Photodecomposition of Lead Bromochloride Film

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The molar extinction coefficient as a function of wavelength between 300 and 700 nm can be calculated for PbBrCl from the absorption measurements reported in this paper. Quantum efficiencies of the production of bromine and chlorine during the photodissociation of PbBrCl have been determined at 300, 350, 475, and 525 nm.

Introduction

Pierrard¹ has studied the photodecomposition of lead bromochloride particles in carbon tetrachloride. However, the absorption spectrum, molar extinction coefficients, and quantum efficiencies of this species have not been reported. We have obtained this information by means of UV-visible, X-ray fluorescence, and X-ray photoelectron spectroscopy (XPS). We believe that this is the first attempt to apply XPS to study the kinetics of photodecomposition.

Aside from the scientific interest, this problem is also important for understanding the transformation of lead compounds in a polluted atmosphere. Most lead in the atmosphere, especially in urban areas, originates from combustion of gasoline containing antiknock additives and is mainly in the form of PbBrCl.² Field experiments indicate that the halogen-to-lead ratio decreases with aerosol age,³⁻⁵ presumably as the result of photodecomposition.

Experimental Section

Thin vacuum-evaporated PbBrCl films were used throughout this study. The films were vaporized in a Varian vacuum vapor deposition chamber ($\sim 10^{-5}$ torr) onto quartz substrates for absorption spectrum measurements, and aluminum substrates for quantum efficiency studies. These substrates were mounted on a glass plate. The thickness of the PbBrCl deposit on the substrate was not measured directly: instead, the thickness of the deposit produced on the glass plate was measured with a Varian interference microscope after a thick coating of gold was deposited on the plate to provide a good optical reflection face.

A sodium lamp (Na D lines at 589.3 and 589.5 nm) was used as a light source to measure the film thickness. The absorption spectra were obtained with a Cary 118 recording spectrophotometer. For the photodecomposition studies, a 200-W high-pressure mercury arc (Osram HBO200W) was used with and without a Bausch and Lomb high-intensity grating monochromator. Light intensities were measured by a Hewlett-Packard 8330A radiant fluxmeter.

The rate of photodecomposition was studied at 525, 475, 350, and 300 nm. The optical band width (full width at half-maximum) was about 6.5 nm at these wavelengths.

The rate of production of metallic lead resulting from the photolysis of PbBrCl was monitored by means of X-ray photoelectron spectroscopy (XPS). XPS spectra reported in this paper were obtained with an AEI ES200 photoelectron spectrometer utilizing Al K α X-rays (1486.6 eV) with a sample chamber pressure of $\leq 10^{-8}$ torr during measurements. Photoelectron peak energies were referenced to the gold (4f_{7/2}) binding energy, 84.0 eV.

XPS peaks corresponding to PbBrCl and metallic lead were periodically monitored during the course of irradiation. The XPS spectrum of the Pb $(4f_{5/2,7/2})$ region was taken for each PbBrCl sample before photolysis. The sample was then rotated so that the surface of the film faced the mercury arc light source, whose beam entered the XPS vacuum chamber through a sapphire window. The geometry of the light beam was adjusted so the entire PbBrCl sample ($\sim 6 \times 12$ mm) was evenly irradiated. After irradiation of the PbBrCl film at room temperature (20 °C) for the desired length of time, the sample was rotated back to its normal position, and the XPS spectrum of the Pb $(4f_{5/2,7/2})$ region was again recorded. This procedure was repeated periodically. In addition to the PbBrCl peaks, two new $4f_{5/2,7/2}$ peaks appeared with binding energies corresponding to those of metallic lead.

Elemental concentrations of lead, bromine, annd chlorine were analyzed by X-ray fluorescence before and after irradiation. The data obtained in these experiments permitted calculation of the quantum efficiencies (see next section).

Results

Figure 1 shows the absorption spectra between 700 and 300 nm of PbBrCl (dashed line), PbBrCl irradiated with natural sunlight (dotted line), and PbBrCl irradiated with a 200-W mercury arc (solid line). For the PbBrCl film at 20 °C, there are three broad absorption regions without any structure: one covers a visible region between 700 and 425 nm; the second starts from the visible region at 410nm and extends into the UV region at 335 nm; and the third starts at \sim 335 nm and extends into the shortwavelength limit. The thickness of the vacuum-evaporated PbBrCl film was 196.5 ± 6.7 nm. Assuming a value of 6 g/cm^3 for the density of the PbBrCl film (based on the unit cell volume given by Calingaert et al.⁶), the molar extinction coefficients of PbBrCl at 525, 475, 350, and 300 nm were calculated to be 9.66 \times 10², 7.06 \times 10², 1.20 \times 10³, and 1.82×10^4 L/mol-cm. The film was exposed to natural sunlight in air for a period of 1 h. This produced a small increase in absorption between 330 and 480 nm (dotted

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Figure 1. Absorption spectrum of PbBrCl thin film at 20 $^{\circ}$ C (dashed line); after a 1-h exposure in air to natural sunlight (dotted line); after a 2-h additional irradiation by a 200-W mercury arc (solid line).

line). The total radiant energy at the time of exposure was 95 mW/cm^2 . The same film was further irradiated for 2 h by a 200-W high-pressure mercury arc, with a total radiant energy of 20 mW/cm². The absorption spectrum of the film after the mercury arc irradiation (solid line) shows a decrease in absorption for wavelengths below 315 nm and above 530 nm, and an increase in absorption between 315 and 530 nm. The PbBrCl film was darker after arc irradiation; its brownish gray color is reflected in the absorption spectrum of the irradiated film as a broad continuous absorption throughout the visible region.

Figure 2 illustrates the use of XPS in monitoring the changes in concentrations of species during the course of the PbBrCl photodissociation. The binding energies of the electrons of PbBrCl are: Cl $(2p_{1/2,3/2})$ 199.4, 197.9 eV; Pb $(4f_{5/2,7/2})$ 143.7, 138.8 eV; and Br $(3d_{3/2,5/2})$ 69.4, 68.6 eV. After a 5-min in vacuo radiation of PbBrCl by the 200-W mercury arc, $4f_{5/2,7/2}$ peaks corresponding to metallic lead appear at binding energies of 141.5 and 136.6 eV.⁷ The intensity of these metallic lead peaks grows as the irradiation time increases, as can be seen in the spectra corresponding to irradiation times of 10, 80, and 140 min. As Figure 2 shows, the rate of production of metallic lead is not constant throughout the entire period of irradiation.

If the metallic lead formed during photolysis is oxidized to PbO, then its XPS lines, which are only slightly shifted from the PbBrCl peaks, can interfere with the determination of both the metal and the halide peak intensities. This was not found to be a problem, however, because the rate of oxidation of metallic lead⁸ to PbO is slow at the pressures maintained in the XPS sample chamber ($\leq 10^{-8}$ torr). For example, the intensity of metallic lead decreased by only ~10% when the sample irradiated for 140 min was left in the vacuum chamber for 40 h. Lead can be oxidized quickly, however, when it is exposed to ambient air, as shown in the spectrum in Figure 2 following a 10-min exposure to air.

Figure 2 also shows the loss of halogen from the PbBrCl film as a result of irradiation, manifested by the decrease in the chlorine and bromine photoelectron peak intensities until they reach a stable value. The observed loss of Br⁻ and Cl⁻ corresponds to the increase in metallic lead within the accuracy of the method $(\pm 10\%)$.

Because of the difficulty in accurately deconvoluting the lead (4f) spectra, we determined the intensity of the metallic lead $(4f_{5/2,7/2})$ peaks by subtracting the spectrum of the unirradiated sample from the spectra taken following each successive irradiation (Figure 3). Although the intensity decrease in the lead halide peaks should equal the increase in the metallic lead peaks, the slow deposition

of a hydrocarbon surface layer on the sample reduced the intensities of these peaks. Thus the apparent decrease in lead halide is greater than the increase in metallic lead. We corrected for this by averaging the intensity decrease in the halide peaks with the intensity increase in the metallic lead peaks to determine a more accurate peak intensity for metallic lead.

Figures 4 through 6 show the experimental results of PbBrCl photolysis, with the ratio of metallic lead to total lead concentration plotted as a function of the irradiation time. Figure 4 shows the results obtained with a sample irradiated by a nondispersed mercury arc. Figures 5 and 6 show the results of irradiation at 350 and 300 nm, with photon fluxes of 5.85×10^{13} and 5.05×10^{13} photons/cm² s. The rate of production of metallic lead is initially fast but approaches saturation with continued irradiation. We did not detect the appearance of the metallic lead photoelectron peaks when the sample was irradiated at 525 or 475 nm.

Angularly resolved XPS measurements⁹ were performed to find out to what degree the PbBrCl photolysis was confined to the sample surface. These measurements involve changing the photoelectron escape angle relative to the sample surface; low escape angles enhance the peak intensities of surface species with respect to those found in layers beneath the sample surface. With this technique, we found the concentration of metallic lead to be distributed nonuniformly in the sample volume. For a sample irradiated by the mercury arc for about 4 h, there is a marked increase in the relative intensity of metallic lead to lead halide when the photoelectron escape angle is low (Figure 7). The increase implies a higher concentration of metallic lead on the surface of the film. The mean free path of electrons in metallic lead¹⁰ is about 2.0 nm at a kinetic energy of 1350 eV. We have calculated the mean free path of electrons in PbBrCl to be about 2.5 nm, using the formula given by Penn.¹⁰ Therefore the ratios of metallic lead to total lead concentration (Figures 4-7) represent only a thin surface layer, not the entire PbBrCl film (~ 200 nm thick). However, we can calculate the bulk lead to lead halide ratio for the entire sample by using the Beer-Lambert equation and the molar extinction coefficients reported earlier. This is done by multiplying the lead to lead halide ratio (for the sample surface) determined from XPS by the factor $(I_0 - I_3)l_1 \cos (90 - \theta)/[(I_0$ $(I_1 - I_1) + (I_2 - I_3)]l_2$. I_0 is the intensity of the radiation incident on the surface of the PbBrCl film; I_1 is the intensity of the radiation after penetrating a distance $l_1 \cos l_2$ $(90 - \theta)$, where l_1 is the electron mean free path and θ is the photoelectron escape angle; I_2 is the intensity of the radiation that reaches the surface layer after it penetrates the entire thickness of the film (l_2) and after it reflects from the aluminum backing; and I_3 is the intensity of the radiation as it emerges from the surface of the sample. From this ratio and from the X-ray fluorescence results, we can calculate the amount of halogen lost as a function of the irradiation time. Quantum efficiency is therefore calculated according to the equation

$$\phi_{\lambda} = \Delta/Jt(I_0 - I_3)/I_0$$

where ϕ_{λ} is the quantum efficiency at wavelength λ , Δ is the amount of bromine or chlorine lost in number of atoms per square centimeter during the irradiation time t (in seconds), and J is the photon flux in number of photons per second-square centimeter. We have calculated the

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Figure 2. XPS spectra of PbBrCI showing changes in intensity of reactant and product peaks with increasing irradiation.



Figure 3. Difference between Pb (4f) XPS spectra before and after irradiation showing a decrease in the lead halide peaks and an increase in the metallic lead peaks.



Figure 4. Ratio of metallic lead to total lead as a function of the irradiation time during the course of irradiation of PbBrCl by a 200-W mercury arc.



Figure 5. Ratio of metallic lead to total lead as a function of the irradiation time during the course of irradiation of PbBrCl at 350 nm.

quantum efficiencies at 350 and 300 nm for chlorine and bromine when the irradiation time (t) approaches zero. The results are listed in Table I. the quantum efficiencies at 525 and 475 nm are negligible because no obvious photolysis of PbBrCl was observed at these wavelengths.

Conclusions

According to Kaldor and Somorjai,¹¹ the mechanism of PbBrCl photodecomposition can be visualized as involving three major steps: (1) the photon-induced charge-trapping at halide ion vacancies, resulting in the release of halogen in the lattice; (2) the charge transfer between the halide ion vacancy and the lead cation leading to the production of lead; and (3) the removal of halogen from the lattice.

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TABLE I: Quantum Efficiencies of the Production of Bromine and Chlorine during the Photodissociation of PbBrCl

wavelength nm	photon flux photons/cm² s	film thickness, nm	total irrad time, h	$\Delta_{Br}^{a}^{a}$ $\mu g/cm^{2}$	$^{\Delta}_{\mathrm{Cl}},^{b}_{\mu\mathrm{g/cm}^{2}}$	$\phi_{\mathbf{Br}}$	ΦCl	
350 300	$\begin{array}{c} 5.85 \times \ 10^{13} \\ 2.5 \times \ 10^{13} \end{array}$	179 179	9.5 2	$\begin{array}{c} 1.72\\ 2.30\end{array}$	0.55 0.90	0.038 0.35	0.027 0.31	

^a $\Delta_{Br} = loss$ of bromine after irradiation. ^b $\Delta_{Cl} = loss$ of chlorine after irradiation.



Figure 6. Ratio of metallic lead to total lead as a function of the irradiation time during the course of irradiation of PbBrCl at 300 nm.



Figure 7. Relative intensity of metallic lead to lead halide photoelectron peaks as a function of the escape angle θ (relative to the sample surface).

They determined the rate-determining step to be the charge-trapping by lead and halide ions rather than the removal rate of halogen from the lattice. Therefore the rate of photodecomposition should not be affected by the sample's being irradiated in vacuum rather than at atmospheric pressure.

The PbBrCl film showed a large increase in production of metallic lead after exposure to the mercury arc in contrast to the exposure to natural sunlight, even though natural sunlight has more radiant energy than the mercury arc. This observation can be explained by differences in the spectral composition of the two light sources and by the fact that the quantum efficiency and molar extinction coefficient of PbBrCl are wavelength dependent. The mercury arc is more intense than natural sunlight in the UV absorption region of PbBrCl, and the quantum efficiency and molar extinction coefficient are greater in the UV-visible absorption region than in the visible absorption region.

Since the thickness of the metallic lead at observed saturation (Figures 4-6) is not great enough to completely block the incident light, we can only hypothesize as to the source of this saturation. It may be due to reaction of metallic lead with halogens migrating from deeper in the film. Whatever the cause, this result should be taken into account when calculating the loss of halogen from PbBrCl particles in the atmosphere.

Ambient photon flux¹² at Los Angeles in summer at noon is approximately 1.85×10^{16} photons cm⁻² s⁻¹ in the region 335-410 nm and 4.0×10^{15} photons cm⁻² s⁻¹ in the region 300-310 nm. With this flux, we would predict that an exposed $0.2-\mu m$ (200-nm diameter) PbBrCl particles would lose 10% of its halogens in less than 1 min, based on the observed production of metallic lead from photolysis of a PbBrCl film at 350 and 300 nm (Figures 5 and 6). Further loss would be at a slower rate because of the saturation phenomena. However, the PbBrCl particles found in the atmosphere are likely to have coagulated with other small particles which are highly light absorbing, e.g., soot, thus reducing exposure of the lead halide to sunlight. Therefore, an undefined particle morphology will also slow the bulk rate of halogen loss to an extent currently impossible to quantify.

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