrm{P} \qquad (7)$$

$$2\mathrm{HgCl}_{n-1}^{(n-2)-} \rightarrow \mathrm{Hg}_2\mathrm{Cl}_2 + (2n-4)\mathrm{Cl}^- \quad (n < 4) \qquad (8)$$

$$2\mathrm{HgCl}_3^{2-} \rightarrow \mathrm{Hg}^0 + \mathrm{HgCl}_4^{2-} + 2\mathrm{Cl}^- \qquad (9)$$

represents a reducing agent, which can be the solvent itself or some organic solute added, and P designates the product formed via oxidation of D. Disproportionation of Hg(I) species (eq 9) plays an important role only in ligand excess, i.e. in the case of tetrachloromercurate(II).

The lifetime of Cl_2^- in a deaerated solution of 10^{-3} M $HgCl_4^{2-}$ (τ = 200 μs) is close to that measured with hexachlorocyclopentadiene in CH_3CN exposed to flash photolysis.[21] Since in the latter case Cl_2^- disappears mostly in reactions 5 and 7, the back-reaction between Cl_2^- and Hg(I) (eq 6) cannot play an important role in this system. A further support to this conclusion is that oxygen does not affect the decay of Cl_2^-, although it very rapidly reacts with Hg(I).[17,26] In the presence of air the overall quantum yield is diminished not only by reaction 3 but via reoxidation of Hg(I) by O_2 too (eq 10). One end product of the latter reaction

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$$HgCl_{n-1}^{(n-2)-} + O_2 \rightarrow HgCl_{n-1}^{(n-3)-} + O_2^- \qquad (10)$$

is peroxide, as it was qualitatively detected in air-saturated solutions irradiated. Besides, O_2 can react with atomic mercury formed via disproportionation, giving Hg_2Cl_2 as an end product.

Addition of ethanol to a deaerated solution of $HgCl_4^{2-}$ significantly enhanced the quantum yield, indicating that EtOH efficiently reacts with one or both of the primary products. Since it does not affect the formation and decay of Cl_2^-, the mercury(I) species, $HgCl_{n-1}^{(n-2)-}$, is the more probable candidate for this reaction. This is confirmed by our recent results with the photolyses of Hg_2^{2+} in water–ethanol mixtures.[20] The suggested primary photoreaction in that system is the cleavage of the Hg–Hg bond, producing very reactive Hg^+ species, which can undergo both reduction and oxidation, depending on the oxygen and alcohol content of the solutions. The $HgCl_3^{2-}$ ion must be similarly reactive; hence, in the absence of O_2, its reduction by EtOH gives atomic mercury (eq 11). In aerated solutions, however, no EtOH

$$HgCl_3^{2-} + CH_3CH_2OH \rightarrow Hg^0 + 3Cl^- + CH_3CHOH + H^+ \qquad (11)$$

effect was observed, indicating that at these concentrations of O_2 (*ca.* 2×10^{-4} M) and ethanol (<0.15 M) reaction 11 is not competitive enough with the oxidation of $HgCl_3^{2-}$ (eq 10) and the atomic mercury formed can also be rapidly reoxidized.

The quantum yields determined for the different $HgCl_n^{(n-2)-}$ complexes (Table II) involve the effect of ligand number on both the primary photoreaction and those with $HgCl_{n-1}^{(n-2)-}$. The efficiency of the overall photoinduced reaction is considerably diminished as the number of the coordinated ligands increases. This tendency is effective in both aerated and argon-saturated systems. The lifetime of any excited state is inversely proportional to the oscillator strength, f,[19b] and in our case the molar absorbance, and thus, f increases upon coordination of more ligands, resulting in a shorter excited-state lifetime and, hence, lower probability for a LMCT reaction. This conclusion is also in accordance with the photoredox behavior of chlorocuprate(II) complexes in acetonitrile.[15,16,27] Besides, the recombination of $HgCl_{n-1}^{(n-2)-}$ to Hg_2Cl_2 may also be hindered by a higher number of ligands (see eq 8), and thus the reoxidation of the Hg(I) monomer (via reactions 3 and 10) can be more efficient.

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