

Flash photolysis and triplet states and free radicals in solution †

Maurice W. Windsor*

Washington State University, Pullman 99164, USA

Received 7th January 2003, Accepted 18th February 2003

First published as an Advance Article on the web 18th March 2003

A personal account is given of the development of microsecond flash photolysis in George Porter's laboratory at Cambridge in the early 1950s. This made possible, for the first time, the observation of the absorption spectra of the lowest triplet states of many polycyclic aromatic hydrocarbons in fluid solutions. The T–T transitions were found to be very intense with oscillator strengths approaching unity in many cases. Detailed kinetic studies showed that triplet state decay was first order and viscosity dependent and strongly quenched by dissolved oxygen. Several aromatic free radicals such as benzyl were also observed in liquid solution for the first time. The advent of the laser in the early 1960s made it possible to extend flash photolysis studies to the ns and ps and eventually the fs time range. Such studies have revolutionized the study of excited states and free radicals and have made possible advances in the understanding of the dynamics of chemical and biological systems that would have been unimaginable 60 years ago.

In 1947 George Porter attended a Faraday Society Discussion on "The Labile Molecule".¹ The meeting was entirely concerned with the study of short-lived chemical substances. In his introduction, H. W. Melville, referring to the low concentrations of radicals normally encountered, stated, "Direct physical methods of measurement simply cannot reach these (low) magnitudes, far less make accurate measurements in a limited period of time, for example a few 10^{-3} milliseconds". At that time free radicals had been implicated in a variety of chemical reactions, particularly those involving combustion and flames or photochemistry, and many had been identified *via* their emission spectra or paramagnetic properties. However, concentrations were typically so small, 10^{-7} to 10^{-10} mol l^{-1} , that detailed kinetic studies were impossible.

George Porter's flash of inspiration was to realize that high intensity flash tubes, as used in night-time aerial photography during WWII, might provide the answer, as Brian Thrush discusses in an accompanying paper,² and generate a concentration of free radicals large enough to be observed spectroscopically. Of course, such observation also had to be made in a brief period of time before the short-lived species underwent chemical reaction or otherwise decayed. As Porter modestly says in his Nobel Prize address,³ "The use of a second flash, operating after a time delay, to record photographically the absorption of the transients must now (1967) seem a very obvious procedure, but it was many months before it became obvious to me." Thus was born the technique of flash photolysis. Beginning in 1948, Porter, in collaboration with Professor R. G. W. Norrish, Head of the Department of Physical Chemistry at Cambridge, and several students, including Brian Thrush, Frank Wright, Margaret Christie, Kerro Knox and M. A. Khan, studied a variety of systems in the gas-phase as discussed by Brian Thrush.²

I went up to Queens' College, Cambridge, in October 1949. It was in my third year of the Natural Science Tripos that I first became aware of the flashes and occasional bangs that were going on downstairs in the basement of the Physical Chemistry Laboratory. Initially intending to specialize in Organic Chemistry, I had the good fortune to have Morris (T. M.) Sugden for supervisions on a one to one basis and decided to switch to physical chemistry. My interest was further enhanced by a course in Photochemistry given by Professor Norrish with guest lectures by Sugden and by Porter. I felt quite disappointed later on when Sugden told me that, owing to lack of lab space, he could not take me on as a research student and suggested I go downstairs and talk with George Porter. Thus began a fascinating and productive career in the flash trade. I have a sneaking suspicion that, apart from my academic credentials, what also motivated George Porter to take me under his wing was that, prior to coming up to Cambridge, I had served 2½ years in the Royal Air Force as a Radar Mechanic. Porter, himself, as Thrush mentions,² had served in the Royal Navy as a Radar Officer and quickly realized that familiarity with high voltage banks of condensers and thyratrons and the like would be very helpful for what he had in mind.

Indeed, what he had in mind was to extend flash photolysis studies from the millisecond range in which the gas phase work was then being done to the microsecond range, so that liquid phase systems could be studied. This task would require smaller condensers (10 μ F), shorter flash lamps and optical absorption cells (20 cm) and an experimental problem involving transient species with much higher absorption coefficients than the gas phase radicals studied previously. He had become aware of the pioneering work of G. N. Lewis and Michael Kasha⁴ on the phosphorescence of aromatic organic molecules, notably the condensed polycyclic aromatic hydrocarbons such as naphthalene, anthracene, *etc.*, in rigid frozen organic glasses and their belief that this emission came from the lowest triplet state of the molecule. Emission from this biradical state with 2 unpaired electrons, is dipole forbidden and so phosphorescence emission lifetimes were typically of the order of seconds.

In 1951, Donald S. McClure⁵ observed what he believed to be the absorption spectra of the phosphorescent state of several such molecules while under illumination in frozen, organic glasses such as EPA (ether, isopentane, ethanol in 5 : 5 : 2 proportions by volume) at liquid nitrogen temperature (77 K). It was believed that these arose from transitions from the lowest triplet level T₁ to a higher state of the same multiplicity and would therefore be fully allowed (Fig. 1). After completing this work, McClure became aware of the flash photolysis work of Porter and Norrish⁶ and at the end of his paper states, "This method should be admirably suited to exploring the triplet states of molecules." It was clear to George Porter that an attempt to observe triplet states in solution would be an ideal test for the faster microsecond flash apparatus. And it was my job to build this apparatus and begin the search.

As Brian Thrush describes, the early gas phase studies employed a 1 m-long flash tube that produced a 2 ms flash.² For

† Dedicated to the memory of Nobel Laureate, Lord George Porter FRSC FRS OM.

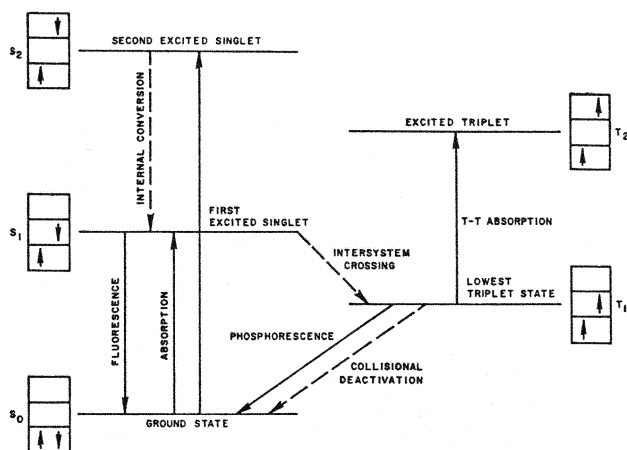


Fig. 1 Formation and deactivation of the triplet state in complex molecules (arrows in boxes indicate electron spin).

our studies, to obtain high conversions, shorter lamps and reaction cells (20 cm), smaller condensers (10 μ F) and higher voltages (10 kV) were needed to produce flashes lasting about 35 μ s for the photolysis flash (P) and 20 μ s for the interrogating spectroscopic flash (S). A triggered spark gap fired P, and S was fired automatically *via* a photocell and preset time delay *via* a thyatron and second spark gap (Fig. 2). The flash lamp and 15 mm diameter quartz reaction vessel were enclosed in a cylindrical MgO coated reflector. To avoid the risk of explosion, a krypton filling of only 5 cm Hg pressure was used in the flash lamps. A quartz reservoir was sealed to the reaction vessel so that the solution could be degassed, and later on a small gas bulb with a breakable seal was added that could be used to introduce known amounts of O₂ or other gases into the solution after the reaction vessel was sealed off (Fig. 3). This permitted kinetic studies of quenching to be carried out. Uranyl oxalate actinometry allowed calculation of the light output per flash, which averaged 7×10^{18} quanta for a 15 kV, 10 μ F charge, giving a conversion factor of electrical energy to luminous energy of about 5%.

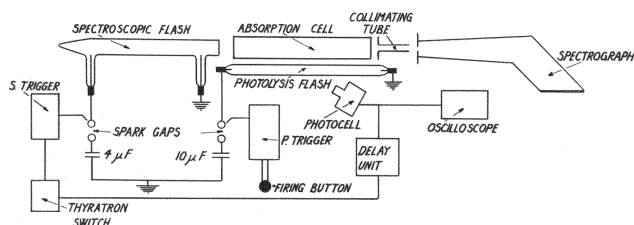


Fig. 2 The flash apparatus.

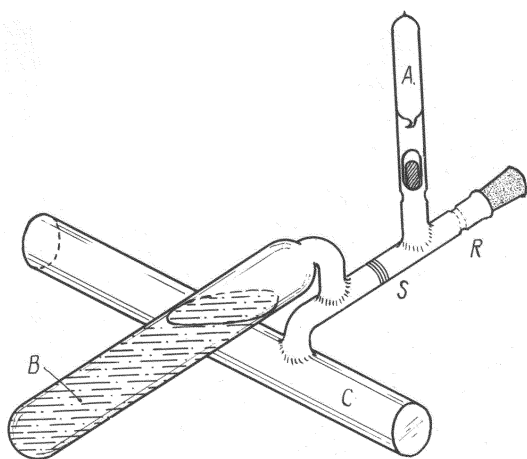


Fig. 3 The absorption cell.

First experiments were made on 10^{-4} M solutions of anthracene in chloroform since Bowen⁷ had suggested that heavy atoms in the solvent might enhance conversion to the triplet state. No transient absorption was observed, with or without removal of dissolved air, and progressive brown coloration indicated that photochemical reaction with the solvent was occurring. In the next series of experiments *n*-hexane was used. With no degassing, neither transient absorption nor chemical reaction occurred. However, with degassed solutions, carried out on a vacuum line with partial freezing of the solvent which facilitated degassing (Fig. 3), strong transient absorption bands were observed (Fig. 4). I shall never forget standing in the dark-room rinsing the developer over the photographic plate and the thrill I experienced as the tell-tale triplet-triplet absorption bands of anthracene began to appear; the first time anyone had ever seen them in solution and so vividly. I took a deep breath. I felt like an explorer entering a new world. By varying the time delay, the decay could be followed over a period of several hundred μ s. The decay was found to be first order. Measurable depletion (*ca.* 20%) of the ground state absorption at the earliest time delays (Fig. 4) made it possible to estimate a value of $118,000 \pm 20\%$ for the absorption coefficient of the 420 nm band in anthracene. This strongly supported assignment to a fully allowed T-T transition, for example T₁ to T₂ in Fig. 1.

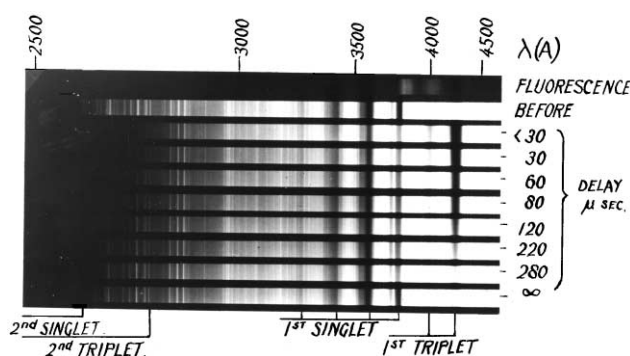


Fig. 4 Decay of triplet anthracene in hexane.

Many subsequent experiments showed that the decay of triplet anthracene was dependent on solvent viscosity, increasing to several ms in liquid paraffin and glycerol, so much so that T-T absorption could be observed in glycerol solutions even without degassing. Subsequent studies showed that as little as 4.5×10^{-5} M of dissolved O₂ completely quenched the triplet in hexane solutions. Since the ground state of O₂ is a triplet electronic state with 2 unpaired electrons, it is likely that quenching involves a paramagnetic interaction and indeed nitric oxide, NO, also paramagnetic, quenched the triplet to about the same extent as O₂. By contrast, much larger amounts of the N₂ failed to produce quenching.

We presented these results at the Faraday Discussion⁸ on fast reactions at Birmingham University in April 1954. Many foreign visitors were in attendance and later visited our laboratory carrying little black books and taking copious notes. It was still a time of relative privation in Britain, with rationing of food and clothing still in effect, and we all experienced some feelings of paranoia that our American colleagues might pick our brains and fly back to the land of plenty and, with their unlimited resources, take advantage of our bright ideas.

Delighted with the success with anthracene, I was motivated to extend our triplet state studies to a wide range of polycyclic aromatic hydrocarbons and their derivatives and found T-T absorption in almost all of them except benzene.⁹ Pyrene was especially pretty, displaying two distinct electronic T-T transitions (Fig. 5). With the aid of stepped optical filters of known optical density, each photographic plate could be calibrated so that, using a recording microdensitometer, it was possible to convert observed triplet absorption bands to absolute optical

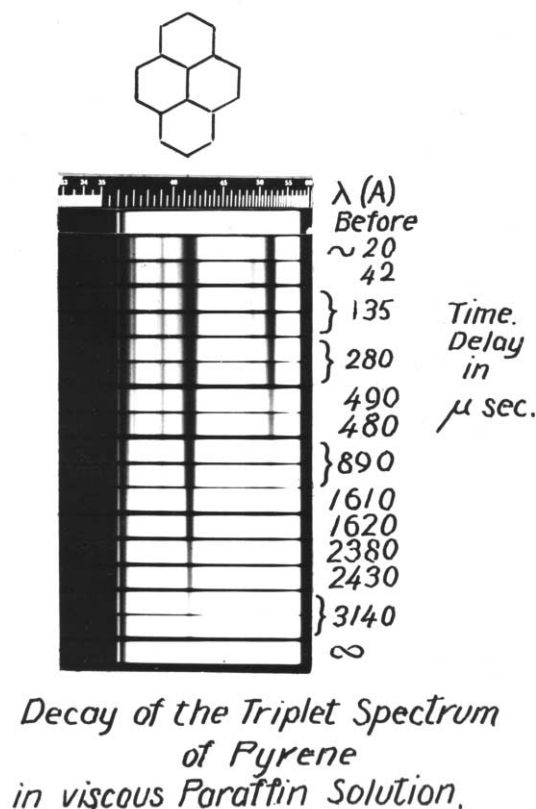


Fig. 5 Decay of triplet pyrene in viscous paraffin.

densities and obtain accurate T–T absorption coefficients.⁹ From calibrated absorption curves the oscillator strength f of the transitions could be calculated. For several molecules f values of the order of unity were calculated, notably for penta-cene, for which initial depletion of the single state reached 80%. Comparisons were made with the theoretical assignments of Pariser.¹⁰

Concurrently with our triplet state studies, Norman and Porter were developing and refining techniques for the spectroscopic detection of free radicals in rigid hydrocarbon glassy solvents at liquid nitrogen temperatures.¹¹ In addition to iodine atoms, CS, ClO, and benzyl, they were able to record the spectra of several other unstable aromatic radicals such as anilino and phenoxy. Attempts to detect phenyl, ethyl, HS and OH were unsuccessful, possibly due to lower activation energies for reaction with the solvent. Based on their observations, we extended our studies to search for short-lived free radicals in solution. The benzyl radical, previously seen in the gas phase by Porter and Wright¹² and in rigid glasses at low temperatures by Norman and Porter,¹¹ was detected following photolysis of benzyl alcohol, chloride, formate or methyl ether in viscous liquid paraffin solution.¹³ Benzoquinone gave the benzosemiquinone radical. These observations were of great significance, since the vast majority of chemical reactions are carried out in the liquid phase. Later on, in collaboration with Robert Livingston,¹⁴ on sabbatical leave from the University of Minnesota, we observed transient absorption spectra in methanol solution for chlorophyll a, chlorophyll b, pheophytin and coproporphyrin dimethyl ester, paving the way for extensive flash photolysis studies of photosynthetic systems in later years.

There is an interesting footnote to my early triplet odyssey that I greatly relish. With my thesis completed, I had to defend it at an oral examination in order to receive my PhD degree. It was July 1955 and both George Porter and my external examiner, the distinguished photochemist E. J. (Ted) Bowen of Oxford, had travel plans. So did I, being scheduled to take up a postdoctoral appointment at Caltech in late August. Fortunately, we would all be attending a spectroscopy conference at

Oxford in mid-July. In consequence, I have the distinction of having undergone my oral exam for the Cambridge University PhD degree at St. John's College, Oxford adorned in a borrowed Oxford gown, with Dr Bowen, who was already very familiar with my research, having read my thesis while traveling by bus to and from the Farnborough Air Show.

These early flash photolysis studies of transient chemical species in solution, especially of the triplet state, greatly spurred and facilitated the elucidation of mechanisms for a wide range of photochemical reactions in solution in later years. Many important reactions in solution, such as those of ketones and quinones, proceed almost exclusively *via* the triplet state.³ The advent of the laser made it possible to extend flash photolysis studies to the nanosecond region^{15–17} in the 1960s and to the picosecond region in the 1970s, and eventually femtosecond studies became possible.¹⁸ With nanosecond laser photolysis, the first excited singlet S_1 state responsible for fluorescence emission in aromatic molecules can also be studied in absorption *via* transitions to higher singlet states ($S_1 \rightarrow S_n$). Picosecond laser photolysis also made possible the first study of the early charge separation steps in the photosynthetic reaction center.^{19–22}

In May 1979, it was very fitting that The Royal Society sponsored a discussion meeting, presided over by Sir George Porter, P. R. S., on “Ultra-Short Light Pulses” in which instrumental developments and applications to a variety of fields in chemistry and physics were discussed.²³

George Porter's flash of insight back in the late 1940s completely revolutionized the study of free radicals, excited states and other labile molecules, and in subsequent decades, together with the invention of the laser, modern computerized instrumentation and the industrious efforts of thousands of researchers worldwide, flash photolysis has made possible advances in the understanding of the dynamics of chemical and biological systems that would have been unimaginable 60 years ago.

Acknowledgements

Fig. 4 is reproduced by permission of the Royal Society of Chemistry.

References

- 1 The Labile Molecule, *Disc. Faraday Soc.*, 1947, **2**, 1–409.
- 2 B. A Thrush, The Genesis of Flash Photolysis, *Photochem. Photobiol. Sci.*, 2003, DOI: 10.1039/b300075n, in the press.
- 3 G. Porter, Nobel Lecture: Flash Photolysis and Some of its Applications, *Science*, 1968, **160**, 1299–1307.
- 4 G. N. Lewis and M. Kasha, Phosphorescence and the Triplet State, *J. Am. Chem. Soc.*, 1944, **66**, 2100–2116.
- 5 D. S. McClure, Excited Triplet States of Some Polyatomic Molecules, *J. Chem. Phys.*, 1951, **19**, 670–675.
- 6 G. Porter, Flash Photolysis and Spectroscopy, *Proc. R. Soc. London, Ser. A*, 1950, **200**, 284–300.
- 7 E. J. Bowen and Miss K. K. Rohatgi, Photochemistry of Anthracene. Part 2, The Photochemical Reaction of Anthracene with Carbon Tetrachloride, *Disc. Faraday Soc.*, 1953, **14**, 146–150.
- 8 (a) G. Porter and M. W. Windsor, Triplet States in Solution, *J. Chem. Phys.*, 1953, **21**, 2088; (b) G. Porter and M. W. Windsor, Studies of the Triplet State in Fluid Solvents, *Disc. Faraday Soc.*, 1954, **17**, 178–186.
- 9 G. Porter and M. W. Windsor, The Triplet State in Fluid Media, *Proc. R. Soc. London, Ser. A*, 1958, **245**, 238–258.
- 10 R. Pariser, Theory of the Electronic Spectra and Structure of Polyacenes and Alternant Hydrocarbons, *J. Chem. Phys.*, 1956, **24**, 250–268.
- 11 I. Norman and G. Porter, Trapped Atoms and Radicals in Rigid Solvents, *Proc. R. Soc. London, Ser. A*, 1955, **230**, 399–414.
- 12 G. Porter and F. J. Wright, Primary Photochemical Processes in Aromatic Molecules, 3: Absorption Spectra of Benzyl, Anilino, Phenoxy, and Related Free Radicals, *Trans. Faraday Soc.*, 1955, **51**, 1469.

- 13 G. Porter and M. W. Windsor, Observation of Short-Lived Free Radicals in Solution, *Nature*, 1957, **180**, 187–188.
- 14 R. Livingston, G. Porter and M. Windsor, Phototropy of Chlorophyll Solutions, *Nature*, 1954, **173**, 485–486.
- 15 (a) J. R. Novak and M. W. Windsor, Laser Photolysis and Spectroscopy in the Nanosecond Time Range: Excited Singlet State Absorption in Coronene, *J. Chem. Phys.*, 1967, **47**, 3075; (b) J. R. Novak and M. W. Windsor, Excited Singlet Absorption in 1,2-Benzanthracene by the use of Nanosecond Laser Photolysis and Spectroscopy, *Science*, 1968, **161**, 1342–1343; (c) J. R. Novak and M. W. Windsor, Laser Photolysis and Spectroscopy: A New Technique for the Study of Rapid Reactions in the Nanosecond Time Range, *Proc. R. Soc. London, Ser. A*, 1968, **308**, 95–110.
- 16 (a) G. Porter and M. R. Topp, *Nobel Symposium 5—Fast Reactions and Primary Processes in Reaction Kinetics*, p.158, Interscience, London and New York, 1967; (b) G. Porter and M. R. Topp, Nanosecond Flash Photolysis and the Absorption Spectra of Excited Singlet States, *Nature*, 1968, **220**, 1228–1229.
- 17 R. Bonneau, J. Faure and J. Jousset-Dubien, Singlet-Singlet Absorption and Intersystem Crossing from the $^1B_{3u}$ State of Naphthalene, *Chem. Phys. Lett.*, 1968, **2**, 65.
- 18 See review by S. C. Pyke and M. W. Windsor, Measurements in the Picosecond and Shorter Time Range, in *Chemical Experimentation Under Extreme Conditions*, in The Techniques of Chemistry Series, ed. B. W. Rossiter, John Wiley and Sons, Inc. New York, 1980, ch. 5, vol. 9, pp. 205–276.
- 19 M. G. Rockley, M. W. Windsor, R. J. Cogdell and W. W. Parson, Picosecond Detection of an Intermediate in the Photochemical Reaction of Bacterial Photosynthesis, *Proc. Nat. Acad. Sci. USA*, 1975, **72**, 2251–2255.
- 20 K. J. Kaufmann, P. L. Dutton, T. L. Netzel, J. S. Leigh and P. M. Rentzepis, Picosecond Kinetic Events Leading to Reaction Center Bacteriochlorophyll Oxidation, *Science*, 1975, **188**, 1301–1304.
- 21 See review by D. Holten and M. W. Windsor, Picosecond Flash Photolysis in Biology and Biophysics, *Annu. Rev. Biophys. Bioeng.*, 1978, **7**, 189–227.
- 22 M. W. Windsor and D. Holten, Picosecond Studies of Primary Charge Separation in Bacterial Photosynthesis, *Philos. Trans. R. Soc. London, A*, 1980, **298**, 335–349.
- 23 Royal Society Discussion on Ultra-Short Light Pulses, *Philos. Trans. R. Soc. London, A*, **298**, 211–414.