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Flash photolysis study of 2,4,6-trimethylpyrylium and 2,4,6-triphenylpyrylium ions: evidence for oxoniabenzvalene intermediate

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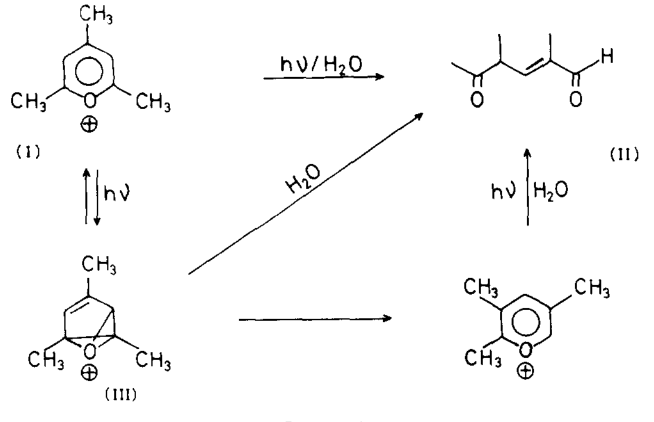
Abstract

A flash photolysis study of 2,4,6-trimethylpyrylium perchlorate (TMP) and 2,4,6-triphenylpyrylium tetrafluoroborate (TPP) was performed in hydroxylic medium. The transient absorptions observed for TMP and TPP in methanol with maxima at 365 and 390 nm respectively are due to the formation of the intermediate oxoniabenzvalene. We also report the triplet–triplet absorption spectrum of TMP in methanol.

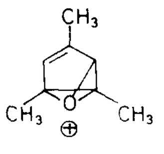
Keywords: Photochemistry; Flash photolysis; Photolysis; Pyrylium ions; Oxoniabenzvalene

1. Introduction

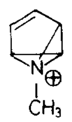
The photochemical transformation of an aqueous solution of 2,4,6-trimethylpyrylium ion (**I**) to a linear product 2,4-dimethyl-5-oxohex-2-enal (**II**) on irradiation with 254 nm light has been proposed to involve the intermediate oxoniabenzvalene (**III**) [1] (Scheme 1). A similar nitrogen analogue of the intermediate azoniabenzvalene (**IV**) has been proposed for *N*-methylpyridinium chloride and similar salts on photolysis in aqueous medium [2]. Here, the azoniabenzvalene intermediate re-aromatizes back to the isomeric aromatic product after reaction with the solvent. These intermediates resemble benzvalene [3]; hydration of the initially formed benzvalene (**V**) [4–7] yields bicyclo-[3.1.0]hex-3-en-2-exo-ol. Benzvalene has been proposed as an intermediate in the isomeric interconversions observed on irradiation of substituted benzenes [8]. Support for this involvement is provided by the rearrangement of isotopically labelled substituted benzenes, such as mesitylene and 1,3,5-tri-tert-butylbenzene, which give the 1,2,4-isomer exclusively, demonstrating that the 1,2-phototransportation of the adjacent ring carbon atoms is accompanied by the substituents [8]. Similar methods have been used to explain the involvement of the azoniabenzvalene intermediate in the photochemical reaction of pyridinium salts [2], but not in the case of pyrylium salts.



Scheme 1.



(III)



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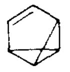
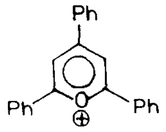


(V)



(VI)

Literature reports reveal that the benzvalene and substituted benzvalene intermediates have an absorption spectrum with a maximum at or beyond 230 nm respectively, the shift in the case of substituted benzvalenes being due to the effect of substituent groups [9–11]. While no spectral evidence has been established for the valence bond intermediates azoniabenzvalene and oxoniabenzvalene, the present investigation deals with the identification of the oxoniabenzvalene intermediate by the flash photolysis technique.

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2. Experimental details

2,4,6-Trimethylpyrylium perchlorate (TMP), prepared following Ref. [12] and 2,4,6-triphenylpyrylium tetrafluoroborate (TPP), purchased from Aldrich and recrystallized, were used in this investigation.

The applied Photophysics KN-020 conventional flash kinetic spectrometer, used for recording the transient absorption spectra, comprised a pair of LR 16 Inotech xenon flash lamps with a half-time of 30 μs, a 100 W tungsten–iodine lamp as monitoring lamp, a Czerny–Turner-type monochromator, an R-928 photomultiplier tube (PMT) and a 25 MHz digital storage oscilloscope. Light from the xenon lamp was used without a filter; for each flash, fresh solutions were used. The optical detection path length was 10 cm and the volume of the sample solution for the conventional flash technique was 7 ml; concentrations of 7×10^{-6} M and 6×10^{-6} M were used for TMP and TPP respectively.

The laser flash photolysis system comprised a Quanta Ray DCR-2(10) Nd-YAG laser with an 8 ns pulse width, a 300 W pulse xenon lamp as the monitoring source, an R-928 PMT coupled with a Czerny–Turner-type monochromator and an HP 54210A 50 MHz digital storage oscilloscope. This was used to record the triplet–triplet absorption spectra of TMP and TPP. The fourth harmonic (266 nm) of the laser was used for the excitation of TMP and the third harmonic (355 nm) for TPP. Argon-purged samples (volume, 4 ml) with a concentration of 3×10^{-5} M were used for both TMP and TPP. Fresh nitrogen-purged samples were used for each flash while recording the triplet–triplet absorption spectrum.

The photolysis set-up used to obtain the photoproduct comprised a 254 nm Penray lamp with a quartz jacket, a thermostatically controlled assembly and a constant mechanical stirring assembly; the total volume of the solution in the cell was 50 ml. The photolysis of a 10^{-3} M solution of the pyrylium salts in methanol and water was performed for 24 h during which the starting material was found to be thermally stable. The photoproduct in methanol medium was isolated after solvent evaporation and separation from the starting material. For aqueous medium, the water was removed by freeze drying the mixture in a Martin Christ Alpha 2-4 freeze dryer, followed by separation of the photoproduct from the starting material.

3. Results and discussion

The photolysis of air-equilibrated aqueous and methanol solutions of TMP leads to a steady decrease in the absorbance over the entire absorption spectrum, indicating the destruction of the aromatic system as proposed earlier [1]; a similar change is also observed in the case of nitrogen-purged aqueous and methanol solutions of TMP. The spectral changes observed during irradiation of a nitrogen-purged solution of TMP in aqueous and methanol media are given in Fig. 1.

Conventional flash photolysis of aqueous and methanol solutions of TMP results in transients in the region 300–500 nm. The transient absorption spectra recorded immediately after the flash give maxima at 360 and 365 nm for aqueous and methanol solutions respectively (Fig. 2). Kinetic analysis of the transients shows that the transient decay obeys first-order kinetics, with rate constants of 9.1 ± 0.2 s^{-1} and 13.1 ± 0.2 s^{-1} for aqueous and methanol solutions respectively (Fig. 3). It should be noted that the decay rates are not influenced by the presence of oxygen, eliminating the possibility of the involvement of competitive processes, such as the formation of oxygenated products and the triplet state. The transient absorption spectrum observed exhibits different absorption features when compared with the triplet–triplet absorption spectrum recorded for TMP by laser flash photolysis (Fig. 2). The triplet lifetime of TMP is 35 μs in methanol, whereas the transients observed in methanol and aqueous solutions have lifetimes of a few hundred milliseconds. On the basis of these arguments, the transient observed cannot be attributed to triplet–triplet absorption. Since the molecular oxygen present in the medium does not perturb the observed transients, the possibility of any oxygenated intermediate can also be ruled out. Thus the observed transients in both water and methanol can be attributed to the oxoniabenzvalene intermediate. The triplet–triplet absorption spectrum of TMP is not reported in the literature; we recorded this spectrum in methanol using excitation at 266 nm; the decay kinetics are influenced by the presence of oxygen. Oxygen is a very good quencher of the triplet state and the enhancement of the decay rate of the triplet in the presence of oxygen provides clear evidence that the observed transient is due to the triplet state of TMP. Triplet quenching by well-known triplet quenchers could not be performed as most of them absorb at 266 nm. Triplet decay of TMP was not observed in dichloromethane or acetonitrile.

The investigation with TPP (**VI**) involved similar experiments, but only in methanol, since TPP is thermally unstable in water. Hydrolysis of TPP results in the formation of enedione [13]; this is favoured in TPP compared with TMP due to steric factors. The photolysis of an air-equilibrated methanol solution of TPP results in a steady, rapid decrease in absorbance over the entire absorption spectrum, indicating the destruction of the heteroaromatic moiety to give various oxygenated products, such as benzaldehyde, phenol, methylbenzoate and benzoic acid [14]; however, in a nitrogen-purged methanol solution of TPP (Fig. 4), a slow, steady decrease in absorbance over the absorption spectrum is observed, indicating the destruction of the heteroaromatic moiety of the TPP molecule to give the linear product (**VII**).

Flash photolysis of an air-equilibrated methanol solution of TPP gives transients in the region 300–500 nm. Similar transients are also observed for a nitrogen-purged methanol solution of TPP and the presence of oxygen does not alter the dynamics of the transients. The transient absorption spectrum recorded immediately after the flash exhibits a maximum at 390 nm (Fig. 5). Kinetic analysis of the transients shows that

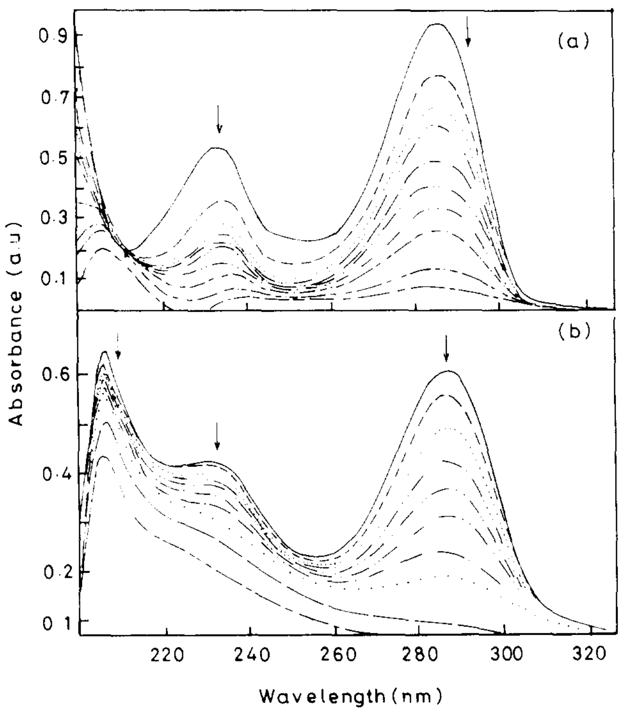


Fig. 1. Absorption spectral changes during steady photolysis of nitrogen-purged aqueous (10^{-4} M) (a) and methanol (6.5×10^{-5} M) (b) solutions of TMP. Spectra monitored at time intervals of 3 min.

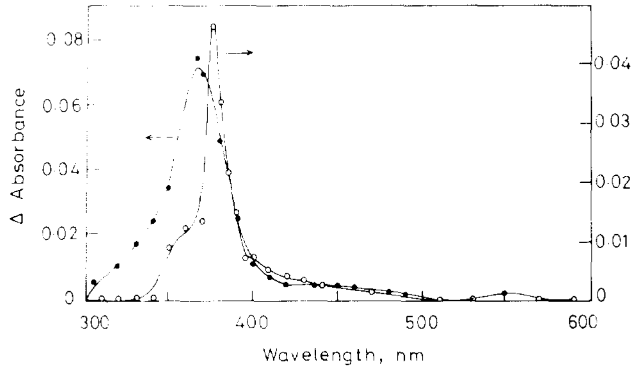


Fig. 2. Triplet–triplet absorption spectrum for a 10^{-5} M solution of TMP in methanol (○) and the transient absorption spectrum of the oxoniabenzvalene intermediate recorded immediately after the flash for a 10^{-6} M methanol solution of TMP (●).

transient decay obeys first-order kinetics with a rate constant of 137 ± 3 s^{-1} (lifetime, 7.2 ms) (Fig. 6). The transient observed cannot be due to the triplet state of TPP as indicated by the lifetime of the triplet (triplet lifetime, 14 μs) and the triplet–triplet absorption spectrum of TPP [15–17], which is very different from the transient absorption spectrum observed. The triplet–triplet absorption spectrum was recorded in methanol using laser flash photolysis and is given in Fig. 5 together with the transient absorption spectrum observed. Thus the observed transient is attributed to the oxoniabenzvalene intermediate.

The photolysis of TMP in methanol at 254 nm for 24 h followed by IR spectral analysis of the photoproduct isolated after separation from the starting material (confirmed by thin layer chromatography (TLC)), gives a spectrum with a characteristic broad band at 1700 cm^{-1} indicating the presence of saturated and α,β-unsaturated ketones in the linear product (**VII**); this is formed as a result of the reaction of the oxoniabenzvalene intermediate with methanol as shown in Scheme 2. Bands are also observed at 1500 cm^{-1} (C–C bending) and 1080 cm^{-1} (C–H bending), characteristic of the formation of the linear product (**VII**). The product resulting from the oxoniabenzvalene intermediate in methanol is similar to that obtained in aqueous solution [1]. On changing

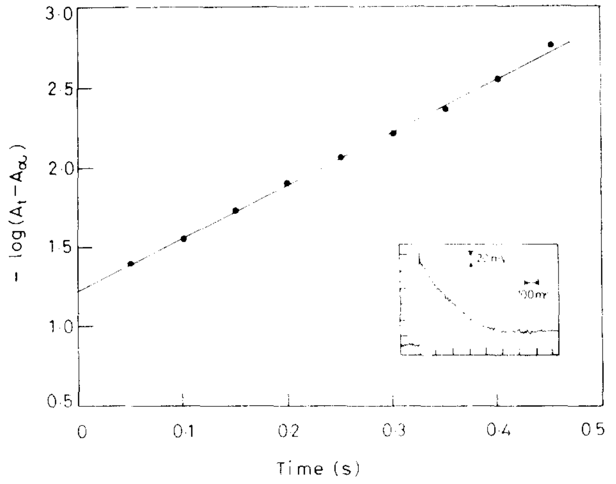


Fig. 3. Kinetic analysis of the transient decay observed for the oxoniabenzvalene intermediate of TMP at 365 nm; inset: the corresponding decay at 365 nm.

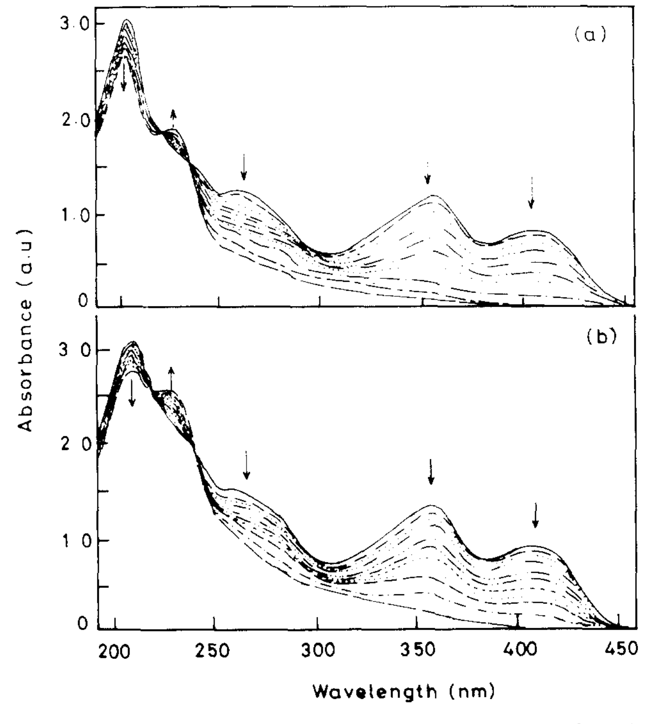


Fig. 4. Absorption spectral changes during steady photolysis of an air-equilibrated methanol solution of TPP (10^{-5} M) (spectra monitored at time intervals of 30 s) (a) and a nitrogen-purged methanol solution of TPP (10^{-5} M) (spectra monitored at time intervals of 3 min) (b).

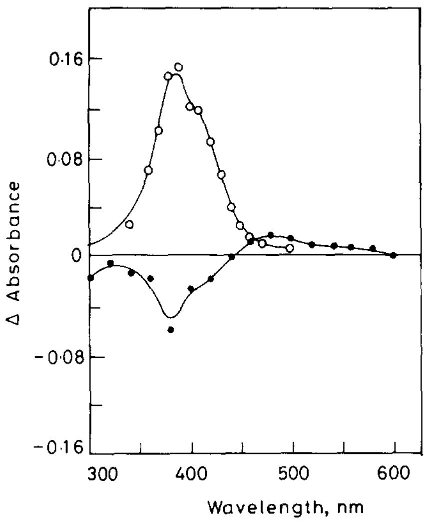


Fig. 5. Triplet–triplet absorption spectrum for a 10^{-5} M solution of TPP in methanol (●) and the transient absorption spectrum of the oxoniabenzvalene intermediate recorded immediately after the flash for a 10^{-6} M methanol solution of TPP (○).

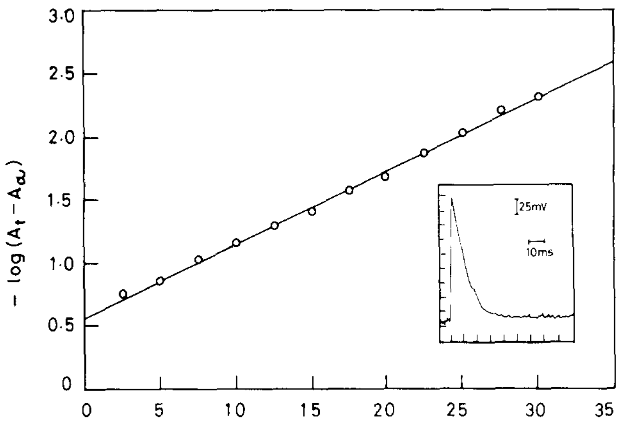
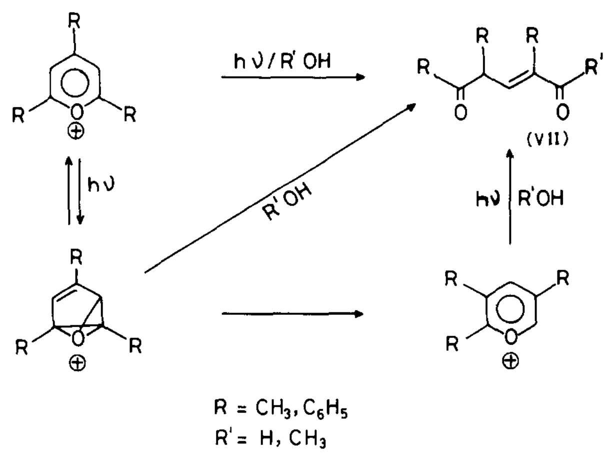


Fig. 6. Kinetic analysis of the transient decay observed for the oxoniabenzvalene intermediate of TPP at 390 nm; inset: the corresponding decay at 390 nm.



Scheme 2.

the solvent from water to methanol, the aldehyde carbonyl becomes ketonic due to the addition of a methyl group from methanol instead of a hydrogen atom from water, resulting in the observation of only one broad band at 1700 cm^{-1} in the product obtained from methanol instead of two bands at 1720 cm^{-1} and 1670 cm^{-1} in the case of aqueous medium. In the IR spectrum of the photoproduct isolated from a methanol solution of TPP, broad bands at 1700 cm^{-1} (characteristic of saturated and α,β-unsaturated ketones) and 1460 cm^{-1} (due to aromatic substitution) are observed in addition to the bands due to C–H bending, indicating the destruction of the heteroaromatic system of TPP and further supporting the involvement of the oxoniabenzvalene intermediate of TPP in methanol.

4. Conclusions

From the above observations and arguments, it can be concluded that the transients observed can be assigned to the oxoniabenzvalene intermediate formed during the production of the linear product, which is obtained after the destruction of the heteroaromatic system of the pyrylium salt. It should be noted that the transients are not observed in acetonitrile and dichloromethane. Since these transients are observed only in water and methanol, the hydroxylic solvents probably stabilize the oxoniabenzvalene intermediate. It is obvious from the lifetimes of the intermediates that TPP has a fairly short-lived oxoniabenzvalene intermediate in comparison with that of TMP due to steric reasons. Since the oxoniabenzvalene intermediate is formed even in the presence of oxygen (the triplet state of pyrylium salts is quenched by oxygen), it is suggested that it is formed through the singlet manifold.

Acknowledgements

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