Graham R. Fleming on

“Flash Photolysis and Spectroscopy: A New Method for the Study of Free Radical Reactions”

G. Porter


The technique of flash photolysis emerged whole and fully formed in the first paper to describe it. That paper has a single author, a postgraduate student at Emmanuel College Cambridge, working under the supervision of Professor R. G. W. Norrish who was well known for his work in photochemistry. The student was George Porter, who had gone to Cambridge in 1946, having been demobilised from the Royal Navy after World War II. George’s original problem was concerned with the methylene radical using a technique based on the time to destroy a metal mirror at a variable distance from the source of gaseous free radicals (the Paneth mirror technique). George’s own view of his first paper is not charitable: “Paper published on this in 1947 (1). Not very good.” In fact the paper was for the 1947 Discussion of the Faraday Society on “The Labile Molecule”. The meeting was entirely concerned with the study of short-lived chemical species such as free radicals, but did not consider direct methods of observation at all. As Harry Melville said in his introductory remarks, in reference to the low concentrations of radicals obtained, “The direct physical methods of measurement simply cannot reach these magnitudes, far less make accurate measurements in a limited period of time, for example $10^{-3}$ s.” George had, in fact, already begun on the development of flash photolysis, the method that was going to revolutionise the study of chemical kinetics, and over the course of the next fifty years would lead to the creation of the new fields of physical, chemical and biological dynamics of molecules down to timescales of hundreds of attoseconds ($10^{-18}$ s).

In papers he left in the Royal Society archives George described how he got the idea for the flash photolysis method and it seems best to use his own words: “I was sent to the Siemens lamp works in Preston to collect a large mercury arc which I wanted for my research and took the opportunity to look around. Siemens was using electronic flash lamps and talked of milliseconds duration and 10,000 J energy. I had been trying to obtain the spectrum of methylene which I knew lived for a millisecond and could be produced by light. My experience in the Navy made me familiar with rapid recording techniques. I went back to my rather sordid hotel room and in the space of about half an hour I knew that here was a new technique for photochemistry and free radicals. I wrote out the idea in detail and Norrish was enthusiastic immediately. I begged and borrowed condensers from the Navy and Air Force. But it was nearly another year before...
I had the idea of using a second flash to record the spectrum having previously wasted much time trying to build a rapid recording grating spectrograph."

Thus the impetus for the technique was the spectroscopic detection and study of free radicals in the gas phase. The first experiment designed to produce organic free radicals certainly showed that the concentration of free radicals would be adequate for detection: photolysis of acetone with a 4000 J flash resulted in total destruction of the acetone and the deposition of filaments of carbon throughout the 1 m long sample cell! It is interesting to speculate if C₆₀ or carbon nanotubes were present in these filaments.

The second paper² written with Norrish describes the effect of such high intensity flashes on photochemical reactions and is clearly aimed at creating high concentrations of radicals. Today it seems a fairly standard paper and gives no hint that three days later (August 9, 1949) George would submit to the Proceedings a single-author paper describing the fully-fledged method of flash photolysis containing spectra as a function of time delay, for several radicals and transient species, including new spectra for the CIO and CH₃CO radicals.³

The method involving an intense "photolysis" flash and a second, delayed "spectro flash", to record the spectrum on a photographic plate at the image plane of a spectrograph, was revolutionary and set in train attempts, in which George was to play a leading role, to record the fastest processes in chemistry that continues to this day.

There are many remarkable aspects of this paper on "Flash photolysis and spectroscopy: A new method for the study of free radical reactions".³ First, as George notes above, his original intention was to record the full two-dimensional surface of time and wavelength (frequency) information for the experimental system, something that is rarely attempted today, and then only with very high repetition rates, ultra-stable, laser sources. Second, George was concerned that the very intense photolysis flash would produce unmanageable quantities of scattered light, and as a result did not use an electronic delay between the two flashes, but instead a rotating wheel which synchronised a shutter to block the photolysis flash, the firing of the photolysis and spectroflash, and an oscilloscope time base. Timing was controlled by the gearing to the wheel for coarse delays and by altering the separation of the two contacts on the wheel which produce the trigger pulses to the two lamps. The condensers (capacitors) required for the discharge were given free by the Royal Navy, who even paid the chemistry department £20 for returning their packing cases!

Equally striking were the long term consequences of the true "basic" research in that first paper more than 30 years after the recording of the CIO spectrum and subsequent careful study of its reactions by George and F. J. Wright; CIO was found to play an important role in the catalytic destruction of stratospheric ozone (the "ozone hole" above Antarctica) via the reactions:
$$\begin{align*}
\text{Cl} + \text{O}_3 & \rightarrow \text{ClO} + \text{O}_2 \\
\text{Cl} + \text{O} & \rightarrow \text{Cl} + \text{O}_2 \\
\text{O}_3 + \text{O} & \rightarrow 2\text{O}_2
\end{align*}$$

with the chlorine atoms being generated by photochemical decomposition of chlorofluorocarbons.

A remarkable burst of activity followed with studies ranging from the explosive reaction of hydrogen and oxygen and the kinetics of HO radicals, fragmentation of organic molecules, the explosive combustion of hydrocarbons to the study of such phenomena as knock, carbon formation and atom recombination reactions.

References

Professor, University of California Berkeley (1997—present), Melvin Calvin
Distinguished Professor of Chemistry (2002—present), Director, Physical Biosciences
Division, Lawrence Berkeley National Laboratory (1997—2005), Associate Laboratory
Director for Physical Sciences (2002—2005), Deputy Laboratory Director (2005—
present), Director (Berkeley), California Institute for Quantitative Biomedical Research,
UCB, UCSF, UCSC (2000—present).