

# CHEMISTRY AND THE SPECTROSCOPE\*

R. G. W. NORRISH, F.R.S.

*Department of Physical Chemistry, University of Cambridge, England*

**T**HE fundamental and detailed work conducted in laboratories must, by its nature, remain sometimes obscure to non-scientists and in some cases even to those who specialise in other branches. Yet it is indirectly of importance to everybody.

For example, flash photolysis and "kinetic spectroscopy", discovered and developed in the Laboratory of Physical Chemistry at the University of Cambridge, England, is a new and powerful method of studying the intimate nature of photo-chemical and thermal reactions over periods measured in millionths of a second. Its applications are immensely varied.

It provides means of examining the nature of explosive processes; can be applied to the study of anti-knock additives in the internal combustion engine; it yields important information about the elementary reactions in the upper atmosphere of vital value to the meteorologists and geochemists and the processes which are now believed to have created the environment on which life, as we know it, depends.

The new method yields objective information about the free radicals and other transient intermediates taking part in photo-chemical and thermal reactions. These intermediates generally have very short lives, measured in millionths of a second; nevertheless it has been possible to photograph their characteristic spectra at successive intervals of time and so to measure the rates of their growth and decay during chemical reaction. Sometimes they are produced in a highly energised state of thermal vibration, yet "cold" as regards their translational and rotational motions, and the study of this has thrown light on the propagation of chain reactions, and the transfer of energy from vibrational to other thermal degrees of freedom.

## A PARAMOUNT CHALLENGE

The "kinetic spectroscopy" method involves the use of the photo-chemical technique of flash photolysis. It was discovered and developed spectroscopically in our Laboratory of Physical Chemistry at Cambridge, as I shall presently describe.

The principles of photo-chemical reaction were first conceived some 50 years ago through the

work of Warburg, Bodenstein, Henri and Weigart and took final shape through the work of others who followed. Into the whole framework have been fitted innumerable photo-chemical and thermal reactions whose postulated mechanisms, involving atoms-free radicals or excited species, are entirely derived from the circumstantial evidence afforded by spectroscopic observations and quantitative measurements involving photo-chemical kinetics, and end products. In general, the consistency of the mechanisms within the framework is so good as to lead to confidence in our conclusions, though the absence of any objective proof of the existence of the postulated intermediates has constituted a permanent challenge to the photo-chemist, and sometimes gave rise to criticism from unbelievers which weakened his position.

It was for this reason that in 1946 we decided to break new ground by endeavouring to obtain direct spectroscopic evidence for the free radicals postulated as intermediates in photo-chemical reactions. This was made possible by the discovery by Porter and myself that very large measures of photolysis could be achieved by the application of a powerful light flash to suitable reactants, such as nitrogen peroxide, iodine, or acetone, contained in a quartz vessel. These early flashes produced by discharging a bank of condensers through argon were of 1-2 milliseconds duration and dissipated up to 10,000 Joules of energy, and it seemed obvious that if free radicals were produced in the reactions, they must momentarily have been at such very high concentrations as to invite efforts to photograph their absorption spectra.

## FIRST ACHIEVED IN 1949

This was achieved in the first instance by Porter in 1949, who, using a second flash as a photographic source triggered mechanically at short intervals after the first by the method of Oldenburg, was able to demonstrate the dissociation of chlorine and to obtain the spectrum of the CS radical by the photolysis of carbon disulphide. This early success was followed by the development of the technique; shorter photolysis flashes of 100 microseconds duration and of 1,000-3,000 Joules were devised, and shorter intervals between the photolysis flash and spectroscopic flash were achieved by using electronic delay circuits capable of precision timing to a few microseconds.

\* Based on his Presidential Address to the Chemistry Section of the British Association for the Advancement of Science's Annual Meeting at Norwich, August and September, 1961.



It soon became apparent that the early results of flash photolysis in the gaseous systems which I have previously exemplified were vitiated by a great rise of temperature, which resulted in thermal as well as photo-chemical dissociation. This arises from the fact that when the intense flash is applied to a suitably absorbing system such as chlorine, or nitrogen peroxide, the absorbed light energy is rapidly degraded to heat: it may be calculated that a reactant at a pressure of 1 mm. absorbing one-thousandth of the emitted energy will instantaneously reach a temperature measured in some thousands of degrees. Only if a relatively large excess of inert gas (say 500 mm. pressure) is present to act as coolant, or the process is carried out in solution, can this temperature rise be kept in check, and so limited to a few—say ten degrees in the case of a gaseous system. Thus under the adiabatic conditions resulting from lack of temperature control thermal cracking or explosion as well as photolysis may be induced in suitable systems and the method of kinetic spectroscopy provides a valuable means for the observation of the rapid elementary reactions of free radicals or atoms occurring in explosive media initiated photo-chemically.

#### COMPREHENSIVE METHOD

We therefore have a comprehensive method which can be applied to "instantaneous" reactions in the gas phase both under adiabatic and isothermal conditions, and also to reactions in solution.

Applications are legion. The very short ultra-violet rays of the sun which do not penetrate our atmosphere bring about reactions in the

upper atmosphere, giving rise to the protective ozone layer and involving atoms and free radicals of the utmost importance to the geochemist and meteorologist; much information can be obtained about these in the laboratory by the methods I have described.

It is now believed that the primitive atmosphere of the earth was reducing, composed mainly of hydrogen, together with methane, hydrogen sulphide, water, carbon monoxide and ammonia, similar to the atmospheres of the major planets as we see them today. If the solar system had a uniform origin there must have been influences which changed our atmosphere and that of Mars from reducing to oxidising. The first is the progressive loss of hydrogen from our relatively weak gravitational field. The second is the photolysis of water and the other compounds, leading to the formation of formaldehyde and oxides of sulphur, phosphorus and nitrogen, which on interaction, according to the fascinating views of Urey and Oparin, deposited the primordial organic scum on the earth and provided the necessary medium for the evolution of life.

Many of the reactions involved can be studied by flash photolysis. Others such as the photolysis of water, methane and other hydrocarbons lie at present outside its scope, and provide a challenge to extend this powerful method to shorter wavelengths of the ultra-violet which at present escape us.

---

*Note:* Full references to the work cited are to be found attached to the report of the full address published by the British Association.

#### SUCCESSFUL OPERATION OF NIMROD INJECTOR

ON August 1 the first proton beam accelerated to the design energy of 15 MeV. was obtained from the linear-accelerator injector which forms the first stage of *Nimrod*, the 7,000 MeV. proton synchrotron under construction at the Rutherford High-Energy Laboratory of the National Institute for Research in Nuclear Science, Harwell. The linear accelerator consists of a cylindrical copper cavity approximately 44 ft. long and 5.5 ft. in diameter, with 48 drift tubes spaced along its axis, the whole being enclosed in a vacuum envelope. Approximately 1 MW. of radio-frequency power is supplied to the cavity at its resonant frequency of 115 Mc./s. to set up the required accelerating fields across the gaps between drift tubes. The function of the drift tubes is to screen the protons from the field when its direction reverses every alternate half-cycle, and they also contain focusing magnets

which constrain the protons to form a proper beam close to the machine axis. The drift tubes increase in length along the tank to correspond with the increase in proton velocity. Protons enter the linear accelerator with an initial energy of 0.6 MeV. from a pre-injection stage which is basically a conventional d.c. accelerator. Pulsed 15 MeV. beams will be delivered by the injector to the synchrotron at rates up to 2 per sec. and at pulse lengths up to 2 m. sec. Within the synchrotron, they will be constrained to a circular path by a suitably varying magnetic field. In this way they will make many revolutions, receiving a small acceleration at a particular point in the orbit until the output energy of 7,000 MeV. is reached. Construction work on *Nimrod* started in August 1957 and is expected to be completed during 1962.—(*Nature*, p. 1,043, Vol. 191, September 9, 1961.)