ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 114 (1998) 95–101

Journal of
Photochemistry
and
Photobiology
A:Chemistry

Spectra, equilibrium and photoredox chemistry of tri- and tetraiodoplumbate(II) complexes in acetonitrile

Ottó Horváth *, Ildikó Mikó

Department of General and Inorganic Chemistry, University of Veszprém, P.O. Box 158, H-8201 Veszprém, Hungary

Received 16 December 1997; accepted 9 January 1998

Abstract

The stepwise formation constant of the kinetically labile PbI_4^{2-} complex was determined in acetonitrile ($K_4 = 27 \pm 4$ dm^3 mol^{-1}). The lowest-energy bands in the absorption spectra of the tri- and tetraiodoplumbate(II) complexes are attributed to ligand-to-metal charge transfer transitions. Photolysis of these complexes in solution results in the formation of Pb(I) and I or I_2^- as primary products. The quantum yield of this reaction is 0.10 ± 0.005 for both complexes at 355-nm excitation. The efficiency of the overall reaction (with the formation of I_3^- as end product) is higher for the PbI_3^- than for the PbI_4^{2-} complexes ($\Phi_3 = 0.026 \pm 0.002$ and $\Phi_4 = 0.010 \pm 0.004$) in air-saturated system, $\lambda_{irr} = 366$ nm, $C_{Pb(II)} = 1 \times 10^{-4}$ mol dm^{-3}) due to the different repulsion towards the negatively charged reactants. The overall quantum yield is essentially determined by the competitive dark reactions of the primary products, mostly by those of I_2^-. One key step in the mechanism is the reaction between the I_2^- intermediate and the ground-state lead(II) complexes, with rate constants of $3.4 \pm 1.1 \times 10^7$ dm^3 mol^{-1} s^{-1} and $7.0 \pm 2.0 \times 10^7$ dm^3 mol^{-1} s^{-1} at 37 and 94 partial molar percentages of PbI_3^-, respectively.

Keywords: Triiodoplumbate(II); Tetraiodoplumbate(II); Photoredox

1. Introduction

Formation of kinetically labile complexes with halo ligands in water and different non-aqueous solvents is typical for main-group metal ions with an s^2 electronic configuration, such as Tl^+, Sn^{2+}, Pb^{2+}, Sb^{3+}, Bi^{3+} and Te^{4+} [1,2]. Numerous of these halo complexes proved to undergo photoinduced charge transfer reactions [3]. Depending on the composition of the complex (types of the metal and the ligand) and the experimental conditions (e.g., the presence of air), both oxidation and reduction of the metal center ions can occur. While in air-saturated solutions the chloro complexes of s^2 metal ions undergo a photooxidation by intermolecular excited state electron transfer to molecular oxygen [4–6], in deaerated systems photoreduction of the metal center and the oxidation of the ligands were observed with the bromo and iodo complexes [4–9]. The diversity in the photoredox behavior of these halo complexes can be interpreted by their excited state properties. While the chloro complexes are characterized by low energy sp excited states [5,6,8], a large ligand-to-metal charge transfer (LMCT) contribution has been shown for the iodo complexes [10]. A confirmation of the LMCT photochemistry was the detection of the I_2^- radical ion by flash photolysis of triiodoplumbate(II) in acetonitrile [10]. No effort has, however, been made to study the effect of the coordination number on the photoredox behavior of these complexes and to elucidate the mechanism of their photoinduced reactions.

Since in organic solvents of low coordinating ability the stepwise formation constants of the kinetically labile halo complexes is considerably higher than in protic media [11–13], a relatively small change in the concentration of the free ligand can significantly influence their complex equilibria. Thus, acetonitrile was utilized as solvent for the photolysis of the tri- and tetraiodoplumbate(II) complexes. The aim of our work was to elucidate how the coordination number affects the photoactivity of these species and what kind of reaction mechanism is operative in this system.

2. Experimental

Stock solutions of reagent grade and properly dried PbI_2 and Et_4NI were used to prepare the solutions of desired metal and ligand concentrations for spectral and photochemical measurements. Dry spectrograde CH_3CN was used as sol-

---

* Corresponding author. E-mail: otto@vegic.sol.vein.hu

1010-6030/98/$19.00 © 1998 Elsevier Science S.A. All rights reserved.
PII S1010-6030(98)00214-7

vent. Iodine of the same quality served for calibration. Deoxygenation of the samples was carried out by purging with CH_3CN-saturated argon for at least 1 h before the measurements. The solutions used for stability constant measurements (at room temperature) contained 10^{-4} mol dm^{-3} Pb(II) (as PbI_2) and 2.63×10^{-3}–6.35×10^{-2} mol dm^{-3} iodide (as Et_4NI), thus, the ionic strength was in the same range.

The absorption spectra were recorded on a GBC UV/VIS 911A spectrophotometer, using 1-cm quartz cuvettes. Typically the irradiations were carried out with 12.5-cm^3 solutions in 5-cm cells at room temperature. For continuous photolysis at different wavelengths an AMKO LTI system consisting of a 150-W high pressure Xe–Hg arc lamp and a monochromator was utilized. Incident light intensity was determined with a thermopile calibrated by ferrioxalate actinometry [14]. Quantum yield measurements were carried out with samples of nearly 100% light absorption.

Time-resolved experiments were performed using a laser flash photolysis system previously described [15]. The excitation laser was either a Spectron SL-402, or a Brilliant (Quantel) NdYAG laser, yielding 355-nm pulses of about 15-ns duration. Aberchrome-540 served as an actinometer for quantum yield determination at 355 nm [16].

Peroxide was quantitatively determined by the method of Ovenston and Rees [17] which is based on the catalytic oxidation of iodide to iodine.

3. Results

3.1. Spectroscopy and equilibrium

Our preliminary investigations showed that in the absence of excess ligand PbI_2 partly dissociates, even in acetonitrile. The stepwise stability constants of kinetically labile ML_n complexes generally decrease with an increase in coordination number n. Thus, for a nearly total conversion of 10^{-4} mol dm^{-3} PbI_2 to PbI_3^- it was necessary to add at least 10 times the stoichiometric amount of ligand. At an added iodide concentration of 2.63×10^{-3} mol dm^{-3} the spectrum of the solution displayed two strong absorption bands in the 300–500-nm range: one at 321 and the other at 366 nm (Fig. 1, curve (a)). These bands were unambiguously assigned to the triiodoplumbate(II) complex [10]. Upon increasing the concentration of the ligand excess up to 6.35×10^{-2} mol dm^{-3}, new bands appeared at 408 nm and below 300 nm, while the peak at 366 nm disappeared, resulting in two isosbestic points at 341 and 381 nm clearly indicating that the lead(II) was distributed between the two complexes, PbI_3^- and PbI_4^{2-} in equilibrium, i.e.

$$PbI_3^- + I^- \Leftrightarrow PbI_4^{2-} \tag{1}$$

The spectra shown in Fig. 1 were determined against reference solutions containing the same amount of added iodide as the samples. Since the molar absorbances of iodide ion at wavelengths longer than 300 nm are several orders of magnitude smaller than those of the complexes studied and the iodide imbalance due to the coordination in the samples was negligible in this concentration range, no correction of the recorded spectra was necessary before quantitative analysis.

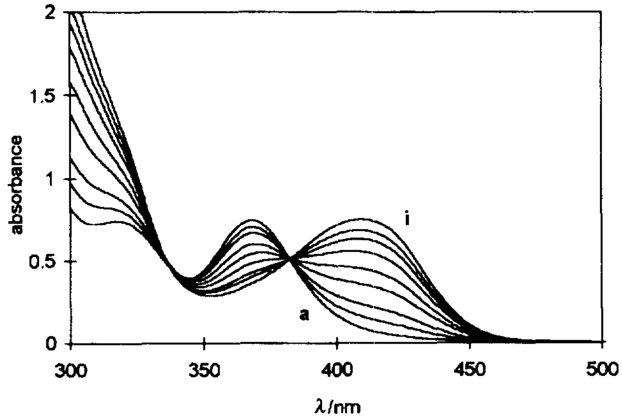

Fig. 1. Absorption spectra changes obtained upon increasing the concentration of the added iodide from 2.63×10^{-3} mol dm^{-3} (a) to 6.35×10^{-2} mol dm^{-3} (i) in acetonitrile containing 10^{-4} mol dm^{-3} PbI_2 ($l=1$ cm).

Since the solubility of Et_4NI limited the ligand excess in this system, a nearly 100% conversion to PbI_4^{2-} could not be achieved. Moreover, the PbI_2–PbI_3^- and PbI_3^-–PbI_4^{2-} equilibria hamper the existence of the PbI_3^- complex alone. Thus, the spectrum of neither the tri- nor the tetraiodoplumbate(II) could be directly determined. Hence, the molar absorbances of both complexes (ε_3 and ε_4) were also treated as unknown in the determination of the stepwise formation constant for the tetraiodo species (K_4).

A Marquardt nonlinear regression was applied to the well-known equation,

$$\begin{aligned}\varepsilon &= (\varepsilon_3+\varepsilon_4K_4[I^-])/(1+K_4[I^-])\\ &= \varepsilon_4+(\varepsilon_3-\varepsilon_4)/(1+K_4[I^-])\end{aligned} \tag{2}$$

where ε (dependent variable) is the molar absorbance of the lead(II) solution and $[I^-]$ is the free ligand concentration (independent variable). Taking the average of the results determined at different wavelengths in the 320–430-nm range, the value of 27 ± 4 dm^3 mol^{-1} was obtained for K_4, the reliability of which is demonstrated by the linearity of the plots of ε vs. $1/(1+K_4[I^-])$ at selected wavelengths (Fig. 2). From this stability constant, the individual spectra of both complexes were determined by simple linear regression using Eq. (2), and these are shown in Fig. 3.

3.2. Continuous photolysis

Upon continuous irradiation in the 320–430-nm range, a new wide band developed at $\lambda_{max}=360$ nm, consistent with the formation of the triiodide anion, I_3^- (Fig. 4). As previous studies showed [10], no side reaction or secondary process occurs in this system, and the presence of oxygen does not affect the course of the reactions, i.e., the absorption spectrum

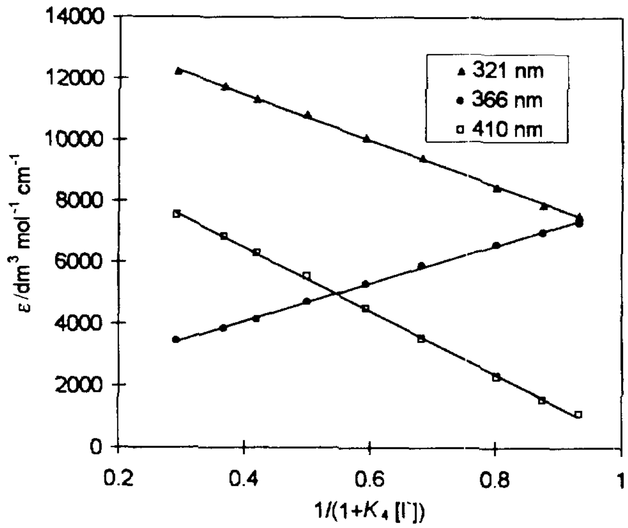

Fig. 2. Molar absorbance vs. $1/(1+K_4[\mathrm{I}^-])$ plots for the Pb(II)–I⁻ system in acetonitrile at selected wavelengths ($C_{\mathrm{Pb(II)}} = 10^{-4}$ mol dm^{-3}, $K_4 = 27$ dm^3 mol^{-1}).

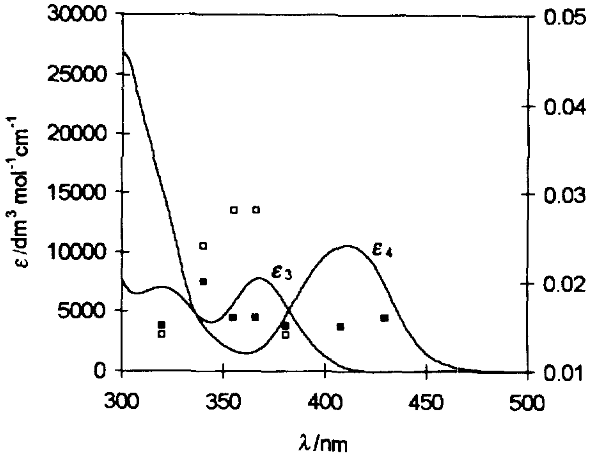

Fig. 3. Individual absorption spectra of $\mathrm{PbI_3}^-$ (ε_3) and $\mathrm{PbI_4}^{2-}$ (ε_4) in acetonitrile and overall quantum yields (Φ, for $\mathrm{I_3}^-$ formation) in solutions containing 2.63×10^{-3} mol dm^{-3} (□) and 6.35×10^{-2} mol dm^{-3} (■) excess iodide ($C_{\mathrm{Pb(II)}} = 10^{-4}$ mol dm^{-3}).

of the solution changes in the same way as in the deaerated system, with only the rate of the change varying. This permitted the use of aerated solutions for the continuous photolysis studies. From the initial rates of absorbance change in irradiated solutions, the quantum yields for the formation of triiodide ion have been determined at different irradiation wavelengths using the molar absorbances of both $\mathrm{I_3}^-$ and the complexes at 360 nm. The dependence of the quantum yield at $\lambda_{\mathrm{irr}} = 366$ nm on the concentration of the excess ligand) (Table 1) indicated that the individual quantum efficiency of the triiodoplumbates(II) is higher than that of the tetraiodo species. The irradiation-wavelength dependence of the quantum yield at lower and higher free ligand concentration (i.e., in solutions containing predominantly triiodo and tetraiodo species, respectively) was also determined (Fig. 3).

The influence of the Pb(II) concentration on the quantum yield was measured at 355- and 366-nm irradiation wavelengths. The quantum yield for the triiodide formation linearly increased with the Pb(II) concentration (Fig. 5). Precipitation of metallic lead was also observed during prolonged irradiation. Peroxide was also detected in air-saturated solutions that were photolysed. In a solution initially containing 10^{-4} mol dm^{-3} $\mathrm{PbI_2}$ and 2.63×10^{-3} mol dm^{-3} added iodide, 2.74×10^{-5} mol dm^{-3} peroxide was formed after 5 min of irradiation at 366 nm, while the concentration

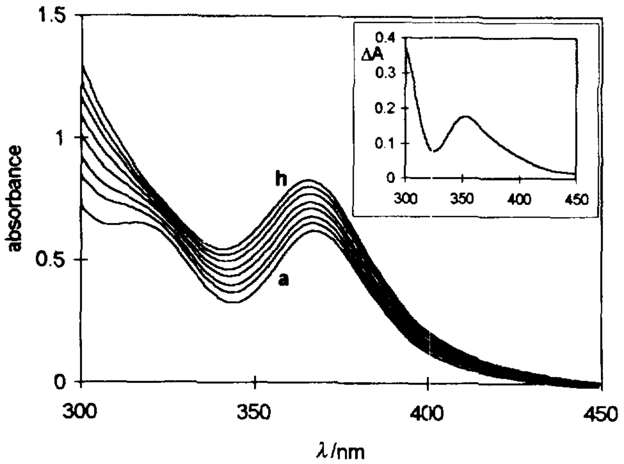

Fig. 4. Temporal spectral changes during the photolysis of 10^{-4} mol dm^{-3} $\mathrm{PbI_2}$ in air-saturated acetonitrile (C_{I}(added) $= 2.63 \times 10^{-3}$ mol dm^{-3}, $\lambda_{\mathrm{irr}} = 366$ nm, $\Delta t = 30$ s, $l = 1$ cm). Curves (*a*) and (*h*) are for 0 and 3-min irradiation time. Inset: difference spectrum (*h*–*a*).

Table 1
The effect of the concentration of the excess ligand (C_{I}(added)) on the quantum yield at $\lambda_{\mathrm{irr}} = 366$ nm (Φ) ($C_{\mathrm{Pb}} = 10^{-4}$ mol dm^{-3})

$10^2(C_{\mathrm{I}}(\mathrm{added})/\mathrm{mol\ dm^{-3}})$	0.263	0.522	0.910	2.52	3.69	6.35
$10^2\Phi$	2.8	2.3	2.1	1.9	2.0	1.6

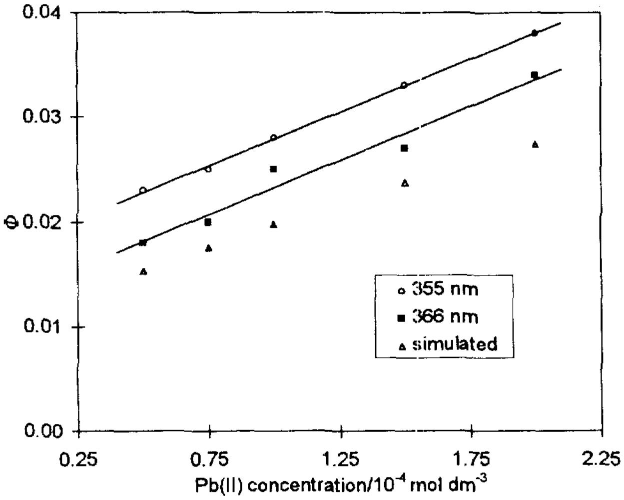

Fig. 5. Overall quantum yields for $\mathrm{I_3}^-$ formation determined by continuous irradiation ($\lambda_{\mathrm{irr}} = 355$ nm and 366 nm) and simulated by the model based on flash photolysis results ($\lambda_{\mathrm{irr}} = 355$ nm) as functions of the lead(II) concentration in air-saturated acetonitrile (C_{I}(added) $= 2.63 \times 10^{-3}$ mol dm^{-3}).

of I_3^- formed was 6.95×10^{-5} mol dm^{-3}. As a comparison, in a degassed solution of the same composition 5.21×10^{-5} mol dm^{-3} I_3^- was measured after a 5-min photolysis at 366 nm. Generally, in the absence of oxygen the quantum yields for the triiodide formation were 25–35% lower than in aerated systems. Addition of ethanol did not significantly affect the photoredox activity of the iodoplumbate(II) complexes in acetonitrile.

3.3. Flash photolysis

Aerated solutions of iodoplumbate(II) complexes were also excited by 15-ns laser pulses at 355 nm. In accordance with our previous observations [10], a short-lived intermediate was detected, which can be attributed to I_2^- (Fig. 6) on the basis of its transient spectrum (absorption bands at 390 and 750 nm) [18]. The disappearance of the Pb(II) species in the primary photochemical reaction, i.e., bleaching, decreases the absorbance by I_2^-. Since the iodoplumbate(II) complexes do not absorb at 750 nm, the diiodide concentration could be determined from A_{750}, and using this value also as the concentration of the Pb(II) species converted, a correction could be made by addition of their absorption spectra to the measured one. The corrected spectrum of I_2^- obtained in this way can also be seen in Fig. 6.

The diiodide intermediate underwent a mixed- (first and second) order decay (Fig. 7). At the end of the transient taken at 390 nm a residual absorbance was detected. The absorption spectrum of this residue taken 100 ms after the pulse was the same as that of I_3^-. The quantum yield for the formation of diiodide was determined from the peak values (at 1.5 ms after the pulse) of the transients at 390 and 750 nm, using 9400 dm^3 mol^{-1} cm^{-1} and 2800 dm^3 mol^{-1} cm^{-1} [18], respectively, as the molar absorbances of I_2^-. Changing the concentration of the ligand excess in the range of 2.63×10^{-3}–6.35×10^{-2} mol dm^{-3} did not significantly influence this quantum yield. Since the partial mole ratio of PbI_3^- decreased from 94% to 37% in this concentration range, both the tri- and the tetraiodoplumbate(II) complexes show the same efficiency ($\Phi = 0.10 \pm 0.005$) for the I_2^- formation. The peak absorbance of the diiodide intermediate proved to be proportional to the pulse energy (in the 6–20-mJ range), indicating a monophotonic process. Since the decay of the I_2^- intermediate involves several reactions (see Section 4), determination of the rate constants for these reactions needed a mathematical analysis of the transient curves taken at different Pb(II) concentrations. The procedure was based on the model suggested in Section 4, and the corresponding results for 2.63×10^{-3} mol dm^{-3} and 6.35×10^{-2} mol dm^{-3} iodide concentrations (C_I(added)) are presented there.

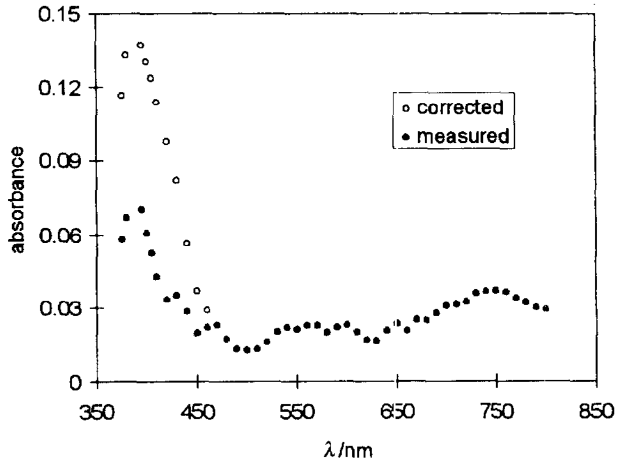

Fig. 6. The measured and corrected transient absorption spectra taken 1.5 ms after a 355 nm laser pulse in acetonitrile solution containing 10^{-4} mol dm^{-3} PbI_2 and 2.63×10^{-3} mol dm^{-3} Et_4NI ($l = 1$ cm).

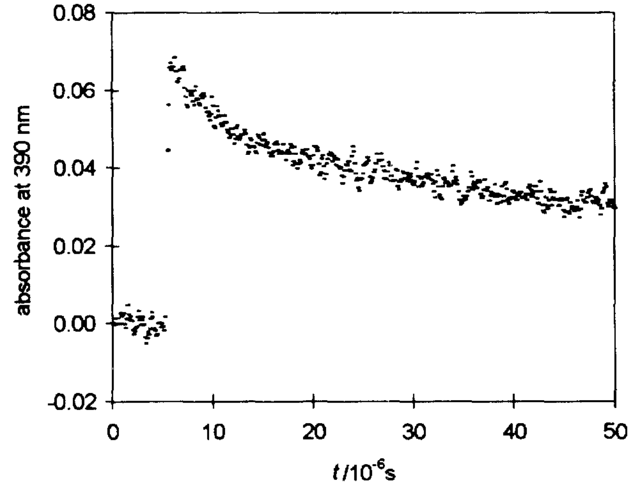

Fig. 7. Transient absorption at 390 nm (conditions as in Fig. 6).

4. Discussion

4.1. Spectroscopy and equilibrium

Whereas in a protic solvent the stepwise stability constants of only the monohaloplumbate(II) complexes could be determined [11–13], in aprotic media such as CH_3CN stability constants of higher coordination number species can be obtained. Thus, similarly to the chloro and bromo systems [9,19], tri- and tetracoordinated iodoplumbate(II) complexes exist in the 10^{-3}–0.1 mol dm^{-3} concentration range

Table 2
Longest-wavelength absorption bands and stepwise stability constants (K_4) of tri- and tetrahaloplumbate(II) complexes in acetonitrile

Complex	λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})	K_4/dm^3 mol^{-1}	Ref.
$PbCl_3$	273 (8100)	8.5×10^{-2}	[19]
$PbCl_4^{2-}$	294 (8200)		
$PbBr_3$	306 (6800)	1.31×10^4	[9]
$PbBr_4^{2-}$	343 (1970)		
PbI_3	366 (8700)	27	this work
PbI_4^{2-}	408 (11 500)		

of the free ligand. When comparing the values of K_4 for the three halo systems (Cl vs. Br vs. I) (Table 2), it can be seen that the value for $PbBr_4^{2-}$ is considerably larger than those of the other halo complexes. Qualitatively this can be explained in terms of hard-soft acid–base theory [20], according to which the bromide ion is a moderately soft base (ligand), while the Pb^{2+} ion is a moderately soft acid (metal center). Thus, the interaction of Pb^{2+} with Br^- can be expected to be significantly stronger than with the harder Cl^- or the softer I^- ions. Since harder bases are less favorable ligands for Pb^{2+} than softer ones, the chloro complex has the lowest stability constant in this series.

As previous studies revealed [9,10,19], the absorption spectra of the PbX_3^- complexes are basically characterized by metal-centered sp transitions. In the case of the tribromo and especially the triiodo complexes, however, the contribution of LMCT transitions is significant as indicated by a red shift of the longest-wavelength band (Table 2). A similar red-shift can be observed in the absorption band of the tetrabromo- and tetraiodoplumbate(II) complexes as well, and the crucial role of LMCT character in this band is demonstrated by the fact that these two complexes undergo photoreduction when irradiated into this band [9,10], whereas the Pb(II) center in the chloro complexes undergoes photooxidation in the presence of air [19] under similar irradiation conditions.

4.2. Photochemistry

Due to the LMCT character of the low-energy transitions of the iodoplumbate(II) complexes their photolysis leads to the reduction of the metal and the oxidation of the iodide ligands. While metallic lead and I_3^- are the final products of the photoinduced processes in these systems, a Pb(I)–I pair (Pb(I) represents PbI_3^{2-} or PbI_2^- complex) is formed in the primary photochemical step (Eq. (3)).

$$PbI_n^{(n-2)-} \xrightarrow{h\nu} PbI_{n-1}^{(n-2)-} + I \tag{3}$$

This pair can undergo a back reaction resulting in the initial ground-state complex (Eq. (4))

$$PbI_{n-1}^{(n-2)-} + I \rightarrow PbI_n^{(n-2)-} \tag{4}$$

or other thermal reactions may occur leading to the final products. Since the concentration of the free iodide was greater than 2.3×10^{-3} mol dm^{-3} in the solutions studied, formation of I_2^- occurred in all cases (Eq. (5)), due to the high value of the corresponding rate constant ($k_5 = 7.6 \times 10^9$ dm^3 mol^{-1} s^{-1}) [21].

$$I + I^- \rightarrow I_2^- \tag{5}$$

This intermediate can react with Pb(I) species (Eq. (6)) or undergo recombination, i.e., dismutation (Eq. (7)).

$$PbI_{n-1}^{(n-2)-} + I_2^- \rightarrow PbI_n^{(n-2)-} + I^- \tag{6}$$

$$I_2^- + I_2^- \rightarrow I_3^- + I^- \tag{7}$$

Both of these reactions should be second-order, but since the I_2^- intermediate exhibited a mix-order decay, at least one reaction of first-order kinetics has to play a significant role in the disappearance of I_2^-. Only the Pb(II) species, other than iodide ion, can be found in substantial (about one order of magnitude) excess compared to the concentration of I_2^- (ca. 1×10^{-5} mol dm^{-3}) in this system, and, therefore, a reaction between I_2^- and the ground-state iodoplumbate(II) complexes may take place (Eq. (8)).

$$PbI_n^{(n-2)-} + I_2^- \rightarrow PbI_{n-1}^{(n-2)-} + I_3^- \tag{8}$$

This conclusion is confirmed by the $C_{Pb(II)}$-dependence of the overall quantum yield for the I_3^- formation (Fig. 5).

The metal center in the Pb(I) intermediates that are formed either photochemically or thermally is finally reduced to the metallic state in an intramolecular ligand-to-metal charge transfer process (Eq. (9)) or via dismutation (Eq. (10)).

$$2PbI_{n-1}^{(n-2)-} \rightarrow 2Pb^0 + I_3^- + (2n-5)I^- \tag{9}$$

$$2PbI_{n-1}^{(n-2)-} \rightarrow Pb^0 + PbI_n^{(n-2)-} + (n-2)I^- \tag{10}$$

Since the presence of air increased the quantum yield for the formation of I_3^- but did not influence the decay of I_2^-, oxygen reacts with another intermediate, possibly Pb(I) (Eq. (11)).

$$PbI_{n-1}^{(n-2)-} + I^- + O_2 \rightarrow PbI_n^{(n-2)-} + O_2^- \tag{11}$$

One end-product of this reaction is peroxide, as was quantitatively determined in irradiated, air-saturated solutions. The O_2^- radical anion can oxidize iodide (Eq. (12)),

$$O_2^- + 3/2I^- \rightarrow O_2^{2-} + 1/2I_3^- \tag{12}$$

and peroxide can also oxidize I^- (even if much slower than O_2^-).

$$O_2^{2-} + 3I^- \rightarrow 2O^{2-} + I_3^- \tag{13}$$

or it decomposes, giving dioxygen.

In order to analyze the transient absorbance curves at 390 and 750 nm involving the decay of I_2^-, it was necessary to develop a mathematical model taking reactions 6–10 into consideration. As a reasonable approximation the concentration corresponding to the maximum absorbance was assumed to be the initial concentration of I_2^- (C_0), and the corresponding time was chosen as the start of its decay ($t = 0$). For the concentration determination at 390 nm, a correction was made for the Pb(II) species converted to Pb(I), using the corresponding molar absorbances (the Pb(I) species does not absorb at this wavelength) [22]. Since the diiodide radical ion disappears in three competitive reactions (Eqs. (6)–(8)) its concentration change is described by the following differential equation:

$$\begin{aligned} d[I_2^-]/dt = & -k_6[I_2^-][Pb(I)] - 2k_7[I_2^-]^2 \\ & -k_8[I_2^-][Pb(II)] \end{aligned} \tag{14}$$

The I_3^- species also absorbs at 390 nm, and therefore its formation has to be taken into account as well:

$$d[I_3^-]/dt = k_7[I_2^-]^2 + k_8[I_2^-][Pb(II)] + k_9[Pb(I)][I^-] \quad (15)$$

Moreover, the change in the concentration of Pb(I) also has to be considered because it takes part in both the formation of I_3^- and the consumption of I_2^-:

$$d[Pb(I)]/dt = -k_6[I_2^-][Pb(I)] + k_8[I_2^-][Pb(II)] - k_9[Pb(I)][I^-] - 2k_{10}[Pb(I)]^2 \quad (16)$$

A preliminary calculation indicated that the order of magnitude for the value of k_6 is 10^{10} dm^3 mol^{-1} s^{-1}. The average initial concentration of I_2^- (as well as that of Pb(I)) was about 1×10^{-5} mol dm^{-3}, and this value was taken for comparison of the rates of reactions with known or estimated rate constants. Since Pb^{2+} does not oxidize I^- in thermal reaction at room temperature, the probability of reaction 9, in which Pb(I) would oxidize iodide, is very low even if lead in this oxidation state is rather labile. Hence, this reaction could be neglected in the numerical analysis, i.e., k_9 was taken to be zero. Furthermore, the rate constant found in the literature for the disproportionation ($k_{10} = 1.7 \times 10^8$ dm^3 mol^{-1} s^{-1}) [22] indicates a minor significance of reaction 10 in the disappearance of Pb(I). Thus, it was necessary to determine k_6, k_7, and k_8, using a fitting procedure giving the lowest sum of the squares of the differences between the measured and calculated absorbances along the decay curves both at 390 and at 750 nm. The changes in the concentrations and, thus, the actual absorbances were calculated point by point (by a simple Euler-method) with 10^{-7} s intervals. The evaluation was done at both 2.63×10^{-3} mol dm^{-3} and 6.35×10^{-2} mol dm^{-3} iodide concentrations. The resulting values for k_6 and k_7 are $2.1 \pm 0.7 \times 10^{10}$ dm^3 mol^{-1} s^{-1} and $1.5 \pm 0.4 \times 10^9$ dm^3 mol^{-1} s^{-1}, respectively, and they proved to be the same at different concentrations of I^-. The magnitude of k_6 is typical for back reactions of product pairs formed in primary photochemical steps, indicating a diffusion controlled process. The value of k_7 is consistent with the corresponding data determined in acetonitrile solutions of iodomercurate(II) complexes [23]. However, k_8 was found to decrease with increasing iodide concentration, with values of $7.0 \pm 2.0 \times 10^7$ dm^3 mol^{-1} s^{-1} at 2.63×10^{-3} mol dm^{-3} I^- vs. $3.4 \pm 1.1 \times 10^7$ dm^3 mol^{-1} s^{-1} at 6.35×10^{-2} mol dm^{-3} I^-.

Using these values for the rate constants (along with the known and estimated ones) and the quantum yield determined for the formation of I_2^- at 355-nm excitation ($\Phi = 0.10$), the overall quantum yields for the production of I_3^- could be calculated at each Pb(II) concentration studied, using the same mathematical model for an interval of 100 ms (after which no change was observed in the absorption residue at 390 nm). The quantum yields calculated at 2.63×10^{-3} mol dm^{-3} I^- are in very good agreement with the values determined by continuous irradiation at 355 nm (Fig. 5). The calculated values are about 30% lower than the measured ones because the flash experiments, which were the basis of the calculations, were carried out with degassed solutions, while the continuous photolyses were with aerated systems.

The effect of oxygen can be attributed to reactions 11–13. The excess of I_3^- formed in the aerated system is due to reactions 12 and 13, i.e., the difference between the I_3^- concentrations measured in aerated and degassed solutions after 5-min irradiations at 366 nm (6.94×10^{-5} mol dm^{-3}–5.21×10^{-5} mol dm^{-3}), plus the peroxide determined in the aerated system (2.74×10^{-5} mol dm^{-3}) are almost equal to the concentration of I_3^- formed in the absence of oxygen. Of course, some peroxide may be decomposed, producing dioxygen instead of I_3^-. This significant effect of oxygen is strongly promoted by the high efficiency of reaction 11, the rate constant of which was determined to be 3.9×10^9 dm^3 mol^{-1} s^{-1} in aqueous system [24].

Since the quantum yields for the diiodide formation are the same for the tri- and the tetracoordinated species, the change in the overall quantum yield (for the I_3^- formation) as a function of $[I^-]$ may be caused by dark reactions involving the initial and/or intermediate complexes of different coordination numbers, i.e., reactions 8 and (much less probably) 9. Since the initial ground-state complexes are involved in these reactions, it is reasonable to examine how the shift in the PbI_3^-–PbI_4^{2-} equilibrium affects the overall quantum yield. The linear relationship between Φ and the partial molar percentage of PbI_3^- ($= 100[PbI_3^-]/C_{Pb(II)}$) clearly indicates the crucial role of the complex equilibrium in these thermal processes (Fig. 8). The significance of reaction 8 is confirmed by the fact that its rate constant at 2.63×10^{-3} mol dm^{-3} I^-, where 94% of Pb(II) exists as PbI_3^-, is substantially higher ($k_8 = 7.0 \times 10^7$ mol^{-1} dm^3 s^{-1}) than at 6.35×10^{-2} mol dm^{-3} I^- ($k_8 = 3.4 \times 10^7$ dm^3 mol^{-1} s^{-1}), where only 37% of Pb(II) is triiodoplumbate(II) and 63% is PbI_4^{2-}. This behavior can be attributed to the stronger repulsion of the latter species towards the negatively-charged reactants. Extrapolation of the plot in Fig. 8 gives the individual quantum yields for the PbI_3^- and PbI_4^{2-} complexes

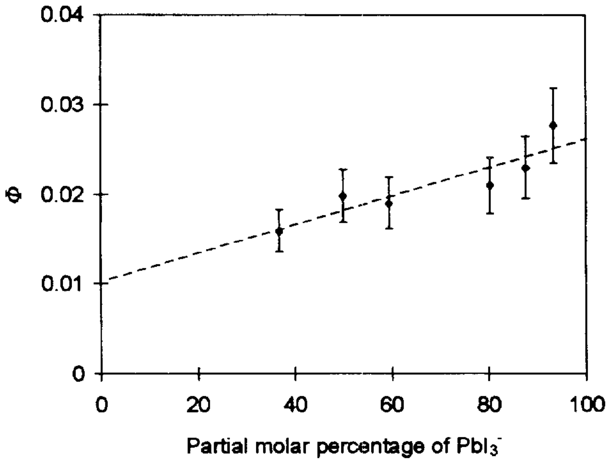

Fig. 8. Overall quantum yield (for I_3^- formation) vs. partial molar percentage of PbI_3^- in air-saturated acetonitrile ($C_{Pb(II)} = 10^{-4}$ mol dm^{-3}, $\lambda_{irr} = 366$ nm).

($\Phi_3 = 0.026 \pm 0.002$ and $\Phi_4 = 0.010 \pm 0.004$). The irradiation-wavelength dependence of the quantum yield (for the I_3^- formation) in solutions containing predominantly triiodo or tetraiodo species (Fig. 3) indicates that the quantum yields characteristic for PbI_3^- are in good agreement with its absorption spectrum in the 340–400-nm range. This confirms the LMCT feature of the transition assigned to the 366-nm band. The quantum yields at higher ligand concentration do not follow the shape of the absorption spectrum of PbI_4^{2-}. They are rather invariable in the 350–440-nm range, perhaps because of a fast internal conversion to a lower-energy excited state, from which the photochemical reaction takes place.

5. Conclusion

Simultaneous analyses of continuous and flash photolysis results provided a detailed model for the mechanism of the photoinduced redox processes that occur upon excitation of iodoplumbate(II) complexes in acetonitrile. The model, which includes appropriate rate constants, gives consistent explanations for the effects of Pb(II), I^-, and oxygen on the system studied. Since iodo complexes of other main-group metal ions with s^2 electronic configuration displayed similar photoredox behavior, the mechanism suggested here may prove to be applicable to the interpretation of those systems as well. New efforts in this direction using iodobismuthate(III) complexes appear to be promising.

Acknowledgements

Support of this work by the Hungarian Ministry of Culture and Education (grant No MKM 175/94) is gratefully acknowledged. We thank K. Oldenburg and Prof. A. Vogler (Universität Regensburg) as well as Prof. A. Horváth (University of Veszprém) for their competent professional assistance. O.H. is indebted to the Alexander von Humboldt Foundation for the donation of the AMKO LTI photolysis system used in this work.

References

[1] N.N. Greenwood, A. Earnshow, Chemistry of the Elements, Pergamon, London, 1984.
[2] F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, Wiley-Interscience, New York, 1988.
[3] O. Horváth, K.L. Stevenson, Charge Transfer Photochemistry of Coordination Compounds, VCH, New York, 1993.
[4] A. Vogler, A. Paukner, Inorg. Chim. Acta 163 (1989) 207.
[5] A. Vogler, A. Paukner, H. Kunkely, Coord. Chem. Rev. 97 (1990) 285.
[6] A. Vogler, H. Nikol, Pure Appl. Chem. 64 (1992) 1311.
[7] A. Vogler, A. Paukner, J. Photochem. Photobiol. A 46 (1989) 227.
[8] A. Vogler, H. Kunkely, in: K. Kalyanasundaram, M. Grätzel (Eds.), Photosensitation and Photocatalysis Using Inorganic and Organometallic Compounds, Kluwer, Dordrecht, 1993, p. 71.
[9] K. Oldenburg, A. Vogler, Z. Naturforsch. Teil B 48 (1993) 1519.
[10] K. Oldenburg, A. Vogler, I. Mikó, O. Horváth, Inorg. Chim. Acta 248 (1996) 107.
[11] A. Martell, L.G. Sillén, Stability Constants of Metal–Ion Complexes, Special Publ. No. 17, The Chemical Society, London, 1964.
[12] A. Martell, L.G. Sillén, Stability Constants of Metal–Ion Complexes, Special Publ. No. 25, The Chemical Society, London, 1971.
[13] E. Högfeldt, Stability Constants of Metal–Ion Complexes, Part A: Inorganic Ligands, Pergamon, Oxford, 1982.
[14] C.G. Hatchard, C.A. Parker, Proc. R. Soc. London, Ser. A 235 (1956) 518.
[15] K.L. Stevenson, R.M. Berger, M.M. Grush, J.C. Stayanoff, A. Horváth, O. Horváth, J. Photochem. Photobiol. A 60 (1991) 215.
[16] V. Wintgens, L.J. Johnston, J.C. Scaiano, J. Am. Chem. Soc. 110 (1988) 511.
[17] C.J. Ovenston, W.T. Rees, Analyst 75 (1950) 204.
[18] G.L. Hug, Optical Spectra of Nonmetallic Inorganic Transient Species in Aqueous Solution, National Bureau of Standards, Washington, 1981, pp. 54–55.
[19] H. Nikol, A. Becht, A. Vogler, Inorg. Chem. 31 (1992) 3277.
[20] D.S. Shriver, P.V. Atkins, C.H. Langford, Inorganic Chemistry, Oxford Univ. Press, Oxford, 1991, pp. 173–175.
[21] J.H. Baxendale, P.L. Bevan, D.A. Stott, Trans. Faraday Soc. 64 (1968) 2389.
[22] M. Breitenkamp, A. Henglein, J. Lilie, Ber. Bunsenges. Physik. Chem. 80 (1976) 973.
[23] O. Horváth, A. Vogler, Inorg. Chim. Acta 221 (1994) 79.
[24] J.H. Baxendale, J.P. Keene, D.A. Stott, J. Chem. Soc., Chem. Commun. (1966) 715.