Classic Paper presentation

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Trapped Atoms and Radicals in a Glass 'Cage'

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THE preparation of highly reactive free radicals and atoms in non-equilibrium concentrations high enough for their direct observation by physical methods has hitherto depended on the use of special rapid techniques such as that of flash photolysis. Here we describe a general method for the preparation of these species under conditions which permit their observation at high concentrations for an indefinitely long period of time. The method involves the photolytic dissociation of a substance dissolved in a transparent rigid solvent at very low temperatures. The only related work which we have been able to find is that of Lewis and Lipkin, who showed that certain rather stable radicals, such as triphenyl methyl, could be detected after photolysis of the parent saturated molecule[1].

The essential conditions to be fulfilled if a reactive species, such as an iodine atom, is to be permanently isolated are: (1) diffusion to the vicinity of another atom must be prevented by using a very viscous solvent; (2) reaction with the solvent must not occur; such reactions are usually accompanied by appreciable activation energies and may therefore be avoided by working at a sufficiently low temperature. We have found that both conditions are fulfilled, for most radicals so far investigated, by using glasses formed from a mixture of hydrocarbons or from ether, alcohol and *iso*pentane at the temperature of liquid nitrogen.

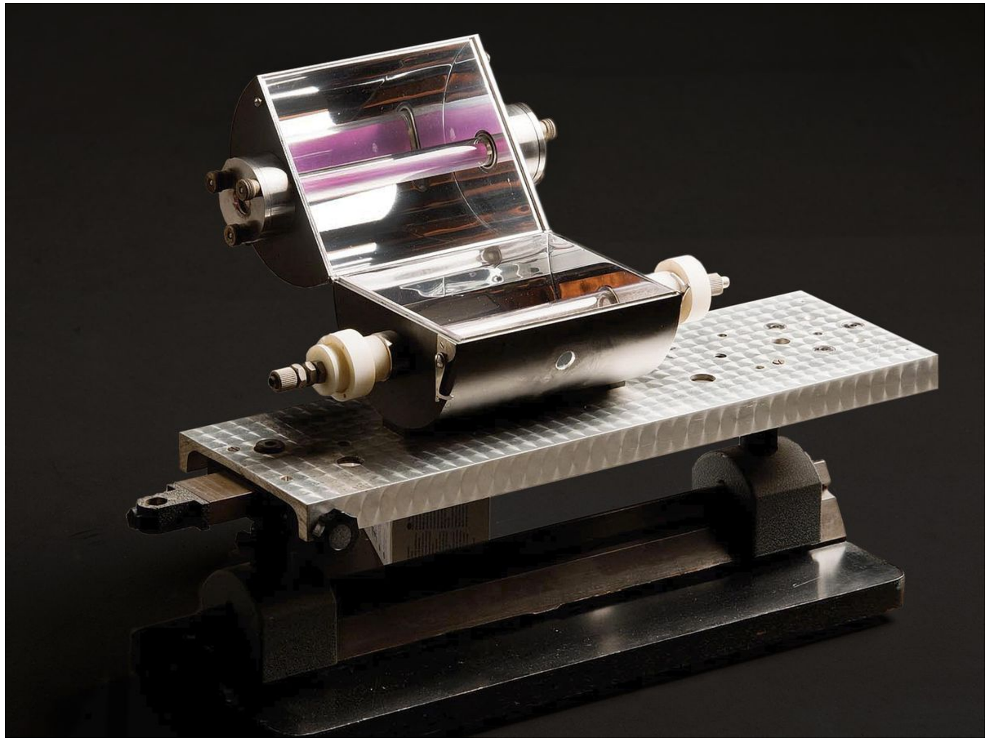
The method was first tested in a very simple manner by irradiating a 10^{-3} *M* solution of molecular iodine in a hydrocarbon glass at 86° K., using a conventional high-pressure mercury arc. The absorption spectrum of the iodine molecule occurs at a wave-length considerably less than that corresponding to the energy of dissociation to normal atoms, and it was believed that this energy might be sufficient to allow the atoms to diffuse apart through the rigid solvent by a process of local softening of the glass. Rapid dissipation of this energy would then result in a system of trapped iodine atoms. In complete accordance with this reasoning, we have found that, on irradiation, such an iodine solution becomes colourless throughout the visible and quartz ultra-violet regions of the spectrum and remains so indefinitely at 86° K. On softening the glass, by warming, the colour returns as the atoms recombine.

(1) *Ethyl iodide*. On irradiation, the spectrum of ethyl iodide decreases in intensity; but no other spectrum appears. On warming, molecular iodine is formed and recooling has no further effect. We conclude that the iodine atoms have been trapped as before, and it seems probable that trapped ethyl radicals were also present.

(4) *Aromatic compounds*. Porter and Wright have recently shown that the gas-phase photolysis of many single-ringed aromatic molecules results in the appearance of transient banded spectra with life-times less than 10^{-4} sec., which are attributed to free radicals such as benzyl[5]. We have observed similar spectra from the same series of compounds for several hours after photolysis in rigid solvents. These spectra vanished completely on warming the glass, and were therefore readily distinguished from the spectra of permanent products.

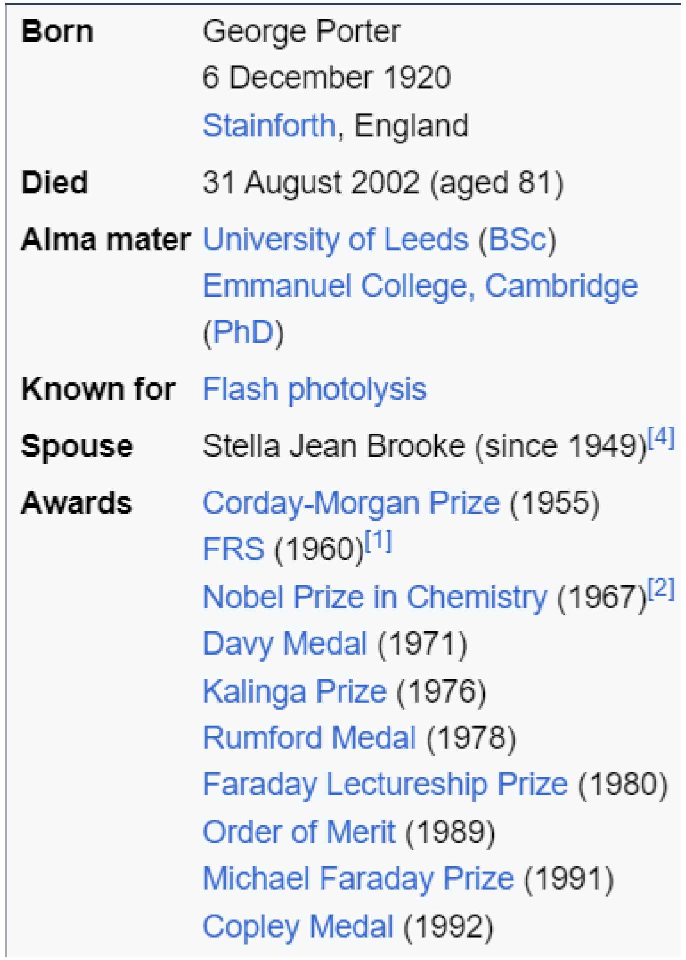
In all these examples the spectra were observed, with undiminished intensity, several hours after photolysis; they were removed by softening the glass and did not reappear on cooling.

This method should have many applications. It may be used for trapping the primary products of photochemical or radiation chemical processes for identification. It makes possible the measurement of properties such as infra-red spectra of free radicals, which has not hitherto been possible owing to the need for rapid recording. Bearing in mind the possibility of using still lower temperatures and other solvents, the method should be applicable to practically all free radicals which can be produced by photolysis.

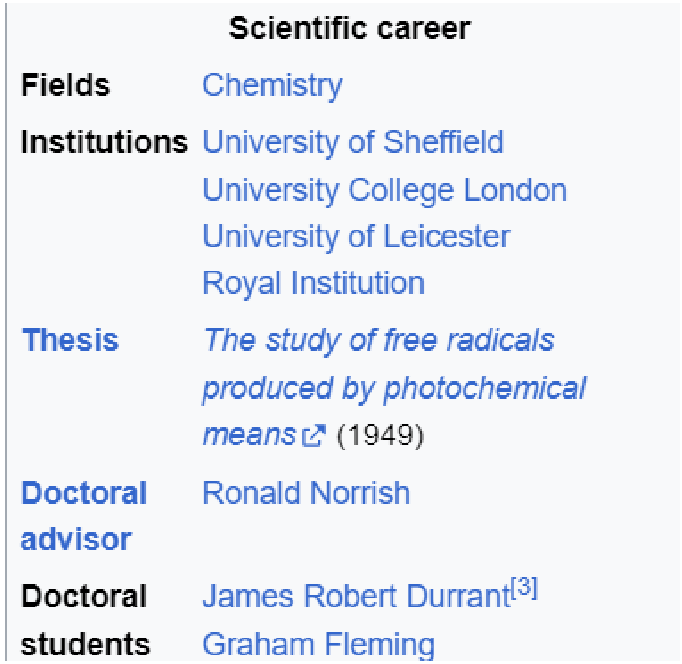


Science is, on the whole, an informal activity, a life of shirt sleeves and coffee served in beakers.

George Porter



Born	George Porter 6 December 1920 Stainforth, England
Died	31 August 2002 (aged 81)
Alma mater	University of Leeds (BSc) Emmanuel College, Cambridge (PhD)
Known for	Flash photolysis
Spouse	Stella Jean Brooke (since 1949)[4]
Awards	Corday-Morgan Prize (1955) FRS (1960)[1] Nobel Prize in Chemistry (1967)[2] Davy Medal (1971) Kalinga Prize (1976) Rumford Medal (1978) Faraday Lectureship Prize (1980) Order of Merit (1989) Michael Faraday Prize (1991) Copley Medal (1992)



Scientific career

Fields	Chemistry
Institutions	University of Sheffield University College London University of Leicester Royal Institution
Thesis	*The study of free radicals produced by photochemical means* (1949)
Doctoral advisor	Ronald Norrish
Doctoral students	James Robert Durrant[3] Graham Fleming