

PHOTOCHEMISTRY OF PYRENYLMETHYLTRIPHENYLPHOSPHONIUM SALTS AND RELATED COMPOUNDS

M. E. C. DIAS REAL OLIVEIRA and L. C. PEREIRA

Molecular Physics Group, University of Minho, 4719 Braga (Portugal)

E. W. THOMAS, R. H. BISBY and R. B. CUNDALL

Department of Biochemistry, University of Salford, Salford M5 4WT (Gt. Britain)

(Received October 22, 1984; in revised form June 14, 1985)

Summary

Pyrenylmethyltriphenylphosphonium salts in alcoholic solutions undergo photochemical solvolysis to form the corresponding alkoxy-methylpyrene and triphenylphosphine compounds in high yield. The analogous naphthylmethyl compounds also undergo similar reactions. The corresponding tri-*n*-butylphosphonium salts, however, are photostable under the same conditions. The first excited singlet is probably involved in the reaction. The photophysical properties of the pyrenyl compounds have been measured and the triplet states have been recorded.

1. Introduction

During the evaluation of a range of phosphonium salts as potential probes of biomembranes [1], the photolability of 1-(pyrenylmethyl)triphenylphosphonium (I) bromide in hydroxylic solvents was noted. In view of the relative paucity of information on phosphonium salt photochemistry [2, 3] a closer investigation of the photochemical properties of I and its tributyl analogue was undertaken.

2. Materials

I(Br⁻) was prepared by quarternization of triphenylphosphine with 1-bromomethylpyrene as described elsewhere [4]. Exchange reactions with silver chloride and silver perchlorate in MeOH (Me ≡ methyl) gave the corresponding chloride and perchlorate salts. The tributylphosphonium (II) analogue (melting point, 175 °C) was prepared from tri-*n*-butylphosphine and 1-bromomethylpyrene and recrystallized from MeOH-diethyl ether

before use. 1-(Methoxymethyl)pyrene was prepared by *O*-methylation of 1-(hydroxymethyl)pyrene. 1-(Naphthylmethyl)triphenylphosphonium chloride was prepared by quarternization of triphenylphosphine with 1-(chloromethyl)naphthalene (Aldrich).

EtOH (Et = ethyl), MeOH, *n*-hexane, CHCl₃ and CH₃CN were all spectroscopic grade. No impurities were detected using fluorescence spectroscopy under conditions of extreme sensitivity. High purity grade potassium ferrioxalate was used for actinometric studies.

Absorption measurements were made using either Perkin-Elmer Lambda 5 or Pye Unicam SP 1800 instruments. Fluorescence excitation or emission spectra were recorded using either Perkin-Elmer MPF 44 or Schoeffel RRS 100 spectrofluorometers. Fluorescence decay times were measured using an Edinburgh Instruments 199 fluorometer; a conventional least-squares method [5] was used to fit the decays. Fluorescence quantum yields were measured relative to pyrene in cyclohexane solution with the appropriate corrections [6]. Photochemical quantum yields were determined by means of potassium ferrioxalate actinometry [7], the irradiation at 340 nm being performed using the MPF 44 light source.

Laser flash photolysis studies were carried out with a frequency-doubled *Q*-switched ruby laser (JK Lasers Ltd.) giving up to 0.5 J flash⁻¹ at 347 nm with a pulse width of 30 ns.

All samples were degassed by bubbling with argon, except for the few experiments carried out in the presence of oxygen, and were freshly prepared. Preparative irradiations were carried out in Pyrex vessels with a medium pressure mercury arc. Photochemical reaction products were isolated by preparative thin-layer chromatography (TLC) (silica gel G; CHCl₃:hexane, 1:2 by volume) and characterized by absorption, emission and mass spectroscopies.

3. Results

The emission spectrum of I(Br⁻) in MeOH (2.5 μM) at room temperature is shown in Fig. 1, curve 1. The spectrum shown is typical of the structured emission of pyrenyl derivatives, and at this low concentration there is no excimer peak at about 470 nm. During irradiation in the fluorometer the intensity of the fluorescence was observed to increase (Fig. 1, curves 2 - 6) indicating photolysis of the starting material and formation of a product in reasonably high yield. The ratio of the emission intensities of the peaks in the fluorescence spectra changed during the photolysis. Measurements of the absorption spectra of the sample during the course of the photolysis also revealed the formation of new absorption bands that are ascribed to the photoproduct (Fig. 2).

The spectral characteristics of unphotolysed I compounds are shown in Table 1.

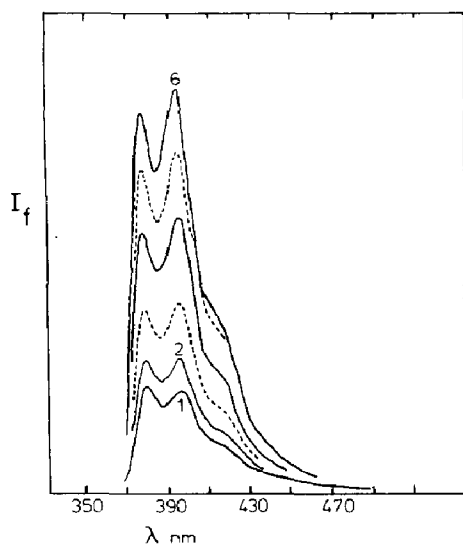


Fig. 1. Uncorrected fluorescence spectra of I in MeOH solutions ($2.5 \mu\text{M}$) at various irradiation times with $\lambda_{\text{ex}} = 350 \text{ nm}$: curve 1, zero time; curve 2, after irradiation for 2 min; curve 6, after irradiation for 60 min.

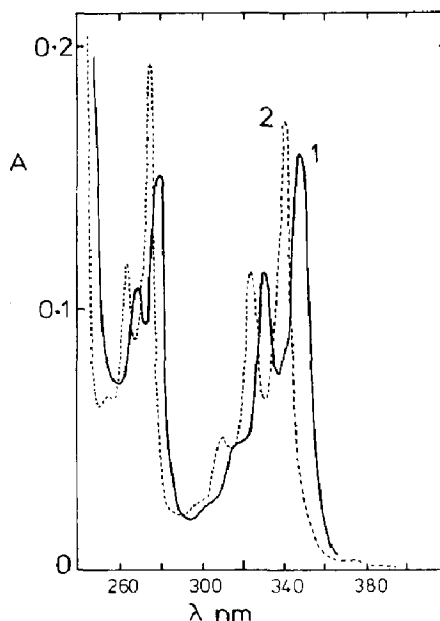


Fig. 2. Absorption spectra of I in MeOH solution: curve 1, zero time; curve 2, fully irradiated.

TABLE 1

Fluorescence quantum yields ϕ_{FL} , extinction coefficients and fluorescence lifetimes τ_{FL} for the compounds under study

Compound	Solvent	ϕ_{FL}	ϵ_{max} ($\text{M}^{-1} \text{cm}^{-1}$)	τ_{FL} (ns)
I(Br^-)	MeOH	0.06	3.2×10^4 (350 nm)	90.4 ± 4.4
	EtOH	0.07	3.0×10^4 (350 nm)	80.3 ± 3.0
I(Cl^-)	Propan-2-ol	0.06	6×10^4 (350 nm)	107.0
	Dioxan	0.28	—	—
	CH_3CN	0.26	—	—
	$\text{CF}_3\text{CH}_2\text{OH}$	—	—	202.1 ± 1.4
I(ClO_4^-)	MeOH	0.06	—	—
	EtOH	0.06	—	—
II(Cl^-)	MeOH	0.73	6.0×10^4 (344 nm)	—
	EtOH	0.67	6.0×10^4 (344 nm)	—
	H_2O	0.30	3.2×10^4 (344 nm)	—
Methoxymethylpyrene (synthetic)	MeOH	0.53	5.9×10^4 (340 nm)	219.0 ± 1.8
Photoproduct from I (in MeOH)	MeOH	0.54	6.0×10^4 (340 nm)	219.0 ± 0.7

Measurements with the chloride and perchlorate salts of I in argon-bubbled solutions showed that changing the counterion had no detectable effect on either the photochemical reaction or the photophysics.

Following prolonged photolysis in MeOH, the photoproducts were isolated by TLC and characterized. Nuclear magnetic resonance spectroscopy, mass spectroscopy and UV spectroscopy showed that the reaction products were methoxymethylpyrene and triphenylphosphine, formed in equimolar amounts in greater than 90% yield. The emission spectra of the photoproduct (before and after isolation) and synthetic methoxymethylpyrene were identical.

The photolysis of I in several hydroxylic solvents was monitored by studying the fluorescence emission of the alkoxyethylpyrenes produced. Photolysis in H₂O led to the formation of 1-(hydroxymethyl)pyrene. The observed rates decreased in the order H₂O > MeOH > EtOH > *n*-BuOH > CH₃COOH ≫ CF₃CH₂OH ≈ dioxan. No breakdown of I was observed in rigid EtOH glasses at -196 °C. At this temperature the fluorescence was very much enhanced but phosphorescence was not detected. In dry acetonitrile solutions at 23 °C there was no photolysis. The rate of photolysis increased with temperature as shown by experiments in MeOH between 24 °C and 60 °C. The photochemical quantum yield for the reaction was measured as 0.15 (MeOH, 27 °C) and 0.12 (EtOH, 27 °C).

The fluorescence quantum yields of the photoproducts are, as indicated previously, much greater than that of I(Br⁻) both in MeOH and EtOH. The fluorescence quantum yields of I in solvents of low polarity were considerably higher than in alcohols and the photolysis rates were negligible. The analogous naphthylmethyltriphenylphosphonium salts showed similar behaviour, the photolysis being monitored by the increase in fluorescence intensity upon irradiation (the results are not shown). Photolysis rates appeared to be slower than for the pyrenyl salts.

In the presence of air, the photoreaction in MeOH still proceeded although at a rate about five times less than that in the absence of oxygen. Oxygen quenched the fluorescence of both I and the photoproduct (the latter more markedly).

II(Br⁻) was found to be photochemically stable in all solvents examined. This was deduced from the absence of any change in absorption, excitation and emission spectra after prolonged irradiation and the absence of products as determined by TLC. The fluorescence quantum yield of the tributyl compound was determined to be in the range 0.30 - 0.71 in the solvents examined (see Table 1).

The photolysis of I in alcohols was accompanied by an increase in the observed fluorescence lifetime. The lifetime of I could not be accurately determined owing to the occurrence of photolysis during the measurement. An upper estimate of about 90 ns was obtained in both MeOH and EtOH compared with about 219 ns for the photoproduct in MeOH. Comprehensive data for lifetimes of starting materials and photoproducts in a range of solvents are included in Table 1.

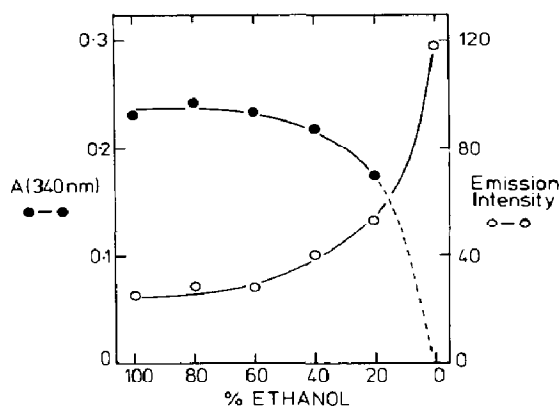


Fig. 3. Changes in photochemical behaviour of $I(Cl^-)$ in EtOH-dioxan mixtures: ○, emission intensity at 400 nm; ●, relative product yield of 1-(ethoxymethyl)pyrene. (Solutions were irradiated for a fixed time period, and the product was assayed at 340 nm after separation by TLC.)

TABLE 2

Laser photolysis of I

Solvent	Triplet extinction coefficient ($M^{-1} cm^{-1}$)	ϕ_T
MeOH	1.8×10^4	0.44
EtOH	1.8×10^4	0.58
Dioxan	1.8×10^4	0.72

The triplet quantum yields of I were measured by laser flash photolysis (30 ns pulse at 347 nm). The yields were measured by comparison of the triplet extinction of I at 415 nm (immediately following the flash) with that produced in a solution of anthracene in cyclohexane. The result was corrected for absorbance of the solution at 347 nm, and a triplet quantum yield of 0.70 for anthracene was assumed [8].

Measurements were also carried out on the photolysis of I (chloride salt) in a series of dioxan-EtOH mixtures. The fluorescence quantum yields increased with increasing proportion of dioxan in the solvent mixture. The rate of photochemical reaction to give ethoxymethylpyrene (as identified by mass spectrometry) decreased with decreasing fraction of EtOH in the solvent as shown in Fig. 3.

Observations of the triplet states of I and the methoxymethylpyrene photoproduct were made by means of flash photolysis. The spectra in different solvents were characterized by peaks at about 415 nm and 485 nm. Absorption at longer wavelengths (above 600 nm) is evident in alcohols, indicating a charge transfer nature for this transition. The triplet yields (relative to anthracene) are given in Table 2.

4. Discussion

Previous studies on the photolysis of benzyltriphenylphosphonium salts in benzene–EtOH mixtures [2] and in acetonitrile [3] have indicated the operation of free radical pathways initiated by an intramolecular charge transfer process involving the counterion. In contrast, the isolation of 1-(alkoxymethyl)pyrenes in higher yield on photolysis of I in alcohols, and the absence of 1-methylpyrene in significant amounts, provides a strong argument against a free-radical-based reaction scheme. A closer analogy is found in the photolysis of benzyldimethylsulphonium salts in alcohols [9, 10] when apparent nucleophilic displacement of dimethyl sulphide occurs as a result of attack by the alcohol on the excited state of the substrate. The heterolytic cleavage of the substrate, producing the benzyl cation, could occur before or at the same time as the attack by solvent. Photosolvolytic has been comprehensively reviewed by Cristol and Bindel [11]. It seems that a similar mechanism applies for the phosphonium salts investigated here, and would also be expected for a large range of arylmethyltriphenylphosphonium salts.

Based on the studies in alcohol–dioxane mixtures, the photoreaction presumably occurs from the first excited singlet state. Thus an *increase* in pyrenyl chromophore fluorescence from I is paralleled by a *decrease* in the photochemical reaction rate. A significant decrease in triplet yields from I in alcohols also supports a reaction mechanism involving the excited singlet state of the substrate. The species absorbing at longer wavelengths than the pyrenyl triplet are probably due to the pyrenyl cation and solvated electron as previously observed [8]. These charged species are formed by biphotonic processes operating under the laser photolysis conditions, and are irrelevant to the steady state photolysis investigations reported here.

The efficiency of photolysis in the various alcohols follows approximately their pK_a values, with the exceptional behaviour of CF_3CH_2OH (the most acidic) being presumably a reflection of the strong intramolecular hydrogen bonding which occurs with this molecule. The photostability of the tri-*n*-butylphosphonium salts is seen to be a consequence of the increased charge density on the phosphorus atoms in the excited state owing to the electron-donating effect of the butyl groups. In the triphenylphosphonium salts, however, heterolytic cleavage of the carbon–phosphorus bond in the excited state must be facilitated by an overall electron withdrawing effect of the phenyl groups.

References

- 1 R. A. Badley, in E. L. Wehry (ed.), *Modern Fluorescence Spectroscopy*, Plenum, 1976, Chapter 3.
M. Shinitzky and Y. Barenholz, *Biochim. Biophys. Acta*, 515 (1978) 367.
- 2 C. E. Griffen and M. C. Kaufman, *Tetrahedron Lett.*, (1965) 773.

- 3 Y. Nagao, K. Shima and H. Sakurai, *Tetrahedron Lett.*, (1971) 1101.
- 4 S. Akiyama, K. Nakasuji and M. Nakagawa, *Bull. Chem. Soc. Jpn.*, 44 (1971) 2231.
- 5 J. N. Demas and G. A. Crosby, *J. Phys. Chem.*, 75 (1971) 991.
- 6 C. A. Parker, *Photoluminescence of Solutions*, Elsevier, Amsterdam, 1968.
- 7 C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, 235 (1956) 518.
- 8 J. T. Richards, G. West and J. K. Thomas, *J. Phys. Chem.*, 74 (1970) 4137.
- 9 A. C. Maycock and G. A. Berchtold, *J. Org. Chem.*, 35 (1970) 2532.
- 10 H. E. Zimmerman and V. R. Sandel, *J. Am. Chem. Soc.*, 85 (1963) 915.
- 11 S. J. Cristol and T. H. Bindel, *Org. Photochem.*, 6 (1983) 327.