

The genesis of flash photolysis †

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A brief account is given of the construction of the first flash photolysis apparatuses at Cambridge and their application to gas phase systems.

George Porter graduated in Chemistry from Leeds University in 1942. As a lieutenant in the Royal Navy Volunteer Reserve he served as a Radar Officer on destroyers in the Second World War. This often required skill in improvisation, for instance, the large black and yellow resistors known as 'tigers' could be repaired with boot polish. On demobilisation in 1945 he came to Cambridge to undertake research in the Physical Chemistry Department with R. G. W. Norrish and became a member of Emmanuel College of which he was later an Honorary Fellow.

During the war Physical Chemistry research in Cambridge had been much oriented towards practical problems. For instance, pre-war research on ignition problems led to work on the suppression of gun flash (dripping toluene down gun barrels worked well, but was not approved by the army). Work on ionisation in flames resulted from the problem that a rocket's exhaust absorbs signals used for its radio control. Post-war, the fundamental aspects of this work were developed by Morris Sugden.

By 1945 it was clear that progress in reaction kinetics was limited by the lack of techniques for observing and studying free radicals and other short-lived intermediates whose

presence could be deduced from kinetic studies and product analysis. Here photochemistry provided a possible way forward because at least the rate of initiation of a reaction could be determined. Here Norrish and Porter¹ used a 7.5 kW mercury arc mounted in a searchlight to produce detectable amounts of CH₂ radicals by the photolysis of a gas flow containing ketene or diazomethane. Partially successful attempts were made to detect these radicals by the Paneth mirror technique in which a tellurium film deposited in the flow tube is removed by the radicals. Fortunately other war-time developments showed a way forward. The use of the Arditron and other high intensity flash tubes for night-time aerial photography provided a possible method for generating large concentrations of free radicals as well as for recording their absorption spectra during their limited lifetime.

After discussion of this idea with Morris Sugden and Tony Harding, George Porter decided to 'run with it'. The Royal Navy gave the condensers free, and even paid the department £20 for returning the packing cases. These were installed in a small basement room from which 2000 µF charged to 4 kV could be discharged through a 1 m long quartz flash tube in approximately 2 ms. This and the reaction vessel were surrounded by a magnesium oxide reflector and the absorption spectrum of the products was recorded using a much smaller flash lasting about 50 µs, the timing of the flashes being determined by a rotating wheel (Figs. 1 and 2).^{2,3} This original apparatus was used to study the kinetics of HO radicals in photosensitised H₂-O₂-NO₂ systems⁴ and with F. J. Wright⁵ to study the kinetics of ClO formation and removal in the flash photolysis of Cl₂-O₂-N₂ mixtures which established the intermediacy of the ClOO species, an example of the complex chlorine oxide chemistry which is so important in stratospheric ozone depletion.

At this stage the relationship of flash photolysis to conventional photochemistry arose. Margaret Christie⁶ established that uranyl oxalate actinometers maintained the same efficiencies up to very high intensities. Kerro Knox⁷ and M. A. Khan⁸ investigated the role of radical-radical reactions in the flash photolysis of aldehydes and ketones but found that the associated temperature rise made the results hard to interpret.

Subsequent flash photolysis apparatus used electronic timing of the two flashes and shorter photolysis flashes (typically 50 µs from a 50 cm tube using 30 µF at 8 kV).⁹ Studies of acetylene-oxygen explosions photosensitised by nitrogen dioxide yielded a plethora of free radical absorption spectra, raising the interesting question as to whether C₂ has a singlet or triplet ground state.^{9,10} Attempts to improve the time resolution by replacing the spectroscopic flash by a xenon arc and photomultiplier cells showed that it was not possible to initiate ignition uniformly enough to prevent formation of detonation waves.¹⁰⁻¹²

At this time Margaret Christie¹³ followed by Anna Harrison¹⁴ used a tungsten lamp and photomultiplier cell to measure the recombination rate of iodine atoms by following the reappearance of I₂ after its flash photolysis. Similar studies at Manchester by Russell and Simons¹⁵ led to some controversy as to which physical property correlated best with the widely differing efficiencies of third bodies.

Professor Brian Thrush was born on 23rd July 1928. He came up to Emmanuel College, Cambridge as an Open Scholar in 1946 and subsequently obtained Firsts in both parts of the Natural Science Tripos. In 1950 he designed and built the first flash photolysis apparatus to use electronic timing, with which he studied hydrocarbon combustions. After a sabbatical year in Washington, D. C. in 1957/1958, he was elected to a fellowship at Emmanuel College and concentrated on spectroscopic and kinetic studies of atoms and free radicals using discharge-flow techniques. In 1976 he became an FRS and was elected to a Professorship of Physical Chemistry. He was subsequently Vice-Master of Emmanuel College and became first Head of the Combined Chemistry Department. He retired in 1995.



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

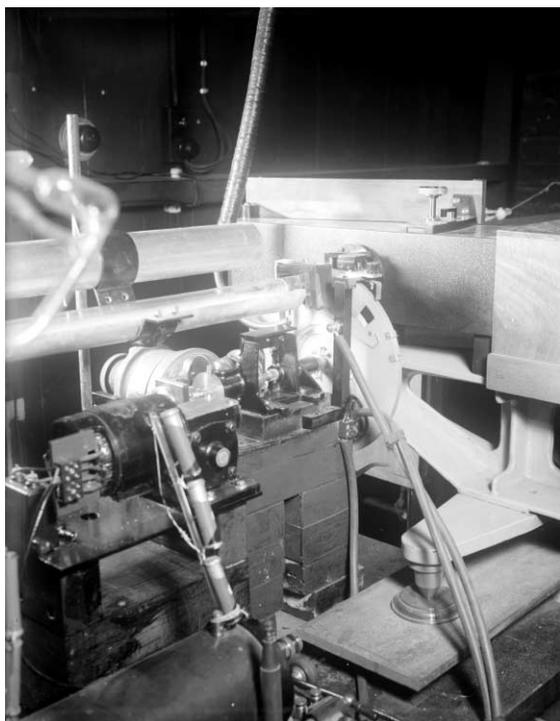


Fig. 1 Photograph of the first flash photolysis apparatus showing the timing wheel.

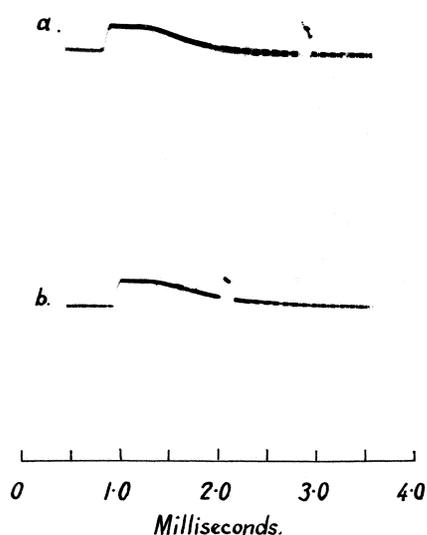
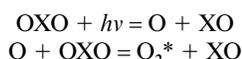


Fig. 2 Intensity-time record for the two flashes in the original flash photolysis apparatus.

Flash photolysis was also very quickly adopted at the National Research Council in Ottawa. There the dispersion of large grating spectrographs yielded visible absorption spectra of NH_2 and HCO , etc.¹⁶ which were beyond the sensitivity range of the prism spectrographs at Cambridge, although the latter produced the first ultraviolet absorption spectra of aromatic radicals,¹⁷ of C_5H_5 ¹⁸ and of N_3 ¹⁹ where quartz spectrographs have high dispersion. Absorption spectra of the triplet states of aromatic molecules were also observed.¹⁷ The flash photolysis of NO_2 and ClO_2 ,^{20,21} and later of O_3 ²² yielded absorption spectra of highly vibrationally excited oxygen molecules, the mechanism being:



however, the width of the vibrational distribution make these systems difficult for studying vibrational relaxation.

The wide ranging potential application of flash photolysis made some selectivity necessary. George Porter concentrated on the study of the condensed phase as described here by Maurice

Windsor, whilst Norrish concentrated on gas phase systems notably on combustion and its relation to engine knock.²³

In 1954 George Porter left Cambridge to become Assistant Director of the British Rayon Research Association. Soon afterwards he was appointed Professor of Physical Chemistry at Sheffield University.

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