

## Exploding Wire as a Light Source in Flash Photolysis\*

GISELA K. OSTER† AND R. A. MARCUS

*Department of Chemistry, Polytechnic Institute of Brooklyn, Brooklyn 1, New York*

(Received December 6, 1956)

The exploding wire technique has been developed for use as a light source in flash photolysis. The method consists of discharging a bank of condensers, via a mechanical switch through a thin Nichrome wire. The wire explodes, emitting light rich in the ultraviolet region in less than a millisecond. The luminous efficiency in the 200 to 330  $m\mu$  region is of the order of 10% of the input. The minimum electrical energy input necessary to produce an explosion is equal to the energy required to vaporize the wire. The light output of the exploding wire as measured by uranyl oxalate actinometry and acetone photolysis is proportional to the electrical energy input. It was found to be highly reproducible. It was further observed that the exploding wire behaves as a line source. Because of the absence of a quartz or Pyrex tube in this source, it may find application in the far as well as in the near ultraviolet and in the visible spectral regions.

### INTRODUCTION

THERE are a number of methods of producing a high-intensity burst of light of short duration. For example, the high intensity produced by a spark has been known for more than a century and was utilized in the early work in high-speed photography, especially in ballistics. In the last twenty years high-speed discharge lamps have been developed particularly by Edgerton<sup>1</sup> for use in high-speed photography. The use of such discharge lamps was systematically applied to the study of a number of chemical systems by Norrish and Porter.<sup>2,3</sup>

In the normal application of discharge lamps a voltage of the order of some thousand volts, stored on a bank of condensers, is applied across the terminals of the lamp, but this is usually not sufficient to discharge the lamp, therefore a trigger voltage of the order 10 000 volts is applied via a third electrode, and this renders the discharge tube conducting. The electrical energy stored in the condenser is then given by  $\frac{1}{2}CV^2$  where  $C$  is the capacitance of the condenser and  $V$  is the voltage on the condenser. The actual luminous efficiency of these lamps is of the order 10% of the electrical input.<sup>3</sup>

Although these discharge lamps have proven to be very valuable for photochemical studies they have certain drawbacks. The cost is, for certain laboratories at least, very large. In the lamps of Porter and Norrish 1-inch tungsten electrodes, requiring special metal-to-glass seals, were used. These workers also report that their lamps decay in luminous efficiency due to deterioration of the surface of the electrodes.

Accordingly, it was decided to consider an alternative method of producing a high intensity flash. The method

chosen was that of the so-called exploding wire, first described as early as 1815<sup>4</sup> and since described by workers in the field of high-speed photography,<sup>5</sup> but its use in photochemical studies has not heretofore been exploited. This source has the advantage of possessing no quartz or Pyrex envelope. This in turn may permit its photochemical application in the far as well as in the near ultraviolet regions of the spectrum.

The method as used in the present work consists of the following. A bank of condensers is charged to a high voltage; the charged condensers are then discharged through a manually operated high-voltage switch through a thin high-resistance wire to ground. The wire explodes producing a very loud noise and a very strong burst of light accompanied by the complete disintegration of the wire. In order to produce another flash a new piece of wire is introduced.

### ELECTRICAL CIRCUIT

A conventional full-wave rectifier having mercury-filled 866 A rectifier tubes was employed. The voltage output ranging from zero to 8000 volts was regulated with a variable transformer applied across the rectifier. This voltage was applied via a high-voltage switch to a bank of condensers consisting of 110 Sprague condensers of 0.3  $\mu f$  each. The charged condensers were discharged via the high-voltage switch through a 30 cm long Nichrome wire (Harris Company BS 40). A small residual voltage remaining after the wire had exploded was removed by discharge through a high-power resistor.

The high-voltage switch consisted essentially of a Bakelite rod fitted at its end with a rectangular brass plate which can be moved manually between the charging and discharging positions. The metal terminals at these two positions are brass plates mounted on a Bakelite board and make a perfectly even contact with the moving brass piece. All the metal parts were chromium-plated, as otherwise the places of contact

\* Abstracted in part from a thesis of Gisela K. Oster, submitted in partial fulfillment of requirements for the degree of Doctor of Philosophy at the Polytechnic Institute of Brooklyn, 1956. (Microfilm available from University Microfilms, Ann Arbor, Michigan.)

† Socony-Vacuum Fellow (1953-1954); Research Fellow (1954-1955) under Contract No. Nonr 839(09).

<sup>1</sup> H. E. Edgerton and K. S. Germeshausen, *Rev. Sci. Instr.* **3**, 553 (1932).

<sup>2</sup> R. G. W. Norrish and G. Porter, *Nature* **164**, 658 (1949).

<sup>3</sup> G. Porter, *Proc. Roy. Soc. (London)* **A200**, 284 (1950).

<sup>4</sup> G. T. Singer and A. Croose, *Phil. Mag.* **46**, 161 (1815).

<sup>5</sup> W. M. Conn, *J. Opt. Soc. Am.* **41**, 445 (1951).

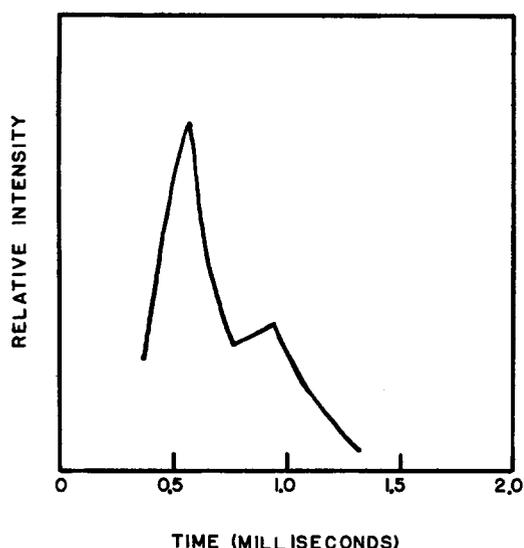


FIG. 1. Trace of the flash.

were slowly oxidized, thereby changing the charging characteristics.

#### SOME PROPERTIES OF THE EXPLODING WIRE

A minimum voltage was required to explode the wire, below which voltage the wire merely burned out without emission of ultraviolet light. For example, when the length of wire was kept at the constant value of 12 cm, it was found that above 1500 volts the wire exploded and disintegrated completely and the condensers were practically completely discharged. Below this voltage, short fragments of the nonexploded wire could be found in the vicinity and the condensers retained nearly all of their original voltage. Hence it is seen that in order to produce an explosion under our experimental conditions the electrical energy input must be 34 joules or greater.

The precise nature of the mechanism of the explosion is not known, but high-speed cinematography<sup>6</sup> of exploding wires has revealed that the wire disintegrates early in the process although the condensers continue to discharge, presumably through a conducting atmosphere of metal ions. It would appear that the electrical energy is dissipated in three ways, firstly, in the vaporization of the metal, secondly, in the formation of a shock wave, and thirdly, in the emission of radiation. The energy in joules necessary to vaporize the wire equals  $4.2\Delta H_s dv$  where the latent heat of sublimation of Nichrome  $\Delta H_s$  equals approximately 1700 cal/g, the density  $d$  equals 8 g/cm<sup>3</sup>, and for the 12 cm 40 gauge wire the volume  $v$  equals  $6.0 \times 10^{-4}$  cm<sup>3</sup>, so that the energy is 33 joules. Since, as was shown above, at least 34 joules of electrical energy input are necessary to produce an explosion, it appears that the major part of the energy input at 1500 volts is used to vaporize the metal. Energy inputs above

<sup>6</sup> Allen, Hendricks, Mayfield, and Miller, Rev. Sci. Instr. 24, 1068 (1953).

1500 volts could then be used for the ionization of the atoms. The ions that may be formed in that metal atmosphere serve as conductors and further ionization might take place by secondary impact cascade processes.

The duration of the flash was determined photoelectrically on an oscilloscope. The phototube used was an ultraviolet sensitive (S-5 response) RCA type 935 whose output was applied across the vertical terminals of a Dumont oscilloscope type 304H having a long duration fluorescent screen. The time axis was applied across the horizontal plates via the linear sweep circuit of the oscilloscope whose frequency was calibrated with a General Radio audio oscillator of exactly 1000 cycles.

Photographs of the amplitude of the photocurrent as a function of time were taken for varying flashing

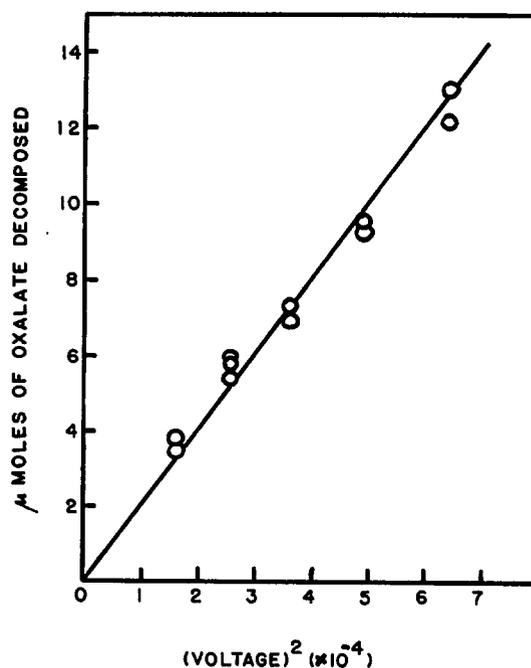


FIG. 2. Decomposition of oxalate per flash as a function of voltage.

voltages. The duration of the flash was unchanged with varying voltages, although the photocurrent increased with increasing voltages. A typical trace is shown in Fig. 1 and consists of two peaks, the smaller one probably due to an oscillation of the electrical circuit, where the leads would serve as inductance. From Fig. 1 it is seen that the major part of the light output has a duration of about one-third of a millisecond.

Spectra of the flash were taken with a small Bausch & Lomb Littrow spectrograph and it was found that the spectrum exhibits all the lines, including those in the ultraviolet region, of nickel and chromium.

#### ACTINOMETRY

The intensity of the ultraviolet light of the flash was determined in an approximate fashion by uranyl oxalate

actinometry.<sup>7</sup> For the purposes of our measurements we assumed a quantum yield of oxalate destruction of 0.57 in the ultraviolet region. In the present experimental arrangement the absorption of light by the uranyl oxalate was essentially 100% between 200 and 310  $m\mu$ ; it was still large at 330  $m\mu$  but became quite small at longer wavelengths. Thus the light output measured in this way is approximately that between 200 and 330  $m\mu$ . A quartz tube of diameter 1 cm was filled with 20 cc of a 0.01  $M$  solution of uranyl oxalate. This tube was placed parallel to the wire, the distance between wire and the center of the tube being 1.5 cm and tube and wire being of equal length. The solution was exposed to a certain number of flashes (1 to 10, depending on the intensity of the flash so as to give about the same amount of decomposed oxalate). It was found that the decomposition per flash was independent of the number of flashes given. The moles of oxalate decomposed per flash as a function of voltage on the condensers are shown in

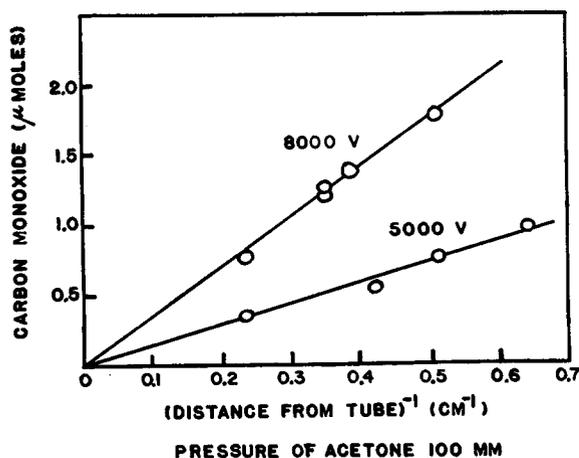


Fig. 3. Carbon monoxide production as a function of the distance of the wire from the center of the reaction tube.

Fig. 2. As is seen, the amount of oxalate destroyed is proportional to the square of the voltage. That is, the energy of luminous output is directly proportional to the electrical energy input. This proportionality also indicates that the spectrum of the flash does not change with varying electrical input.

The order of magnitude of intensity of light falling on the cell can then be calculated. For example, at 8000 volts, one flash decomposed  $1.27 \times 10^{-5}$  mole of oxalate. Assuming a quantum yield of 0.57 and total absorption of light falling on the vessel, it follows that  $2.23 \times 10^{-5}$  einstein are falling on the vessel. At a wavelength of 280  $m\mu$  a quantum of light has an energy of  $7 \times 10^{-12}$  erg. Therefore  $2.23 \times 10^{-5}$  einstein correspond to 9.5 joules falling on the vessel. The total output of the lamp is then calculated by integrating over a circle and gives 93 joules. The electrical input into the wire, on the other

<sup>7</sup> P. A. Leighton and G. S. Forbes, *J. Am. Chem. Soc.* **52**, 3139 (1930).

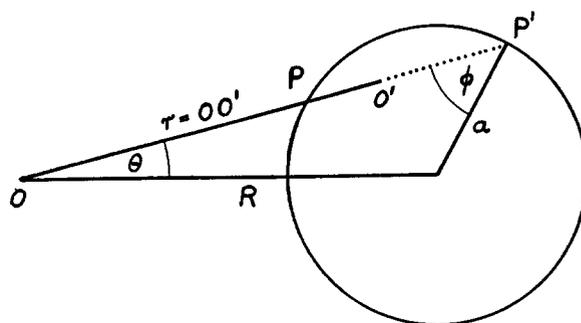


Fig. 4. Cross section of wire and reaction tube arrangement.

hand, was 1056 joules and hence the wire is approximately 10% efficient in the production of ultraviolet light in the spectral region 200 to 330  $m\mu$ .

A still further and perhaps more convenient method of actinometry was that of the gasometric measurement of carbon monoxide production in the photodecomposition of gaseous acetone. For an acetone pressure of 100 mm, it was found that the amount of carbon monoxide produced by a flash was directly proportional to the square of the applied voltage. Since it has been shown that the intensity is proportional to the square of the applied voltage, it follows that carbon monoxide production is directly proportional to the intensity.

It was found that the carbon monoxide production increased linearly with the inverse distance of the wire from the center of the reaction tube, if the wire were flashed at a constant voltage, as is shown in Fig. 3. The proportionality of carbon monoxide to the square of the applied voltage was maintained irrespective of the chosen distance. The geometric factors governing light absorption in the present experimental arrangement can then be calculated. In all experiments the wire was parallel to the long axis of the cylindrical reaction vessel of radius  $a$ . A cross section of the system is illustrated in Fig. 4 where  $R$  is the distance of the wire to the center of the reaction vessel, and  $r$  is the distance to any point. If the wire is considered as a line source whose intensity output per unit length is proportional to  $1/r$ , then the total incident intensity on the tube will be proportional to  $\int (dA/r)$ , the integration being over every area element of the tube cross section. This integral equals<sup>8</sup>  $(\pi a^2/R)(4B/\pi)$ , where  $B^9$  is a complete elliptical integral, whose modulus  $k$  equals  $(a/R)$ . For any given  $a$  the integral  $B$  decreases steadily from 1 to  $\pi/4$  as  $R$  increases from  $a$  to infinity. Over the range of  $(a/R)$ 's given in Fig. 4,  $B$  changes<sup>9</sup> only by 10%. Thus, Fig. 4 shows that the wire behaves as a line source.

<sup>8</sup> Referring to Fig. 4 and integrating first over  $r$  we obtain  $\int \int r d\theta dr/r = \int (PP') d\theta$ . We note that  $(PP') = 2a \cos \phi$ , and express  $d\theta$  in terms of  $d\phi$  using the relation  $\sin \phi = (R/a) \sin \theta$ .

<sup>9</sup> E. Jahnke and F. Emde, *Tables of Functions* (Dover Publications, New York, 1957), pp. 73 and 82.

$$B = \int_0^{\pi/2} [\cos^2 \phi / (1 - k^2 \sin^2 \phi)^{3/2}] d\phi.$$

## CONCLUSION

The foregoing experiments have shown that the exploding wire is a light source of considerable brilliance and excellent reproducibility and should, therefore, be of use in flash photochemistry. Since the wire is a line source, the light beam could be rendered very parallel by reflectors or lenses with the wire at the focal point. The spectral output of this source can be changed at will by choosing the appropriate metals (e.g., it was found that exploding copper wires emitted very intense green light). As noted earlier it may be suitable in the far ultraviolet

region as well as in the near ultraviolet and visible. Experiments in the far ultraviolet using sapphire reaction vessels are being planned.

The duration of the flash can be decreased by choosing a lower resistance wire. Alternatively, high voltage-low capacity condensers may be employed. Since the problems of mechanical switching at extremely high voltages become greater, thyratron<sup>10</sup> or series spark gap<sup>11</sup> electrical circuits can be used instead.

<sup>10</sup> R. Marshall and N. Davidson, *J. Chem. Phys.* **21**, 659 (1953).

<sup>11</sup> G. Porter and M. W. Windsor, *Discussions Faraday Soc.* **17**, 178 (1954).

## Electronic Spectral Shifts of Nonpolar Molecules in Nonpolar Solvents

H. C. LONGUET-HIGGINS AND J. A. POPLE

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

(Received November 20, 1956)

A theory of the red shift of low-lying electronic bands of nonpolar molecules in nonpolar solvents is presented. The difference between the dispersion forces in the ground and excited states is investigated by perturbation theory and an approximate formula is derived according to which (in dilute solution)

$$\text{Red shift} = \frac{1}{6} \alpha_A \alpha_B \bar{R}^{-6} \left\{ \frac{1}{2} E \alpha_A + M^2 \right\},$$

where  $\alpha_A$  and  $\alpha_B$  are the molecular polarizabilities of the solute and solvent, respectively,  $M$  and  $E$  are the dipole moment and energy of the transition, and each solute molecule is supposed to be surrounded by  $z$  solvent molecules at a mean distance  $\bar{R}$ .

## 1. INTRODUCTION

THE frequency of a molecular electronic absorption band is generally displaced when the molecule is immersed in a solvent medium such as a liquid or a foreign gas under pressure. These shifts are usually towards longer wavelengths although the opposite is sometimes observed.<sup>1</sup> They arise from solute-solvent interaction and a theory of their magnitude has to be based on a comparison of the solvent stabilization of the ground and excited states. If the interaction is greater when the solute molecule is in the excited state, then the electronic band will be shifted in the red direction.

There are essentially two types of theory of the origin of the spectral changes produced when a molecule is perturbed by its environment. These are, respectively, impact and statistical theories. In the impact theories explicit account is taken of the time dependence of the Hamiltonian for the absorbing system; in the statistical theories, which have been discussed particularly by Margenau,<sup>2</sup> the translational motion of the molecules is neglected, though account is taken of the statistical distribution of molecular configurations. The present paper describes a statistical theory of the electronic spectral shifts of a nonpolar solute in a nonpolar solvent.

Previous theoretical work on this problem includes a paper by Bayliss<sup>3</sup> in which it was assumed that the shift of a band is proportional to the solvation energy of the transition dipole, but no attempt was made to justify this hypothesis quantum-mechanically. Perhaps the most thorough quantum-mechanical discussion of the problem is that of Ooshika.<sup>4</sup> Ooshika's theory is concerned with both polar and nonpolar solutes and solvents. He concludes that the dispersive interactions are important in the red shift which is normally observed, but his formulas for the spectral shifts are somewhat complicated. In the present paper we follow the same lines as Ooshika, but introduce certain approximations which lead to a final formula in which the spectral shift is related to other simple properties of the solute and solvent.

A simple approach based on interactions involving only the lowest excited state of the solute molecules suggests that the magnitude of the shift is closely related to the polarizability of the solvent and to the oscillator strength of the transition under examination.<sup>5</sup> Some experimental data suggest, however, that the effect of

<sup>3</sup> N. S. Bayliss, *J. Chem. Phys.* **18**, 292 (1950).

<sup>4</sup> Y. Ooshika, *J. Phys. Soc. Japan* **9**, 594 (1954).

<sup>5</sup> H. C. Longuet-Higgins, *Molecular Quantum Mechanics Conference Abstracts*, University of Texas (1955).

<sup>1</sup> H. M. McConnell, *J. Chem. Phys.* **20**, 700 (1952).

<sup>2</sup> H. Margenau, *Phys. Rev.* **82**, 156 (1951).