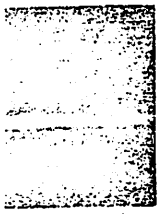

FIG. 7. Image of the explosion process of a 4-cm, 5-mil gold filament.

FIG. 6(d). Explosion of gold wire. The spikes represent trajectories of vaporized segments of the wire ejected from the region of the explosion.

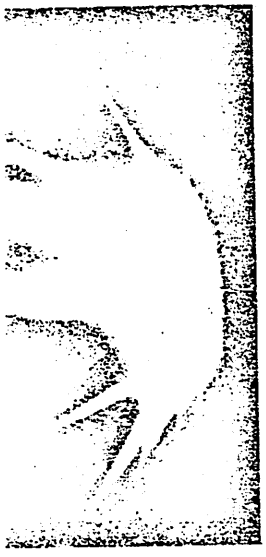

FIG. 6(c). Explosion of a 5-mil gold wire image process, by the sensitization method.

APPLICATION OF THE EXPLODING WIRE TECHNIQUE IN PHOTOCHEMISTRY*

R. A. Marcus

Polytechnic Institute of Brooklyn, Brooklyn, New York

The study of photochemical reactions through the use of an extremely intense light flash is one of considerable interest. In its most important type of application, spectroscopic observation of many short-lived species has become possible. Flash lamps have been employed for this purpose. In a second type of application, for which both flash lamps and exploding wires have been used, the stable chemical reaction products are measured. Here, the free radicals are produced in such high concentration that they tend to combine with each other rather than undergo complicating secondary reactions. This behavior should ultimately permit a more direct correlation between the reaction products and the initial photochemical processes than is possible for low light intensities.

The reproducibility of the light output, the characteristics of the emitted spectrum, the duration of the light flash, its intensity and variation, and the geometrical arrangement are all factors important to the applications of the exploding wire to photochemistry and to any comparison of the relative merits of flash lamps and wires. These features are discussed in this paper and illustrations are given from studies performed in the author's laboratory on the flash photolysis of acetone.

* This research was supported in part (1956-1959) by the U.S. Air Force under Contract No. AF 33(616)3887, monitored by WCRRC, Aeronautical Research Laboratory, Wright Air Development Center.

INTRODUCTION

Photochemistry primarily involves shining light on molecules which can absorb it and measuring the chemical reaction products formed in the process. By making such measurements—while varying the following conditions: light intensities, concentrations of the absorbing gas or of substance in solution, amounts of added compounds, and temperatures of the reaction system—it has been possible to learn much about the nature and reactions of the unstable species formed as intermediates in the process, particularly the free radicals [1]. Information has also been deduced about the initial photochemical processes. The free radicals themselves are of interest partly because they play a similarly important role in many chemical reactions and industrial processes.

About ten years ago, photochemistry received a considerable impetus through the introduction of flash lamps into this field [2]. Extremely high instantaneous free radical concentrations were produced because of the high light intensities. It became possible actually to observe these free radicals spectroscopically, most of them for the first time. Their chemical behavior could be studied also by spectroscopically measuring their rate of disappearance under various conditions.

The flash technique was used also simply as a means of producing a photochemical reaction at extreme light intensities and measuring the reaction products at various experimental conditions. Because of their unusually high instantaneous concentration, these species tended to combine with each other to form stable products, rather than to undergo the many other competitive types of chemical reactions found in low light intensity systems. It is anticipated, therefore, that a study of the reaction products will reveal the free radicals (and electronically excited molecules) formed in the initial photochemical processes more directly and unambiguously than is possible at low intensities.

In this chapter, desirable photochemical characteristics of flash sources are described and illustrated with exploding wire photochemical studies performed by Slagg [3] and by Oster [4, 5] in the author's laboratory.

ON

shining light on molecules
chemical reaction products
such measurements—while
intensities, concentrations
n solution, amounts of added
reaction system—it has been
nature and reactions of the
iates in the process, partic-
ation has also been deduced
ocesses. The free radicals
cause they play a similarly
ions and industrial processes.

try received a considerable
lash lamps into this field [2].
radical concentrations were
tensities. It became possible
cals spectroscopically, most
chemical behavior could be
measuring their rate of dis-

also simply as a means of
at extreme light intensities
cts at various experimental
ally high instantaneous con-
combine with each other to
to undergo the many other
ns found in low light intensity
, that a study of the reaction
ls (and electronically excited
otochemical processes more
possible at low intensities.

ochemical characteristics of
lustrated with exploding wire
Slagg [3] and by Oster [4, 5]

DESIRED PHOTOCHEMICAL CHARACTERISTICS IN A FLASH SOURCE

Reproducibility

The reproducibility of the light output per flash is naturally a necessity in photochemical work. In the exploding wire source and geometry used by us and described later, this reproducibility was excellent, being about several percent when averaged over a few flashes [4].

Spectral Output

The chemical fate of a molecule which has absorbed light depends on the wavelength of the light absorbed. In our work, light filters were used to select various portions of the spectrum emitted by the wire [3]. Data on the spectral output of these exploding wire sources, for various wires and conditions of flash, would be of considerable help, however, in selecting the best wire for the given wavelength region. Because of the small amount of reaction products formed per flash and the desirability of avoiding many flashes, this information assumes a special importance.

One spectral region which has been of increasing interest to photochemists is the far ultraviolet region at wavelengths in the range of 1000 to 2000 A [6]. Many chemical compounds absorb light only in this region. Flash lamps constructed of sapphire, which is transparent to this radiation, have been made [7]. They have had only a limited success, however, because of their instability. An exploding wire does not suffer from this defect and may be a rather promising source for this far ultraviolet spectral region.

Duration of Light Flash

For spectroscopically observing the more reactive free radicals, an intense light flash of very short duration is naturally appropriate. For example, an energy input of the order of 1000 joules and a duration of light of perhaps 10 μsec is suitable.

On the other hand, a long flash time is frequently desired (say, 300 μsec or more) when the reaction mechanism is to be deduced instead from measurements of the stable reaction products. The differential equations for the time dependence of the free radical concentrations become considerably simplified when the duration of the light is much longer than the lifetimes of the free radicals present. A steady state for their concentrations is then achieved and the quantitative interpretation of the data becomes easier.

Light Intensity

The source used in the present studies [3—5] had an input of 1000 joules and was sufficiently intense so that only several light flashes were needed to obtain measurable reaction products when unfiltered light was employed. When light filters were used, a source of perhaps ten- or even twenty-five-fold intensity would have been preferable. A chemical measurement [4] made of the efficiency of production of the unfiltered light output in a portion of the ultraviolet (2000 to 3300 A) indicated it to be of the order of 10%.

Geometrical Arrangement

The light intensity is an important photochemical variable (it controls the free radical concentration), and it is desirable that the intensity be variable in a known manner. Using chemical methods, we found it to be proportional to the square of the applied voltage [4]. However, to ensure a constancy of the spectral output, the light intensity was varied (in our experiments described later) by varying the distance between the exploding wire and the reaction vessel. A particularly convenient geometrical arrangement was one having cylindrical symmetry. A long thin wire was placed external but parallel to a cylindrical reaction vessel. The light intensity averaged over this vessel was found by chemical methods to be inversely proportional to the distance between the axis of the vessel and the wire except at small distances [3, 4]. The wire behaved, therefore, as a line source.

In other types of ex
much light as possible
aperture and where a
the intensity is not nee
is preferable. A short w
lens system. An advan
smaller reaction vesse
flashed compound per
interferes with the ph
products (as it can do in g
an appreciable percent
in this way with fewer fl

In future possible ap
the flashed species by el
be best to concentrate
aperture in the microwa
ment would be appropria

Compa

The exploding wire
lamps in spectral outp
its adaptability to differ
easy manner in which i
quantitative fashion. On
are needed to obtain
source is not convenient.
wire tends to deposit on
cleaned with acid from ti
however, through use of
the case of short wires, a

EXAMPLE OF A

As an example of so
we shall examine a po
reaction and some of t
an exploding wire [3—5].

.me is frequently desired
ıction mechanism is to be
.e stable reaction products.
e dependence of the free
rably simplified when the
than the lifetimes of the
for their concentrations
interpretation of the data

y

studies [3–5] had an input
ntense so that only several
easurable reaction products
/hen light filters were used,
ıty-five-fold intensity would
easurement [4] made of the
red light output in a portion
ıdicated it to be of the order

ıgement

tant photochemical variable
ntration), and it is desirable
nown manner. Using chemical
al to the square of the applied
ıstancy of the spectral output,
experiments described later)
xploding wire and the reaction
geometrical arrangement was
A long thin wire was placed
cal reaction vessel. The light
vas found by chemical methods
e distance between the axis of
mall distances [3, 4]. The wire

In other types of experiments where it is desired to admit as much light as possible into a small reaction vessel or into an aperture and where a simple method of quantitatively varying the intensity is not needed, a different geometrical arrangement is preferable. A short wire can be placed at the focus of a suitable lens system. An advantage of "concentrating" the light into a smaller reaction vessel is that the percent conversion of the flashed compound per flash is increased. When this compound interferes with the physicochemical analysis for the reaction products (as it can do in gas chromatography or mass spectrometry), an appreciable percent conversion is desired and is achieved in this way with fewer flashes.

In future possible applications such as a possible detection of the flashed species by electron spin resonance techniques, it would be best to concentrate as much light as possible into a small aperture in the microwave cavity, and this geometrical arrangement would be appropriate.

Comparison with Flash Lamps

The exploding wire may have certain advantages over flash lamps in spectral output, particularly in the far ultraviolet, in its adaptability to different geometrical arrangements, and in the easy manner in which its intensity can be varied in a predictably quantitative fashion. On the other hand, when numerous flashes are needed to obtain measurable reaction products, the wire source is not convenient. Again, the vaporized metal of the exploding wire tends to deposit on the reaction vessel, which then must be cleaned with acid from time to time. This effect can be minimized, however, through use of the self-generated magnetic field or, in the case of short wires, an applied one.

EXAMPLE OF A PHOTOCHEMICAL APPLICATION

As an example of some of the considerations just discussed, we shall examine a postulated mechanism of a photochemical reaction and some of the evidence obtained for it by the use of an exploding wire [3–5].

The source used in the present work consisted of a bank of condensers, 30 μf capacity, charged to 8 kv and discharged through a 12-in. length of Nichrome wire (BS 40). A slightly longer quartz cylindrical reaction vessel of 1 in. diam was placed parallel to, and close to, the wire. The duration of the light flash was determined with the aid of a phototube and scope to be about 300 μsec.

Acetone was the gas selected for the study since it had been intensively investigated at low light intensities and its photochemistry showed a number of interesting features [1].

Our experimental results suggest that an acetone molecule, $(CH_3)_2CO$, decomposes in at least two ways upon absorption of light. (A third possible way leading ultimately to a minor product, methane, is omitted for simplicity.)

$$(CH_3)_2CO + \text{light} \rightarrow 2\,CH_3 + CO \qquad (1)$$

$$(CH_3)_2CO + \text{light} \rightarrow (CH_3)_2CO^* \rightarrow CH_3CO + CH_3 \qquad (2)$$

$$(CH_3)_2CO^* \xrightarrow{M} (CH_3)_2CO \qquad (3)$$

The first path (1) involves the production of two methyl radicals (CH_3) and a stable reaction product, carbon monoxide (CO), while the second involves the production of a high-energy (electronically excited) acetone molecule. This molecule, indicated in (2) by the asterisk, could then either decompose into one acetyl radical (CH_3CO) and a methyl radical, or instead lose its excess energy upon collision with any other molecule M, such as acetone, to yield the ordinary acetone molecule. The free radicals combine to yield stable products: ethane (C_2H_6, resulting from the combination of two CH_3's), biacetyl ($CH_3CO\ COCH_3$, arising from two CH_3CO's), and acetone (arising from a CH_3CO and CH_3 combination).

According to reaction (1), the carbon monoxide formed should be directly proportional to the amount of absorbed light. This quantity, in turn, is proportional to the incident light intensity and, at the acetone pressures used, to the acetone pressure. These observations were tested and confirmed experimentally.

Again, according to
(and therefore the et
intensity but less than
molecules since the la
molecules by process
methyl radicals in rea
experimentally.

Measurements were
reaction temperature
acetone and deuterate
information.

The effect of wavele
fates of an acetone mol
should depend on the
that is, upon the wavel
C_2H_6 should depend on
various chemical solutic
with the reaction vesse
and was found to be co
opposite sense of that
and suggests that the m
is indicated by the simpl
the gap between low
investigate this point.

Experiments were al
oxygen. The reactions c
of considerable current
work performed at low
disentangle this reactior
ically excited molecules
produced in flash syster
each other rather than re
is fairly high. Thus, we
between these two oxyg
acetone molecules occur
the other involving free

rk consisted of a bank of
:v and discharged through
. A slightly longer quartz
n was placed parallel to,
ight flash was determined
: about 300 μsec.

ıe study since it had been
ıtensities and its photo-
g features [1].

:hat an acetone molecule,
ways upon absorption of
nately to a minor product,

(1)

→ $CH_3CO + CH_3$ (2)

$(CH_3)_2CO$ (3)

:ion of two methyl radicals
arbon monoxide (CO), while
high-energy (electronically
:ule, indicated in (2) by the
ıe into one acetyl radical
tead lose its excess energy
ule M, such as acetone, to
The free radicals combine
$_6$, resulting from the com-
:O $COCH_3$, arising from two
CH_3CO and CH_3 combination).

bon monoxide formed should
unt of absorbed light. This
the incident light intensity
the acetone pressure. These
d experimentally.

Again, according to this sequence, the number of methyl radicals (and therefore the ethane) should be proportional to the light intensity but less than proportional to the concentration of acetone molecules since the latter also deactivate the energetic acetone molecules by process (3), thereby reducing their tendency to form methyl radicals in reaction (2). This behavior was also confirmed experimentally.

Measurements were also made of the slight effect of the initial reaction temperature on the products as well as of mixtures of acetone and deuterated acetone to obtain further mechanistic information.

The effect of wavelength is of particular interest. The relative fates of an acetone molecule which has absorbed light, (1) and (2), should depend on the energy of the quantum of light absorbed, that is, upon the wavelength. Correspondingly, the ratio of CO to C_2H_6 should depend on wavelength. By using filters consisting of various chemical solutions placed in a cylindrical vessel concentric with the reaction vessel, this effect was studied experimentally and was found to be considerable. However, the trend was in the opposite sense of that observed in low light intensity experiments and suggests that the mechanism may be more complicated than is indicated by the simple sequence (1) to (3). Experiments bridging the gap between low and high light intensities are planned to investigate this point.

Experiments were also performed to study the effect of added oxygen. The reactions of free radicals with oxygen are a subject of considerable current chemical interest, but in photochemical work performed at low light intensities it has been difficult to disentangle this reaction from that between oxygen and electronically excited molecules. At the extremely high light intensities produced in flash systems, the radicals will tend to combine with each other rather than react with oxygen unless the oxygen pressure is fairly high. Thus, we felt that it might be possible to distinguish between these two oxygen reactions, the one involving excited acetone molecules occurring at both low and high oxygen pressures, the other involving free radicals occurring only at high pressures.

Experimental measurements were made with an exploding wire source of the effect of oxygen pressure in the reaction vessel on the amounts of ethane, carbon monoxide, and additional oxygenated products formed. Our results do indeed indicate two distinct oxygen pressure regions of chemical behavior. Further experiments in which the effect of light intensity is being studied are in progress to determine whether one of these regions does indeed correspond to the reaction of an excited molecule with oxygen. The general study of such unusual types of reactions is at present in its infancy. Further work is planned using molecules other than oxygen.

REFERENCES

1. E.g., E. W. R. Steacie, Atomic and Free Radical Reactions (Reinhold Publishing Company, New York, 1954).
2. R. G. W. Norrish and G. Porter, Nature 164, 658 (1949); cf. R. G. Norrish and B. A. Thrush, Quart. Revs. (London) 10, 149 (1956).
3. N. Slagg and R. A. Marcus (unpublished results), presented in part at the 132nd National Meeting of the American Chemical Society, New York City (1957); cf. R. A. Marcus, Can. J. Chem. 36, 102 (1958).
4. G. K. Oster and R. A. Marcus, J. Chem. Phys. 27, 189 (1957).
5. G. K. Oster and R. A. Marcus, J. Chem. Phys. 27, 472 (1957).
6. Cf. H. A. Taylor, Ann. N. Y. Acad. Sci. 67, 477 (1957).
7. L. S. Nelson and D. A. Ramsay, J. Chem. Phys. 25, 372 (1957).

A RELIABLE
WI

Explosive Res

This chapter de
three-channel wi
features as abilit
time delays of fro
of energy levels a
inductance circui
thorough shieldin
circuits from po
graphic measurem
gering in pulse-se

In the experimental
need for a reliable multi
controlled time delays
used for a number of d
with a series of high-sp
was a highly desired at
been used both for deto
placed upon its construc
for both purposes. In con
a series of *a priori* req

1. The ability to de
high energy pulses, in mi
energy losses.