ELSEVIER

Journal of Photochemistry and Photobiology
A: Chemistry 86 (1995) 81–84

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A:CHEMISTRY

Sensitized photolysis and intercalation of PbI_2 by anilines and ammonia

G.I. Gurina *, K.V. Savchenko

Departments of Polymeric Composite Materials and Physical Chemistry, Polytechnic University, Kharkov, 310002, Ukraine

Received 16 November 1993; accepted 2 August 1994

Abstract

The kinetics of PbI_2 photolysis sensitized by para-substituted aniline were studied by reflectivity measurements. Photolysis and PbI_2 intercalation are overlapping processes at aniline concentrations exceeding the intercalation threshold, leading to a decrease in the efficiency of photolysis. Linear Hammett-type correlations between the logarithm of the photolysis rate constants, the average shifts of the IR absorption bands of the N–H bond after intercalation and the Hammett constants σ_p^* allow the similarity between the photolysis and intercalation mechanisms to be determined. The effect of ammonia concentration changes on the photoconductivity of PbI_2 thin films was ascertained.

Keywords: Photolysis; Intercalation; Anilines; Ammonia

1. Introduction

The efficiency of PbI_2 photolysis becomes appreciable at temperatures exceeding 450 K [1–3]. A decrease in the photolysis temperature by more than 100 K has been established on irradiation of PbI_2 samples in gaseous or liquid amine media [4–6]. Spectral measurements of the photolysis efficiency have shown [5–7] that amines (ammonia, aniline, 2-aminoethanol) can act as chemical sensitizers, i.e. the spectral region of photolysis activity of the samples in amine medium corresponds to the PbI_2 absorption band. When amine molecules (ammonia or 2-aminoethanol [6]) are intercalated into the PbI_2 matrix and the PbI_2 energy gap is increased (for $PbI_2(C_2H_7NO)_2$ to 3.02 eV and for $PbI_2(NH_3)_4$ to 2.69 eV) or decreased (for $PbI_2(C_2H_7NO)_1$ to 2.14 eV), the spectral region of the photoactivity of the intercalated sample is shifted in conformity with the PbI_2 absorption band shift after intercalation [6].

A study of the relationship between the intercalation and photolysis of PbI_2 has allowed a kinetic similarity to be revealed which results from intercalated compound formation during PbI_2 photolysis in ammonia medium [6].

The photochemical reactions of lead iodide in various media containing amines have been studied during the development of non-silver-photosensitive materials [4] and have been used as a method for the determination of amines in non-reducing media [7].

In this paper, the results of a PbI_2 photolysis sensitization study and the effect of aniline para substitution on the photolysis efficiency are reported. The similarity between the mechanisms of sensitized photolysis and amine intercalation of PbI_2 is discussed.

2. Experimental details

A spectroscopically pure powder of PbI_2 was used. *Para*-substituted anilines (4-nitroaniline, 4-iodoaniline, *p*-toluidine, *p*-anisidine, 1,4-phenylenediamine and aniline) were purified using distillation, recrystallization or sublimation methods; the purity was checked by IR spectroscopy.

The kinetic measurements were carried out using an automatic apparatus [6] for the digital recording of reflectivity and photoconductivity under a polychromatic light flux of about 10^{-2} W m^{-2}. The reflectivity and photoconductivity changes were measured in real time using a transcryptor data acquisition system. The recording of the kinetics was carried out at 0.10, 0.50 or 1.00 s intervals. The photolysis efficiency in anilines

---

* Corresponding author. Fax: +7 (0)572-400-601.

1010-6030/95/$09.50 © 1995 Elsevier Science S.A. All rights reserved
SSDI 1010-6030(94)03937-2

was estimated using a value of PbI_2 surface blackening ($H = (R_0 - R_t/R_0$, where R_0 and R_t are the reflectivities before and after irradiation respectively). The concentration of the phase formed was taken to be proportional to the value of H. The logarithm of the photolysis rate constant k_{ph} was computed from the equation $-dH/dt = k_{ph}(1-H)$ using the least-squares fitting method.

The intercalated compounds were prepared by exposure of PbI_2 samples to amine media [8]. The IR spectra were registered using a Specord IR-75 double beam spectrophotometer. KBr pellets contained 1%–2% of the intercalated compounds. The average shift of the absorption bands of the N–H bond after intercalation was determined as: $\Delta\nu_{av}(N\text{–}H) = (\Delta\nu_s + \Delta\nu_{as})/2$, where $\Delta\nu_s$ and $\Delta\nu_{as}$ are the wavenumber shifts of the symmetric and antisymmetric modes of the N–H bond respectively.

Thin films of PbI_2 (0.1–2.0 μm) were deposited in vacuum (10^{-3} Pa) by a resistive method at a deposition rate of about 100 Å s^{-1}. The substrate temperature was about 423 K during the deposition. Ohmic Ga–In contacts for electric measurements were used. The photoconductivity was measured using a low-current gauge with a signal output to a digital voltmeter.

In the structural studies, an X-ray powder diffractometer (Cu Kα radiation) was used.

3. Results and discussion

The substituent at the para position of aniline has an important effect on the efficiency of sensitized photolysis of lead iodide. The kinetics of PbI_2 photolysis for the series $R\text{–}C_6H_4\text{–}NH_2$, where R is $-NH_2$, $-O\text{–}CH_3$, $-CH_3$, –H, –I and $-NO_2$, were studied at a temperature of 322 K and an aniline concentration $c_1 = 0.01$ M in benzene. The photoreaction rate constants k_{ph} were calculated as described above. The correlation between the logarithm of the rate constants ($\ln k_{ph}$) and the Hammett constants σ_p^* is presented in Fig. 1 (line a). The slope (ρ) and the linear correlation coefficient (r) are as follows: $\rho = 0.63$ and $r = 0.981$. This correlation confirms the mechanism proposed in Ref. [6], involving charge transfer interaction between an atom of nitrogen and an atom of lead on photolysis.

The aniline concentration c_1 was chosen to eliminate aniline intercalation at 322 K into the interlayers of the PbI_2 matrix. Intercalation occurs at amine concentrations exceeding the intercalation threshold [9]. c_1 was chosen from the dependence of the photolysis efficiency H on $\ln c$ at 322 K. The dependence H vs. $\ln c$ for 1,4-phenylenediamine in the 0.001–0.04 M range in benzene at times of 5.0, 10.0, 15.0 and 20.0 s from the start of the reaction is presented in Fig. 2 (curves a–d). A decrease in H at concentrations $c > c_1$ is caused by the formation of the intercalation phase. A similar case has been observed in ammonia [6].

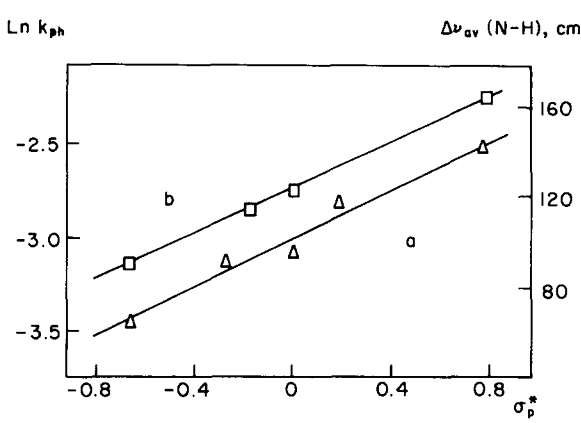

Fig. 1. Correlations between the logarithm of the rate constant ($\ln k_{ph}$, line a) of the aniline-sensitized photolysis of PbI_2, the average shift in the IR absorption bands of the N–H bond after PbI_2 intercalation ($\Delta\nu_{av}$(N–H), line b) and the σ_p^* constants.

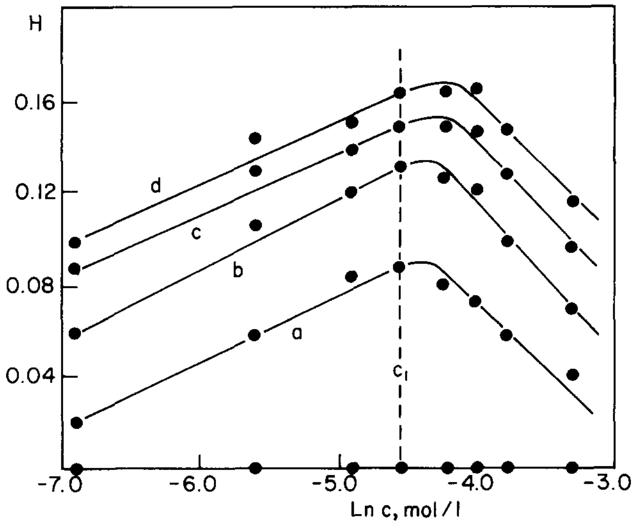

Fig. 2. Plots of the PbI_2 photolysis efficiency (H) vs. the logarithm of the 1,4-phenylenediamine concentration ($\ln c$) at 5.0 s (curve a), 10.0 s (curve b), 15.0 s (curve c) and 20.0 s (curve d) from the start of the photoreaction at 322 K.

The formation of the intercalation phase in the PbI_2–1,4-phenylenediamine system and the other systems studied was confirmed by the aniline absorption band changes in the IR spectrum. The PbI_2 matrix is transparent in the IR region of the spectrum, and therefore the vibrational spectra of incorporated molecules can be analysed to determine the mechanism of intercalated complex formation [9–12]. During PbI_2 intercalation, an expansion in the c axis of PbI_2 and a pronounced shift in the absorption bands of the N–H bond occur for a number of amines. The same effect has been observed during the intercalation of sheet aluminosilicate montmorillonite [13].

Fig. 3 shows the IR absorption band changes of the N–H bond for aniline after intercalation; softening of the symmetric ν_s (from 3375 to 3253 cm^{-1}) and antisymmetric ν_{as} (from 3455 to 3310 cm^{-1}) modes occurs.

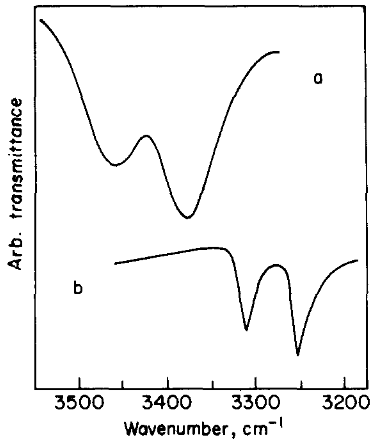

Fig. 3. Symmetric and antisymmetric modes of the N–H bond in the IR spectra: (a) pure aniline sample; (b) aniline-intercalated PbI_2 sample.

A similar softening of the N–H modes for the PbI_2–NH_3 complex has also been reported in Ref. [14].

Our study of the X-ray structure confirms an expansion of 3 Å in the c axis during aniline intercalation [15,16]. The diffraction pattern of aniline-intercalated PbI_2 has a different intensity distribution and a larger number of peaks than that in Ref. [16] because textured thin films of aniline-intercalated PbI_2 were studied.

The shifts in the absorption bands ν(N–H) after intercalation for 1,4-phenylenediamine were 69 and 110 cm^{-1}; the absorption bands ν(N–H) of 4-nitroaniline (3480 and 3360 cm^{-1}) were shifted to 3285 and 3225 cm^{-1} respectively. Shifts in the ν(N–H) absorption bands are typical of all aniline-intercalated PbI_2 samples.

In recent years, the charge transfer interaction between nitrogen atoms and matrix atoms after amine intercalation has been widely studied both theoretically [16–19] and experimentally [9–12,15,20,21]. The development of single-charged ions Pb^+ has been observed in samples of PbI_2 intercalated by some amines, including aniline [20,21], which has been considered as evidence for a charge transfer interaction between the electron-donating organic molecules and the matrix atom of Pb. Furthermore, the existence of strong Pb–N interactions has been demonstrated by IR and Raman spectroscopy for PbI_2 intercalation by a number of amines [14].

However, the theoretical calculations described in Refs. [16] and [19] show that the main changes in the band gap of PbI_2 on intercalation of amine are related to the perturbed iodine orbitals, since the guest molecules are confined between the iodine atomic planes. The increase in the band gap after intercalation was modelled by computing the changes in the band structure resulting from the electrostatic interaction of the $-NH_2$ dipole of aniline with the iodine $5p_z$ electron and from the PbI_2 lattice expansion of 3 Å in the c axis [16].

Our IR spectral study of aniline-intercalated PbI_2 has led to the establishment of a linear Hammett-type correlation between the average wavenumber shift of the absorption bands of the N–H bond after intercalation ($\Delta\nu_{av}$(N–H)) and the $\sigma_p{}^*$ constants (Fig. 1, line b) with $\rho = 52$ and $r = 0.98$. The existence of this dependence, as well as the linear dependence determined earlier [10] between $\Delta\nu_{av}$(N–H) after intercalation of MeX_2 ($MnBr_2$, $CoBr_2$, CoI_2, $CdCl_2$, CdI_2, ZnI_2, $ZnCl_2$ and PbI_2) by aniline or by p-toluidine and the sum of the first and the second ionization potentials of the metal atom in MeX_2, allow the following conclusions to be made: (a) the degree of charge transfer on intercalation is defined by the electron-donating ability of the N–H group of the incorporated amine molecule; (b) the transferred charge localizes at the atom of lead in full agreement with Refs. [10,14,20,21].

The theoretical treatment [16,19] describes the amine–PbI_2 system energy without taking into account the electrostatic interaction of intercalated molecules with each other. This interaction has been taken into consideration in Refs. [17] and [18] and results in a decrease in the degree of charge transfer and a decrease in the interaction energy between the guest molecule and the matrix.

The linear Hammett-type correlations (Figs. 1(a) and 1(b)) and the photolysis of PbI_2 intercalation phases [6] indicate a similarity between the mechanisms of sensitization of PbI_2 photolysis by anilines and PbI_2 intercalation by anilines. In both photolysis and intercalation, charge transfer interaction between an atom of nitrogen and an atom of lead occurs. However, on photolysis of PbI_2 and intercalated PbI_2, the degree of charge transfer is higher than that on intercalation; clearly, this is caused by excitation of the Pb–I bond on irradiation with light quanta, the energy of which exceeds the forbidden gap width of PbI_2.

It is worth noting that, up to the concentration c_1, the linear parts of the semilogarithmic plots of H vs. ln c for the sensitized photolysis of PbI_2 allow the gaseous and liquid amine content in non-reducing media to be determined [7]. Moreover, the sensitivity of the method [7] in gaseous amine media may be increased by using PbI_2 thin films and by measuring the photoconductivity during photolysis. Experiments were carried out to compare the sensitivity of these methods in ammonia medium at 322 K. Thus, at a concentration $c_{NH_3} = 0.001$ M in the measuring chamber, a rise in the NH_3 concentration by 0.001 M led to an increase in the thin film photoconductivity by 20% s^{-1} at 1.0 s from the start of the reaction. However, during reflectivity measurements at a higher concentration $c_{NH_3} = 0.007$ M in the measuring chamber, an increase in the NH_3 concentration by the same value of 0.001 M led to an increase in the H value by 10.5% s^{-1} at 1.0 s from the start of the reaction. The photoconductivity changes on PbI_2 photolysis are now being investigated and will be reported in due course.

Acknowledgement

The authors would like to thank Mr. I.I. Melnik for useful discussions.

References

[1] R.I. Dawood and A.J. Forty, *Philos. Mag., 8* (1963) 1003–1008.

[2] A.W. Buckman and N.H. Hong, *J. Opt. Soc. Am., 67* (1977) 1123–1125.

[3] M.R. Tubbs, *Phys. Status Solidi, B, 67* (1979) 11–57.

[4] N. Pangelova, M. Pancheva, A. Katsev, T. Petrova and N. Tomova, *Z. Signalaufzeichungs Materialen, 7* (1979) 261–273.

[5] G.I. Gurina, A. Yu. Kobyakov, V.D. Evtushenko and V.M. Koshkin, *Zh. Teor. Eksp. Khim. (Ukr. J. Theor. Exp. Chem.), 21* (1985) 757–759.

[6] V.M. Koshkin, G.I. Gurina and K.V. Savchenko, *J. Photochem. Photobiol. A: Chem., 64* (1992) 369–373.

[7] G.I. Gurina, A. Yu. Kobyakov, V.D. Evtushenko and V.M. Koshkin, Method for the quantitative determination of amines in non-reducing media, *Author Certificate of the USSR, 1991, No. 1684639*, Bulleten izobretenii i otkrytii, No. 38, 15.10.1991.

[8] V.M. Koshkin, *Izv. Akad. Nauk Latv. SSR, 6* (1981) 90–98.

[9] G.I. Gurina, V.D. Evtushenko, V.M. Verchovod and V.M. Koshkin, *Zh. Teor. Eksp. Khim. (Ukr. J. Theor. Exp. Chem.), 21* (1985) 123–127.

[10] G.I. Gurina, V.D. Evtushenko, N.A. Gritskaya and V.M. Koshkin, *Zh. Neorg. Khim. (Sov. J. Inorg. Chem.), 31* (1986) 826–829.

[11] G.I. Gurina, V.D. Evtushenko, O.A. Muraeva, V.P. Ignatyuk and V.M. Koshkin, *Ukr. Khim. Zh. (Ukr. J. Chem.), 51* (1985) 1154–1158.

[12] G.I. Gurina, *Ph.D. Thesis*, Kharkov State University, 1987.

[13] G.I. Gurina and K.V. Savchenko, *Zh. Teor. Eksp. Khim. (Ukr. J. Theor. Exp. Chem.), 29* (1993) 88–92.

[14] R.F. Warren and W.Y. Liang, *J. Phys.: Condens. Matter, 5* (1993) 6407–6418.

[15] V.M. Koshkin, V.V. Kukol, A.P. Milner, Yu.R. Zabrodski and K.A. Katrunov, *Fiz. Tverd. Tela (Sov. Solid State Phys.), 19* (1977) 1608–1612.

[16] V. Mehrotra, S. Lombardo, M.O. Tompson and E.P. Giannelis, *Phys. Rev., B, 44* (1991) 5876–5790.

[17] S.A. Safran and D.R. Hamman, *Phys. Rev. Lett., 44* (1980) 939–942.

[18] Yu.R. Zabrodski, K.A. Katrunov and V.M. Koshkin, *Fiz. Tverd Tela (Sov. Solid State Phys.), 25* (1983) 908–911.

[19] R. Al-Jishi, C.C. Coleman, R. Treece and H. Goldwhite, *Phys. Rev., B, 39* (1989) 4862.

[20] K.A. Katrunov, V.M. Koshkin and V.M. Kulakov, *Ukr. Fiz. Zh. (Ukr. J. Phys.), 27* (1982) 226–227.

[21] K.A. Katrunov, *Ph.D. Thesis*, Institute for Low Temperature Physics, Kharkov, 1984.