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Photophysics and photochemistry of main group metals with an s^2 electron configuration. Luminescence quenching and photoreduction of trihydroxoplumbate (II) by hydroxide

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Abstract. The luminescence of $Pb(OH)_3^-$ in deaerated aqueous solution is quenched by hydroxide with $k = 1{\cdot}87 \times 10^5\,L\,mol^{-1}\,s^{-1}$. It is suggested that this quenching is associated with an electron transfer from hydroxide to $Pb(OH)_3^-$ in its $^3P_1$ *sp*- excited state. This assumption is supported by the photochemical behaviour of $Pb(OH)_3^-$ which is photoreduced to metallic lead. The efficiency of the photolysis increase with hydroxide concentration.

Keywords. Photochemistry; luminescence; lead(II); hydroxo complex.

1. Introduction

Recently we observed that the photolysis of $Pb(OH)_3^-$ in deaerated basic solution leads to the deposition of metallic lead (Becht and Vogler 1993). Further studies of this reaction revealed intriguing details which are the subject of this publication. We were able to show that electronically excited $Pb(OH)_3^-$ is reduced by hydroxide which is present in the bulk solution. Our results are of general interest under various aspects of inorganic photochemistry. The photoreduction of coordination compounds to elemental metals gains increasing attention. Light-induced metal deposition may be used for catalyst preparation, water purification, production of electronic devices and other processes (Borgarellow *et al* 1986; Cameron and Bocarsly 1986; Vogler *et al* 1988). Moreover, our observation that hydroxide acts as an outer-sphere reductant represents a new type of light-induced water oxidation which is of great importance in the design of photochemical water splitting systems (Zamaraev and Parmon 1980, 1983; Kiwi *et al* 1982). While transition metal complexes have been studied intensively the photochemistry of main group metal complexes (Vogler *et al* 1990; Vogler and Nikol 1992; Horváth and Stevenson 1993) has hardly been considered for such applications.

2. Experimental

2.1 *Materials*

Solutions of $Na[Pb(OH)_3]$ were obtained by dissolving yellow PbO (Merck, extra pure) in aqueous NaOH (Garrett *et al* 1939; Carell and Olin 1960). The water used

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in the photochemical experiments was triply distilled. All solutions were deaerated by saturation with argon.

2.2 *Photolyses*

The photolyses were carried out at room temperature in 1-cm quartz cells. The light source was a Hanovia Xe/Hg 977 B-1 (1 kW) lamp. Monochromatic light ($\lambda_{irr} = 254$ nm) was obtained by means of a Schoeffel GM 250-1 high-intensity monochromator. During irradiations the solutions were stirred using a small magnetic stirrer. For quantum yield determinations, the complex concentrations were such as to have essentially complete light absorption. The total amount of photolysis was limited to less than 5% to avoid light absorption by the photoproduct. Absorbed light intensities were determined by a Polytec pyroelectric radiometer, which was calibrated and equipped with an RkP-345 detector.

2.3 *Spectroscopy*

Absorption spectra were recorded with a Uvikon 860 double-beam spectrophotometer. Emission spectra were obtained on a Hitachi 850 spectrofluorimeter which was equipped with a Hamamatsu 928 photomultiplier. The luminescence spectra were corrected for monochromator and photomultiplier efficiency. Absolute emission quantum yields were determined by comparison of integrated emission intensity of $Pb(OH)_3^-$ with that of quinine sulfate in 0·5 M H_2SO_4 ($\lambda_{max} = 452$ nm; $\phi = 0{\cdot}546$) (Demas and Crosby 1971) under identical conditions such as exciting wavelength, optical density, and apparatus parameters.

3. Results

The absorption spectrum of $Pb(OH)_3^-$ ($\lambda_{max} = 239$ nm; $\varepsilon = 4500\ \mathrm{L\,mol\,cm^{-1}}$) (Becht and Vogler 1993) in aqueous sodium hydroxide solution was independent of the hydroxide concentration at $[OH^-] > 0{\cdot}01$ M. However, the emission of $Pb(OH)_3^-$ ($\lambda_{max} = 570$ nm) (Becht and Vogler 1993) was quenched by hydroxide (table 1). In 0·1 M NaOH the emission lifetime was $\tau = 45 \pm 5\ \mu s$.

Table 1. Absolute emission quantum yields ($\lambda_{em} = 570$ nm; $\lambda_{ex} = 254$ nm) of $4{\cdot}0 \times 10^{-4}$ M $Pb(OH)_3^-$ in deaerated aqueous solutions at various NaOH concentrations.

[NaOH] ($\mathrm{mol\,L^{-1}}$)	$\phi_{em} \times 10^3$	[NaOH] ($\mathrm{mol\,L^{-1}}$)	$\phi_{em} \times 10^3$
0·01	5·3	0·2	0·8
0·03	3·8	0·4	0·4
0·05	2·6	0·6	0·3
0·08	1·8	0·8	0·2
0·1	1·5	1·0	0

Table 2. Irradiation times and relative quantum yields (see text) of the photoreduction of $1{\cdot}2 \times 10^{-3}$ M $Pb(OH)_3^-$ to elemental lead in deaerated aqueous solutions at various NaOH concentrations ($\lambda_{irr} = 254$ nm).

[NaOH] (mol L^{-1})	t_{irr} (s)	ϕ_{rel}
1·0	270	1
0·7	315	0·86
0·5	390	0·69
0·3	600	0·45
0·1	—[a]	0

[a] Deposition of elemental lead was not observed

The photolysis of $Pb(OH)_3^-$ in argon-saturated basic solution with $\lambda_{irr} = 254$ nm led to the formation of metallic lead as a black colliod. The metal deposition took place after an induction period which may be caused by two effects. A residual amount of oxygen in the solution would lead to an oxidation and not a reduction of Pb^{2+} in the beginning of the photolysis (Becht and Vogler 1993). In addition, the metal colloid is formed in an agglomeration process which becomes visible only if the particles have reached a certain size (Vogler *et al* 1988). These problems hampered the determination of absolute photochemical quantum yields. However, relative rates of metal deposition were determined spectrophotometrically. The formation of the colloid is accompanied by an apparent increase of the optical density of the solution over the entire UV/visible wavelength region. The irradiation time which was required to reach a certain absorbance ($A = 0{\cdot}21$) at a selected wavelength (350 nm) where only the product absorbs was measured as a function of the hydroxide concentration under the same experimental conditions such as complex concentration, light intensity, and apparatus parameters. The reliability of these measurements is based on the assumption that with regard to particle size and size dispersion colloid formation occurs reproducibly. These measurements (table 2) show clearly that the lead deposition was much faster at higher hydroxide concentrations.

The photolysis of $Pb(OH)_3^-$ could be driven to completion. After continuous irradiation the metal was removed by centrifugation. The solution did not contain any more $Pb(OH)_3^-$ as indicated by the absence of the absorption maximum at 239 nm. Potential oxidation products of the photolysis are hydrogen peroxide and/or oxygen. Since H_2O_2 was not detected, hydroxide was apparently photoxidized to O_2.

4. Discussion

In basic solution, lead(II) exists as $Pb(OH)_3^-$ (Garrett *et al* 1939; Carell and Olin 1960; Birss and Shevalier 1987). The UV spectrum of the complex displays a single absorption band ($\lambda_{max} = 239$ nm; $\varepsilon = 4500$ L mol cm^{-1}) which is assigned to the metal-centered $^1S_0 \rightarrow {}^3P_1$ *sp* transition (Becht and Vogler 1993). The $^3P_1$ state is emissive ($\lambda_{max} = 570$ nm) under ambient conditions with $\tau = 45\,\mu$s at $[OH^-] = 0{\cdot}1$ M. From the Stokes shift ($\Delta E = 24300$ cm^{-1}) the energy of the $^3P_1$ state is estimated to be roughly 29,700 cm^{-1} or 3·7 eV.

$Pb(OH)_3^-$ can be oxidized to $Pb(OH)_6^{2-}$ at $E^0 = 0{\cdot}330$ V and reduced to metallic lead at $E^0 = -0{\cdot}540$ V (Galus 1985). Since the reduction and oxidation are two-electron processes, these ground-state potentials may not be used to calculate excited state redox potentials which are based on one-electron transfer steps. However, taking into account the large excitation energy, electronically excited $Pb(OH)_3^-$ is certainly a very strong reductant and oxidant. Accordingly, $Pb(OH)_3^-$ is expected to undergo intermolecular photoredox reactions. In fact, it has been shown recently that the photooxidation of $Pb(OH)_3^-$ to $Pb(OH)_6^{2-}$ by O_2 is a facile process (Becht and Vogler 1993). Other s^2 metal ions such as Tl^+ (Kirkbright *et al* 1972; Vogler and Nikol 1992), Sn^{2+} (Pringsheim and Vogels 1940) and Sb^{3+} (Vogler and Paukner 1989) can be also photooxidized by oxygen. On the contrary, photoreductions of s^2 ions by excited state electron transfer have not yet been observed. Here we report the first example of this reaction type.

In deaerated solution the luminescence of $Pb(OH)_3^-$ is quenched by hydroxide (table 1). Assuming a simple dynamic quenching, standard Stern–Volmer kinetics should be operative (ϕ_0 and τ_0 are the luminescence quantum yield and the lifetime in the absence of hydroxide):

$$\frac{1}{\phi} = \frac{1}{\phi_0} + k_q \frac{\tau_0}{\phi_0}[OH^-]. \qquad (1)$$

The Stern–Volmer plot (figure 1) yields a straight line with an intercept of 125 and a slope of 5600 L mol^{-1}. From the intercept ϕ_0 is calculated to be $8{\cdot}0 \times 10^{-3}$. This is, however, a hypothetical value since $Pb(OH)_3^-$ exists only in basic solution (Carell and Olin 1960). The luminescence lifetime ($\tau = 45\,\mu s$ at $[OH^-] = 0{\cdot}1$ M) can now be used to obtain the quenching constant ($k_q = 1{\cdot}87 \times 10^5$ L mol^{-1} s^{-1}).

We suggest that the quenching is caused by excited state electron transfer from hydroxide to $Pb(OH)_3^-$. The one-electron oxidation of OH^- requires a potential of

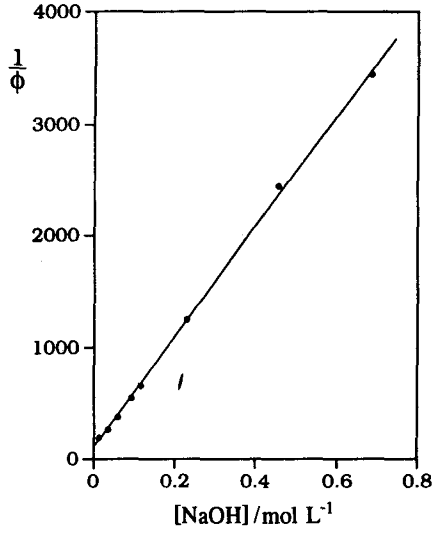

Figure 1. Stern–Volmer plot of the inverse emission quantum yield ($\lambda_{em} = 570$ nm; $\lambda_{ex} = 254$ nm) of $4{\cdot}0 \times 10^{-4}$ M $Pb(OH)_3^-$ versus NaOH concentration.

$E^0 = 2{\cdot}8$ V (Endicott 1988). Although the redox of the excited complex is not known (see above) the large excitation energy ($\approx 3{\cdot}7$ eV) should provide sufficient driving force for a facile reduction by OH^-.

The assumption that the luminescence quenching of $Pb(OH)_3^-$ by OH^- is caused by excited state electron transfer is strongly supported by photochemical evidence. In deaerated solution $Pb(OH)_3^-$ undergoes a photoreduction to metallic lead with an efficiency which increases with the hydroxide concentration (table 2).

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