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"The Triplet State"

NAME OF AUTHOR

George Porter,
Professor of Physical Chemistry,
University of Sheffield,
England.

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The principal projects carried out during the period of this report were

(a) A thorough investigation of the factors controlling the duration of an electronic flash. Dr. E. R. Wooding.

(b) Completion of work on energy transfer between triplet states. Dr. F. Wilkinson.

(c) Initiation of work on first order radiationless decay of triplet states in solution. Dr. M. Z. Hoffman.

Dr. Wooding carried out an investigation of flash photolysis apparatus and the principles underlying its design from January to October 1961.

A novel flash photolysis apparatus was constructed and examined. It consisted of a 10 microfarad capacitor bank arranged radially about the base of a flash tube. The capacitor leads consisted of a disc transmission line which was coupled to a coaxial line containing the flash tube. A spark gap was connected in series with the flash tube to enable it to be fired at a chosen time. This construction enabled the stray inductance to be reduced to 10 nanohenry. With a 1 c.m. flash tube filled with argon, durations of 2 microsecond were obtained. The addition of 30% hydrogen halved the flash duration but the argon pressure was not important in the range 1 to 100 torr.*

* mm. Hg pressure

New methods of constructing flash tubes were examined with a view to reducing the self inductance still further. From the experience gained, a new capacitor bank and flash tube were designed.

It is possible to obtain light pulses of 10 nanosecond duration but the stored energy is very low (G. Porter and E.R. Wooding, J. Sci. Instrum. 1959, 36, 147). Other devices have been examined and attempts have been made to increase the energy. The problem consists mainly of obtaining a capacitor with a large value of $\left(\frac{C}{L}\right)^{\frac{1}{2}} \frac{1}{2}Vo^2$ and connecting to a flash tube of resistance equal to $\left(\frac{L}{C}\right)^{\frac{1}{2}}$ but without introducing further inductance.

A number of capacitors were constructed or obtained from manufacturers and by connecting to spark gaps or flash tubes, light pulses having durations between 10 and 50 nanoseconds were obtained when energies of up to 0.1 joule were discharged. These sources have been described in a paper which is about to be published in the Journal of Photographic Science. One hundred copies will be sent on as soon as they are available.

A circuit was designed for the simultaneous firing of four flash through a single vessel.

Some of the processes leading to radiation from a plasma were examined.

Fuller details of this work will be submitted as a technical

note. Part of the results will be published in book form as "Flash Photolysis" by G. Porter and E.R. Wooding, Oxford University Press.

Application of the work on flash discharge characteristics made it possible for Dr. F. Wilkinson to complete his measurements on triplet state energy transfer in fluid solvents. Wilkinson was employed on this contract from July - September 1960 although he had worked on a related problem in this department for the previous three years. The rate constants of transfer by the process

$$D_T + A_S \longrightarrow D_S + A_T$$

where D and A denote donor and acceptor and T and S denote triplet state and singlet ground state, were measured for a variety of donors and acceptors. In all cases where the triplet excitation energy of the acceptor was considerably less than that of the donor energy transfer rate constants were diffusion controlled. No case of transfer was found when the triplet donor energy was less than that of the acceptor. When the triplet energies of donor and acceptor were nearly equal energy transfer took place but the rate constant was less than the diffusion controlled rate. A theoretical study of these processes leads to the conclusion that overlap of orbitals of donor and acceptor is necessary for transfer to occur and that the Förster resonance type transfer is not applicable.

A full account of this work is in course of preparation and will be submitted later as a technical note.

One of the principal remaining problems in the field of triplet state kinetics is the mechanism of the first order radiationless decay (see Technical Note No. 1, Porter and Wright). A new investigation of this problem by Dr. Hoffman is under way. An apparatus capable of kinetic measurements within 30 μ seconds of flash initiation has been successfully completed and a comparison of naphthalene and anthracene kinetics at different oxygen pressures is in progress.