QUARTERLY REVIEWS

FLASH PHOTOLYSIS AND KINETIC SPECTROSCOPY

By R. G. W. Norrish, Sc.D., F.R.I.C., F.R.S.,
and B. A. Thrush, M.A., Ph.D.
(Department of Physical Chemistry, The University, Cambridge)

The recognition of the importance of short-lived intermediates such as atoms and free radicals in many chemical reactions and photochemical processes has done much to stimulate interest in rapid reactions where detectable quantities of these species are present and their reactions can be studied directly. In this type of work two main problems arise, those of initiation and of observation. The reaction must be started so homogeneously that the chemical processes themselves and not their propagation through space are rate-determining. For certain reactions this can be achieved by rapid mixing, or by adiabatic compression, including the use of shock waves.

Flow systems are generally more useful than static systems where the time of mixing is the limiting factor. This limit is much more serious for gases [1] where it is more difficult to obtain adequate turbulent mixing than for liquids where reaction times as short as one millisecond can be observed.[2]

Among the methods used for premixed systems, those in which reaction is initiated by contact with a heated surface are seriously limited by the incidence of heterogeneous processes and of the temperature gradient which must always be present. The Paneth mirror technique [3] is one of the most interesting systems of this type. Adiabatic compression [4] has been used to obtain rapid homogeneous heating, but this method unfortunately has been applied mainly to combustion reactions which are so rapid as to require a higher rate of production of reaction centres than can be realised by this method, resulting in an insufficiently homogeneous system. Direct mechanical compression is now being superseded as a technique by the use of shock waves [5] and their corollary in combustion–detonation waves.[6] In these systems considerable temperature rises can occur in times as short as 10^{-8} sec., but difficulties arise in observing processes occurring in a rapidly

---

[1] Johnston, *Discuss. Faraday Soc.*, 1954, **17,** 14.

[2] Hartridge and Roughton, *Proc. Roy. Soc.*, 1923, *A*, **104,** 376.

[3] Paneth, *Ber.*, 1929, **62,** 1335.

[4] Jost, " Third Symposium on Combustion ", Williams and Wilkins, Baltimore, 1949, p. 424.

[5] Greene, *J. Amer. Chem. Soc.*, 1954, **76,** 2127.

[6] Berets, Greene, and Kistiakowsky, *ibid.*, 1950, **72,** 1080.

moving wave-front, and there is uncertainty about the rate of transfer of energy from translation to other degrees of freedom.

Spectroscopic methods, where practicable, are the best for following rapid reactions. The use of a thermocouple,[7] resistance thermometer, or interferometer [8] to follow reactions is restricted to relatively simple systems, and the mass-spectrometer [9, 10] appears to provide the best alternative to optical spectroscopy. Although this method is very sensitive, sampling of the system without serious disturbance of the reaction presents a considerable problem. Also the need to prevent further reaction in the time between sampling and ionisation limits the beam current and hence the time resolution. Great strides are, however, being made at present to overcome these difficulties.

The development of the high-intensity flash-discharge lamp was due in the first instance to Edgerton and his co-workers [11] who worked with energies of up to 400 J per flash. Photochemical systems require much higher energies, and lamps capable of dissipating 10,000 J corresponding to about 3×10^{-3} einsteins of ultraviolet light were made by Norrish and Porter [12, 13] who first applied these tubes to chemical systems. These high light intensities make it possible to obtain appreciable photochemical changes in times which are comparable with the lives of the radicals or excited molecules formed. Part of the light absorbed will appear as kinetic energy of the photolysis products, as will the heat liberated by radical reactions or degraded from excited molecules in collisions. Reactions in solution are sufficiently isothermal owing to the thermal capacity of the solvent, but in the gas phase a large excess of an inert non-absorbing gas must be added if it is desirable to maintain approximately isothermal conditions. On the other hand this temperature rise provides a useful method of initiating explosions homogeneously over a relatively large volume.

The flash discharge also provides an excellent method of following fast reactions, as it can be used as a source to photograph the absorption spectrum of the system with high dispersion in a very short time. Absorption spectroscopy is probably the most satisfactory method of following these reactions, since, while it does not disturb the system, it provides a measure of the concentration of the species observed. Its value is, however, limited, as many important reaction intermediates, particularly atoms of the non-metallic elements, do not absorb in the accessible region of the spectrum (2200—7000 Å) or have unidentifiable continuous spectra ; fortunately most diatomic radicals and aromatic species have strong and characteristic electronic transitions in this range. Of the other regions of the spectrum, the vacuum-ultraviolet is rendered very difficult experimentally by the strong continuous absorption which many species show in this region. In

---

[7] Garvin, Guinn, and Kistiakowsky, *Discuss. Faraday Soc.*, 1954, **17**, 32.

[8] Burnett, Deas, and Melville, *ibid.*, p. 173.

[9] Eltenton, *J. Chem. Phys.*, 1942, **10**, 403.

[10] Ingold and Lossing, *ibid.*, 1953, **21**, 368.

[11] Murphy and Edgerton, *J. Appl. Phys.*, 1941, **12** 848.

[12] Norrish and Porter, *Nature*, 1949, **164**, 658.

[13] Porter, *Proc. Roy. Soc.*, 1950, *A*, **200**, 284.

the infrared, the main limitations are the absence of intense light sources and the poor response time of most detectors.

Emission spectra, since they are determined by the populations of upper electronic states, can only be observed in high-temperature systems and, because they are frequently affected by anomalous excitation conditions, the use of light emission as a measure of the concentration of the emitter is limited.

Experimental Methods

Whilst the exact form of apparatus used in flash-photolysis experiments depends to a large extent on the nature of the problem, an arrangement similar to that shown in Fig. 1 has been used in most cases, either for the entire problem, or in a preliminary search for the spectra present.[13, 14]

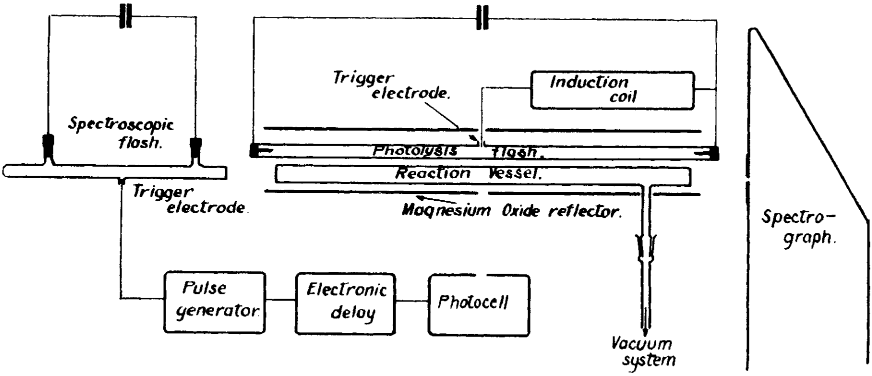


FIG. 1

Typical flash-photolysis apparatus.

The reactants are placed in a cylindrical quartz vessel normally 50 cm. long and 2 cm. in diameter. The photolytic flash tube is placed alongside the reaction vessel on to which the light is concentrated by a cylindrical reflector coated with magnesium oxide. This flash lamp is a krypton-filled quartz tube having the same length as the reaction vessel ; the main discharge occurs between heavy tungsten electrodes placed at the ends and connected to a bank of condensers. After the condensers have been charged to the required voltage, the discharge is initiated by applying a triggering pulse to a small central electrode. Alternatively the trigger pulse can be applied to a spark-gap in series with the flash tube ; in this case no voltage is applied to the lamp until it is triggered, thus making it possible to operate at high voltages with low filling pressures. In these circumstances the flash duration is reduced at the expense of luminous efficiency.

A lower-energy flash lamp of different shape but basically similar design is used to photograph the absorption spectrum of the system through the full length of the reaction vessel. This lamp is triggered between 10^{-5} and 1 sec. after the photolytic flash by an electronic timer which is initiated

---

[14] Norrish, Porter, and Thrush, *Proc. Roy. Soc.*, 1953, *A*, **216**, 165.

photoelectrically by the light from this flash. The performances of typical flash-discharge lamps are summarised in Table 1.

TABLE 1

Type	Length (cm.)	Capacity (μF)	Voltage (kV)	Energy (J)	Effective duration (μsec.)
Photolytic	50	30	6	540	70
,, ...	50	40	10	2000	120
,, ...	100	480	4	3840	2000
Spectroscopic (Hilger E.1 instrument)	30	25	4	200	50
Spectroscopic (Hilger E.3 instrument)	15	10	10	500	30*

* Used with spark gap.

With an apparatus of the type described above it is necessary to perform a separate experiment for each point on a radical-concentration–time curve. As an alternative, photomultiplier cells recording on a cathode-ray oscillograph have been used in some cases to follow the change of light emission or absorption with time. For combustion work, a high-pressure xenon arc has been used as background source, and this light is observed by two photomultiplier cells which are mounted in place of the spectrograph plateholder.[15] In this way, it has been possible to follow concentration changes and measure electronic excitation temperatures with a time resolution of 2 μsec. on the more intense spectra.

For the study of recombination of iodine atoms a very simple photoelectric apparatus has been used.[16] In this case, a tungsten-filament bulb used in conjunction with a liquid filter and a photomultiplier cell was sufficient to monitor the I_2 absorption from which the iodine-atom concentration could be deduced. Though the iodine absorbed only about 10% of the monitoring light, it was possible to measure its concentration to better than 1%. If a photographic technique had been used, the reproducibility of the plates would probably have been insufficient to show even the continuous I_2 absorption. In this case, a spiral flash tube is coiled round the reaction vessel to give a high light intensity, and a filter is used to remove the light which would be absorbed by the iodine without producing dissociation.

Radical-concentration Measurements.—Whilst the actual observation and identification of the transient absorption spectra of atoms or free radicals in many systems is of interest in itself, and these spectra have in some cases yielded valuable information about the structure of the radicals concerned, it is important from a kinetic viewpoint to obtain values for the absolute concentrations of the species present, or failing this, to find a sound

---

[15] Norrish, Porter, and Thrush, " Fifth Symposium on Combustion ", Reinhold, New York, 1955, p. 651.

[16] Christie, Norrish, and Porter, *Proc. Roy. Soc.*, 1953, *A*, **216**, 152.

method of comparing the relative amounts of a radical present under different conditions. If we wish to obtain the absolute concentration of a free radical, it is necessary to know the identity of all the species present, and to have sufficient information to obtain a material balance. So far this has only been possible with ClO and the aromatic triplets, although an upper limit can be set to the concentration of particular radicals in other systems. In the work on the recombination of iodine atoms, their concentration was inferred from the amount of iodine decomposed. If the absolute concentration of the radical cannot be determined, it is in theory possible to compare concentrations under different conditions, since the number of absorbing molecules is proportional to the integral of the extinction coefficient with respect to frequency over the whole of the band system used. For a completely diffuse spectrum, this integral can easily be determined, but the range of temperature is usually sufficiently limited for the extinction coefficient at one wavelength to be an adequate measure of concentration. For discrete spectra, very high resolution, which is not available in flash experiments, is needed to determine the true line contour and hence this integral. Under the conditions of constant temperature and pressure, the apparent intensity of any spectral line will be determined only by the number of molecules in the absorbing path. In many of the systems studied, even to a large extent in explosions, the radical concentrations change very much more rapidly than the pressure or temperature, and it can be assumed that, if the same apparent intensity is observed in the same system at different times by using path lengths in the ratio 2 : 1, the concentrations at these times will be in the ratio 1 : 2. By this means,[14] it is possible to measure half-lives and establish a relative concentration scale without knowing the absolute concentration at any point. Unfortunately, pressure broadening prevents comparison of amounts of the species present at different total pressures, as for example in the work described below on excited oxygen.

Free Radicals and Excited Molecules

Several completely new radical spectra have been obtained by flash photolysis ; in other cases spectra have been observed in absorption for the first time, or obtained with much greater intensity, thus yielding new information about molecular structure and stability.

Though it is generally believed that the " hydrocarbon flame bands " are due to the HCO radical, this cannot be regarded as proved, and the discovery by Ramsay [17] of bands at longer wavelengths due to this radical in the flash photolysis of aldehydes is of great interest. By analysis of these bands [18] the structure of this radical has been determined, showing that it has a bent lower and a linear upper state. Other spectra of polyatomic species which have been obtained for the first time by flash photolysis are those ascribed to HS_2[19] and N_3[20] as well as many spectra of aromatic radicals

[17] Ramsay, *J. Chem. Phys.*, 1953, **21**, 960.

[18] Herzberg and Ramsay, *Proc. Roy. Soc.*, 1955, *A*, **233**, 34.

[19] Porter, *Discuss. Faraday Soc.*, 1950, **9**, 60.

[20] Thrush, *Proc. Roy. Soc.*, 1956, **235**, 143.

and triplet states, which are discussed in a later section. The absorption spectra of C_3[21] and NH_2[22] were also first observed by this technique.

Flash photolysis provides an easy method of observing many diatomic-radical spectra in absorption. Of these Porter [13] obtained the absorption spectrum of ClO for the first time and was thus able to determine its dissociation energy and vibration frequencies. He was also able to determine the vibration frequencies of SH and SD.[19] Other diatomic-radical spectra obtained in absorption for the first time or much more strongly include those of C^2, CH, CN,[14] CS,[13] and SO. The first named is of some interest, as both the Mulliken and Swan bands which arise from the lowest singlet ($^1\Sigma_g{}^+$) and lowest triplet ($^3\Pi_u$) states have been obtained in absorption by explosions and it cannot be regarded as certain whether C_2 has a singlet or a triplet ground state; at present, evidence appears to favour the former, although the two states clearly have closely similar energies.

The ClO Radical.—The ClO radical has probably been studied in more detail by flash photolysis than any other species. Its spectrum was first detected in emission from flames containing chlorine by Pannetier and Gaydon [23] and it was obtained in absorption by Porter [13] who determined its dissociation energy and with Wright [24] studied the mechanism of formation and removal of this radical in systems containing small amounts of chlorine, and rendered isothermal by a great excess of oxygen and sometimes nitrogen. In these experiments the primary photochemical act is clearly to produce chlorine atoms, but the reaction

$$Cl + O_2 = ClO + O \quad . \quad . \quad . \quad . \quad (1)$$

is far too endothermic to occur. The ClO formation must therefore proceed in the following way:

$$Cl + O_2 = Cl\text{–}O\text{–}O \quad . \quad . \quad . \quad . \quad (2)$$

$$Cl\text{–}O\text{–}O + Cl = 2ClO \quad . \quad . \quad . \quad . \quad . \quad (3)$$

In this scheme, the ClO_2 formed is not conceived as the stable molecule of this formula, but a loosely bound intermediate, whose stability could be judged from experiments in which part of the oxygen was replaced by nitrogen; these showed that the formation of ClO by reactions (2) and (3) above was 46 times as fast as the recombination of chlorine atoms with nitrogen as the third body. It was also found that the amount of ClO formed was independent of temperature in the range 25—300°. The rate of removal of the ClO radical by reaction (4) was found by plate photometry

$$ClO + ClO = Cl_2 + O_2 \quad . \quad . \quad . \quad . \quad (4)$$

to be of the second order, constant over the same temperature range and independent of chlorine, oxygen, or nitrogen pressure. Porter and Wright were only able to obtain the rate constant of this reaction in terms of the unknown extinction coefficient of ClO, since the chlorine decomposition was not measurable. Fortunately ClO_2 is a much stronger absorber than

---

[21] Norrish, Porter, and Thrush, *Nature*, 1952, **169**, 582.

[22] Herzberg and Ramsay, *J. Chem. Phys.*, 1952, **20**, 347.

[23] Pannetier and Gaydon, *Nature*, 1948, **161**, 262.

[24] Porter and Wright, *Discuss. Faraday Soc.*, 1953, **14**, 23.

chlorine, and in excess of an inert gas it is almost completely converted into ClO and O_2 by the flash (Fig. 2), most of the ClO_3 formed being decomposed by the flash. By assuming that the amount of ClO formed was the difference between the ClO_2 decomposed and the ClO_3 formed, Lipscomb, Norrish, and Thrush [25] have obtained values for the extinction coefficient of ClO and the rate constant for its removal. In the absence of ClO_2, they found that ClO radicals reacted at approximately one collision in 7000, and the slopes of their graphs were in good agreement with those of Porter and Wright. There is an apparent inhibition of this reaction by ClO_2 which has been tentatively interpreted in terms of an equilibrium,

$$Cl_2O_3 = ClO + ClO_2 \quad . \quad . \quad . \quad . \quad (5)$$

The bimolecular ClO removal is unusual for a radical–radical reaction in having a very low frequency factor, Porter and Wright having found that it has no activation energy.

Excited Molecular States.—In the experiments with chlorine dioxide, Lipscomb, Norrish, and Thrush [25] observed the absorption spectra of oxygen molecules in the electronic ground state with up to eight quanta of vibrational energy immediately after flashing (Fig. 2). As they used between 300- and 2000-fold excess of nitrogen to eliminate the temperature rise, this provides clear evidence for the formation of vibrationally excited molecules in a chemical reaction. Oxygen molecules with a similar energy distribution are also formed in experiments with nitrogen dioxide diluted with a great excess of nitrogen, and it is thought that the oxygen is formed by the analogous reactions :

$$NO_2 + h\nu = NO + O \quad . \quad . \quad . \quad . \quad (6)$$

$$O + NO_2 = NO + O_2^* \quad . \quad . \quad . \quad . \quad (7)$$

$$ClO_2 + h\nu = ClO + O \quad . \quad . \quad . \quad . \quad (8)$$

$$O + ClO_2 = ClO + O_2^* \quad . \quad . \quad . \quad . \quad (9)$$

Reactions 7 and 9 are 46 and 61 kcal. exothermic respectively, and the vibrational-energy distribution of the oxygen formed is such that there are approximately equal numbers of molecules in the levels $v'' = 5$, 6, and 7, and many fewer with $v'' = 8$ which is the highest level observed and has an excitation energy of 33·6 kcal./mole. The formation of excited oxygen in these systems is of interest since they are almost the only cases where it can be shown that the energy liberated in a simple reaction shows considerable deviations from both the Maxwell–Boltzmann distribution law and equipartition, in that the oxygen vibration is receiving an unexpectedly high proportion of the energy liberated. Since O_2 has no electric dipole moment and this energy can consequently only be lost exceedingly slowly by radiation, measurement of the half-life of the vibrationally excited oxygen provides a new method of studying the degradation and transfer of vibrational energy in collisions ; it has the advantage over sound dispersion and fluorescence measurements that it is applicable to the higher vibrational levels of the ground state which are of particular interest in high-temperature reactions, especially combustion. In general, the measurements so far made

---

[25] Lipscomb, Norrish, and Thrush, *Proc. Roy. Soc.*, 1956, *A*, **233,** 45·5

confirm the work with sound dispersion, stressing the efficacy of resonant transfer to molecules with similar vibration frequencies and of removal by free radicals.

Aromatic Molecules.—In aromatic systems we have to consider the possibilities that the excited state will fluoresce, decompose, or undergo a radiationless conversion by collision to form a relatively long-lived phosphorescent state. In some cases, magnetic susceptibility measurements [26] have shown that these phosphorescent states of polynuclear aromatic molecules are triplets, and this nomenclature will be adopted for all long-lived excited states of such molecules, even where the susceptibilities have not been measured. Absorption spectra of triplet states have been observed by flash photolysis for a large number of polynuclear aromatic molecules in the gas phase by Porter and Wright,[27] in solution by Porter and Windsor,[28] and in rigid glasses by McClure and Hanst.[29] The radiationless conversion of the excited singlet state into a triplet occurs remarkably freely with almost all polynuclear aromatic compounds ; for instance, in dilute hexane solution for several hydrocarbons it approaches 50% with a flash of moderate energy. It is, however, probable with a substance like anthracene, which has a very high extinction coefficient and a short fluorescent life, that many of the molecules are raised to the excited singlet state more than once during the flash. The formation and decay of the triplet, together with the depletion and reappearance of the singlet state of anthracene in hexane, are shown in Fig. 3 ; in this case, the rate of disappearance of the triplet is of the first order and independent of the initial anthracene concentration over a wide range. In the absence of oxygen, the rate constant is about 12,000 sec.$^{-1}$ in *n*-hexane, and for a number of solvents of widely different character the first-order rate constants were found to be roughly inversely proportional to the square root of the viscosity ; in the more rigid solvents and glasses, however, the rate tends to the radiative phosphorescence value which is of the order of 10 sec.$^{-1}$. In the gas phase, the lives of the triplet states were too short to be measured with the apparatus used.

The mechanism of deactivation of the triplet state cannot be regarded as satisfactorily explained, and the viscosity relationship given above is probably fortuitous ; it does not fit any of the current theories of reactions in solution. It appears that this process is a radiationless transition which is inhibited by the intermolecular forces determining the viscosity of the solvent.

Aromatic Radicals.—In contrast to the polycyclic aromatic molecules which give triplet states, derivatives of benzene yield free radicals such as $C_6H_5\cdot CH_2\cdot$, $C_6H_5\cdot NH\cdot$, $C_6H_5\cdot O\cdot$, and $C_6H_5\cdot S\cdot$ on photolysis. These have been observed in the gas phase by Porter and Wright [30] and in solution by

---

[26] Lewis, Calvin, and Kasha, *J. Chem. Phys.*, 1949, **17**, 804 ; Evans, *Nature*, 1955, **176**, 777.

[27] Porter and Wright, *Trans. Faraday Soc.*, 1955, **51**, 1205.

[28] Porter and Windsor, *Discuss. Faraday Soc.*, 1954, **17**, 178.

[29] McClure and Hanst, *J. Chem. Phys.*, 1955, **23**, 1772.

[30] Porter and Wright, *Trans. Faraday Soc.*, 1955, **51**, 1469.

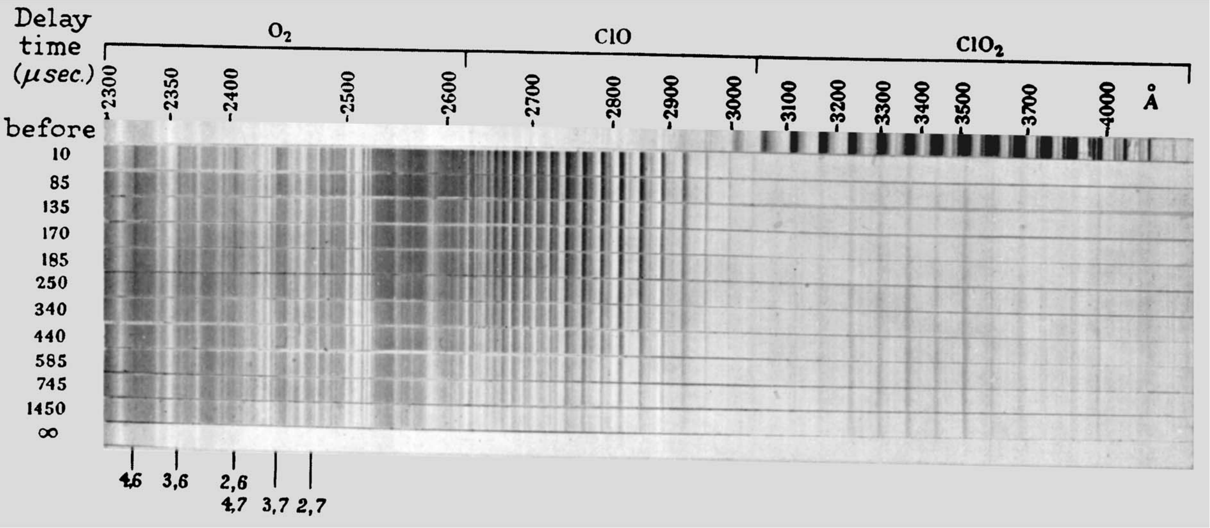


FIG. 2

Spectra of chlorine dioxide and its products of photolysis, showing formation and decay of ClO *and vibrationally excited oxygen.*

[Reproduced with modification, by permission, from *Proc. Roy. Soc.*, 1956, *A*, **233,** 457.]

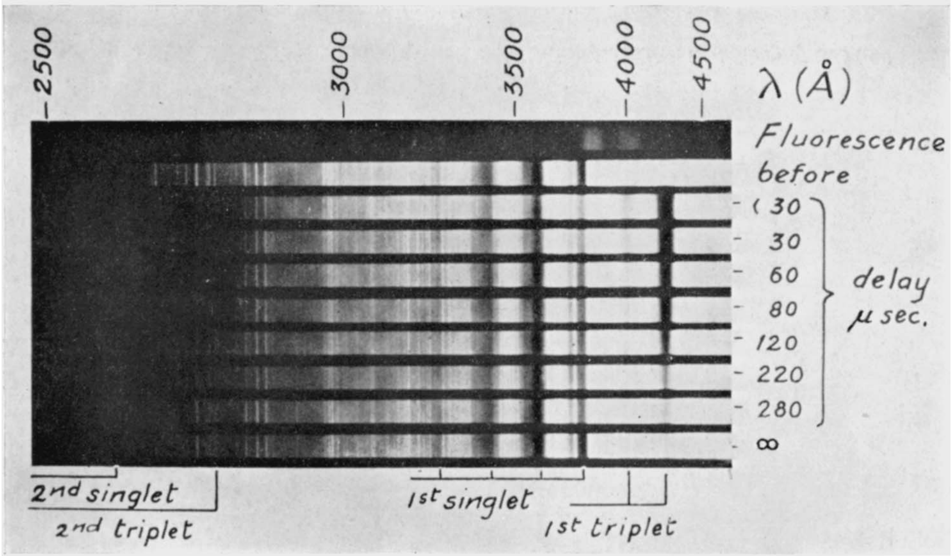


FIG. 3

Series of triplet spectra of anthracene in hexane.

[Reproduced, by permission, from *Discuss. Faraday Soc.*, 1954, **17,** 181.]

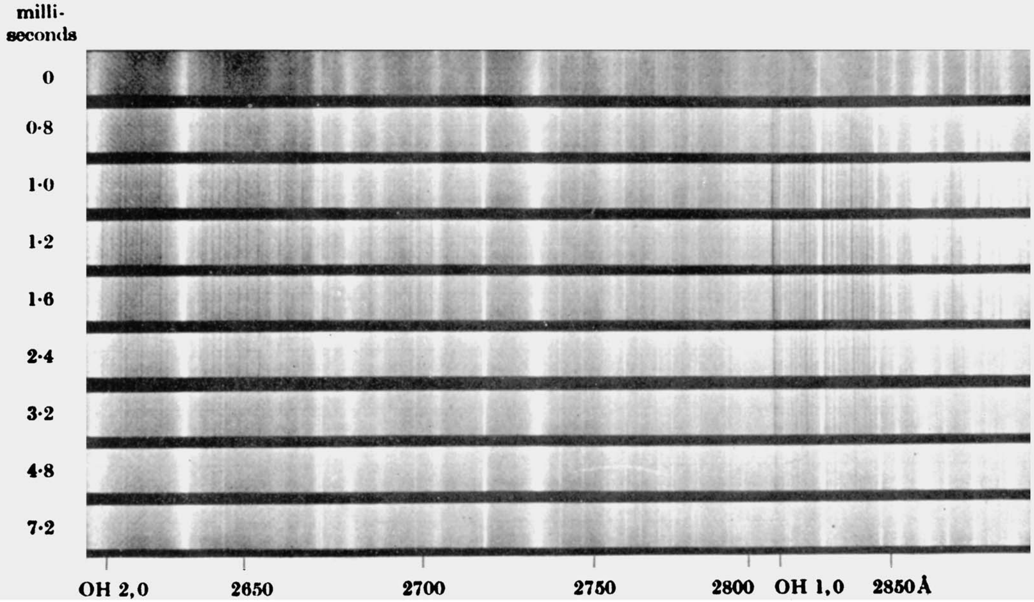


FIG. 7

Intensity of OH (1,0) *and* (2,0) *bands during course of explosion. Original mixture :* $P(\mathrm{H}_2) = 10$ *mm.* ; $P(\mathrm{O}_2) = 5$ *mm.* ; $P(\mathrm{NO}_2) = 0{\cdot}75$ *mm.*

[Reproduced, by permission, from *Proc. Roy. Soc.*, 1952, *A*, **210**, 447.]

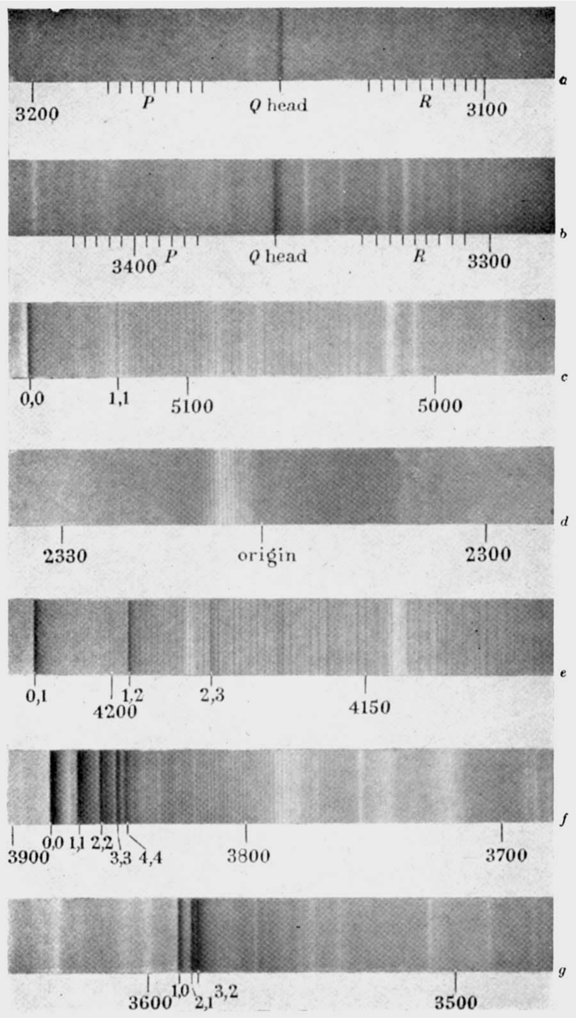
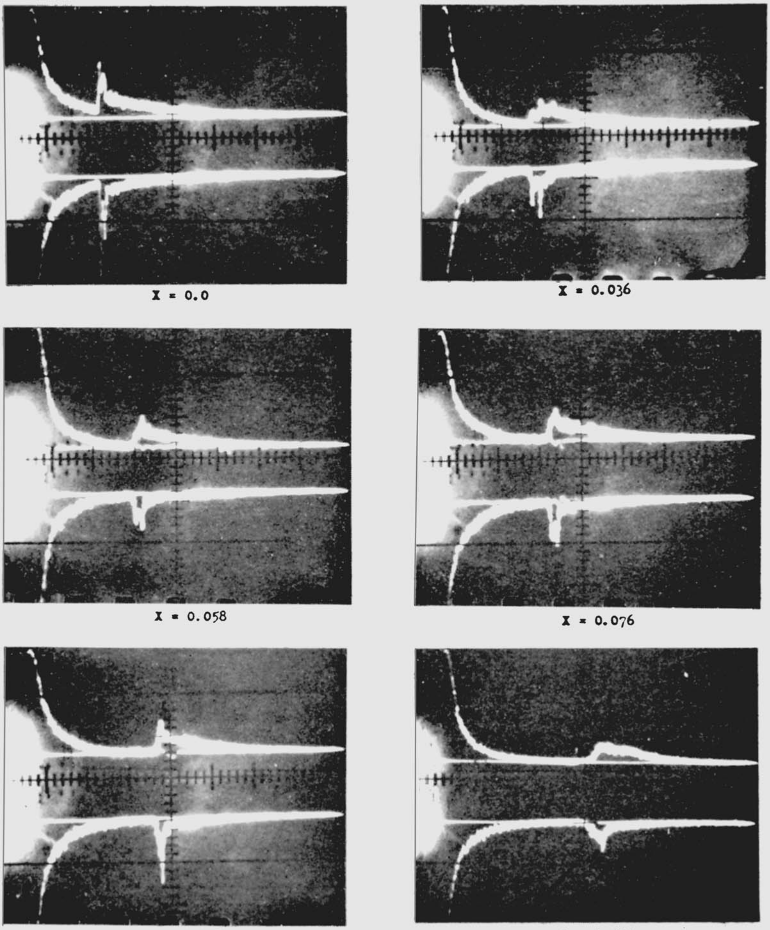


FIG. 8

Radical spectra in acetylene–oxygen–nitrogen dioxide explosions.

(*a*) CH ; (*b*) NH ; (*c*) C_2 " Swan " bands ; (*d*) C_2 " Mulliken " bands ; (*e*), (*f*), and (*g*) CN " violet " bands.

[Reproduced, by permission, from *Proc. Roy. Soc.*, 1953, *A*, **216** 182.]



X = 0.0

X = 0.036

X = 0.058

X = 0.076

X = 0.129

X = 0.185

FIG. 15

The effect of tetraethyl-lead on the induction period. 4 *mm.* $C_5H_{11}\cdot O\cdot NO$ + 3·3 *mm.* C_2H_2 + 15 *mm.* O_2 + x *mm.* $PbEt_4$. *Flash energy* 1000 J.

[Reproduced, by permission, from *Proc. Roy. Soc.*, 1956, *A*, **234,** 182.]

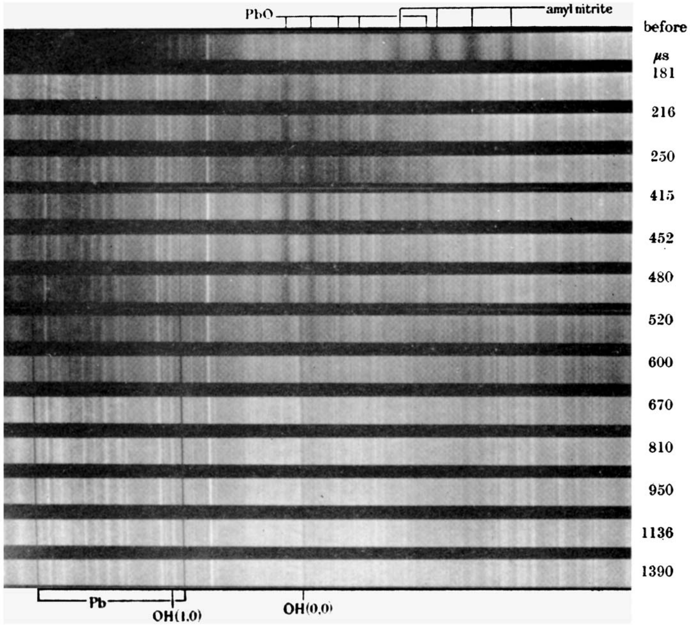


Fig. 16

Spectra v. time. 4 *mm.* C_5H_{11}·O·NO + 3·3 *mm.* C_2H_2 + 20 *mm.* O_2 + 0·17 *mm* $PbEt_4$. *Flash energy* 1000 J.

[Reproduced, by permission, from *Proc. Roy. Soc.*, 1956, *A*, **234,** 182.]

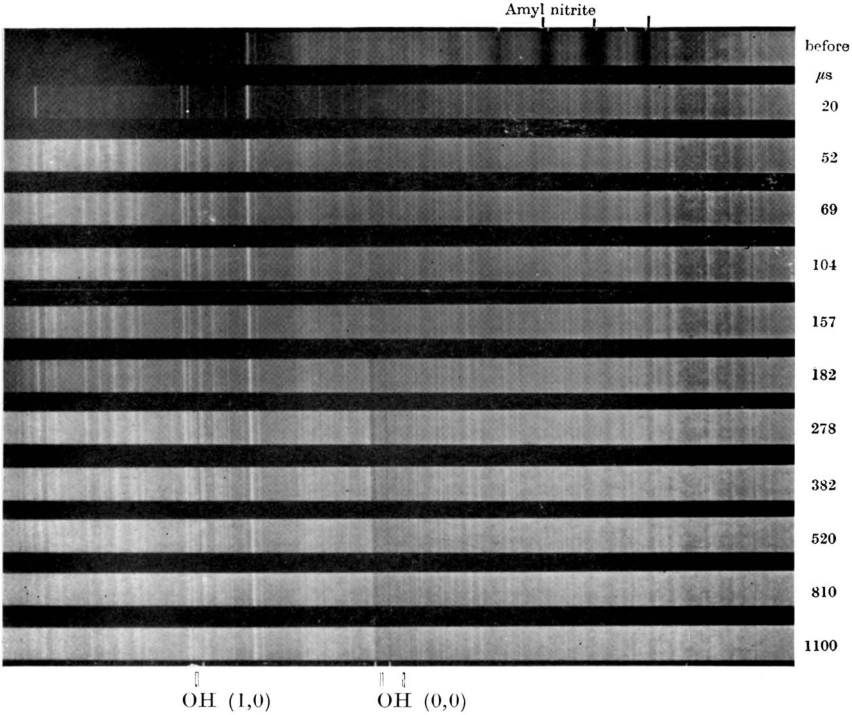


FIG. 17

Spectra v. time. 4 *mm.* $C_5H_{11}\cdot O\cdot NO$ + 3·3 *mm.* C_2H_2 + 20 *mm.* O_2. *Flash energy* 1000 J.

[Reproduced, by permission, from *Proc. Roy. Soc.*, 1956, *A*, **234**, 182.]

Porter and Windsor.[31] Their formation can be distinguished from that of a triplet state by several criteria : the same radical is produced by the photolysis of more than one substance, for instance the spectrum attributed to the benzyl radical is obtained from toluene, benzyl chloride, benzylamine, ethylbenzene, etc., but not from benzylidene chloride or benzotrichloride. Further, the compound photolysed shows a permanent decomposition, which does not usually occur if a triplet state is observed. In rigid media at low temperatures these radicals can be trapped almost indefinitely, whereas under these conditions triplet states show lives which are normally less than one second ; for this reason flash photolysis has not yet been used to study radicals in these systems. It is interesting that acetophenone, benzophenone, and 1-methylnaphthalene form triplet states rather than radicals.

Atomic Reactions

Flash photolysis has provided a very convenient method of studying the recombination of iodine atoms, and it has been used by several groups of workers [16, 32, 33, 34] to extend the measurements originally made with a steady-state system by Rabinowitch and his colleagues.[35] In all the more recent work similar techniques have been used, the concentration of iodine molecules being monitored by a photocell using a tungsten-filament lamp and a suitable filter. The photocell output is displayed on the Y-plate of a cathode-ray oscillograph which is triggered by the flash which decomposes the iodine. Dissociations of the order of 80% can readily be obtained although smaller values are normally used so as to limit the temperature rise. The recombination of the iodine atoms is measured by the reappearance of the iodine absorption. For the different inert gases, the rate of recombination was found to be proportional to the square of the iodine-atom concentration and to the inert-gas pressure. Typical bimolecular plots of the reciprocal of the iodine-atom pressure against time are shown in Fig. 4, and all the workers found that the second-order law was obeyed quite well over a ten-fold concentration range. The absolute rates determined by the various authors differed, however, by more than their estimated experimental errors and for this reason the reaction in the presence of the inert gases has been investigated over a very wide range of conditions by Christie, Harrison, Norrish, and Porter.[34] They examined all the possible sources of error and corrected for the concentration gradient in the reaction vessel ; this is due to the temperature gradient which is produced as the heat absorbed from the flash is removed by conduction. The apparent rate constant of the recombination increased linearly with the ratio of I_2 to inert-gas pressure (see Fig. 5), owing to the high efficiency of I_2 as a third body for the iodine atom recombination, the values of the rate constants being given in Table 2. These rates stress the stability of I_3 as an intermediate and, for the inert

---

[31] Porter and Windsor, unpublished work.

[32] Marshall and Davidson, *J. Chem. Phys.* 1953, **21**, 659.

[33] Russell and Simons, *Proc. Roy. Soc.*, 1953, *A*, **217**, 271.

[34] Christie, Harrison, Norrish, and Porter, *ibid.*, 1955, *A*, **231**, 446.

[35] Rabinowitch and Wood, *J. Chem. Phys.*, 1936, **4**, 497.

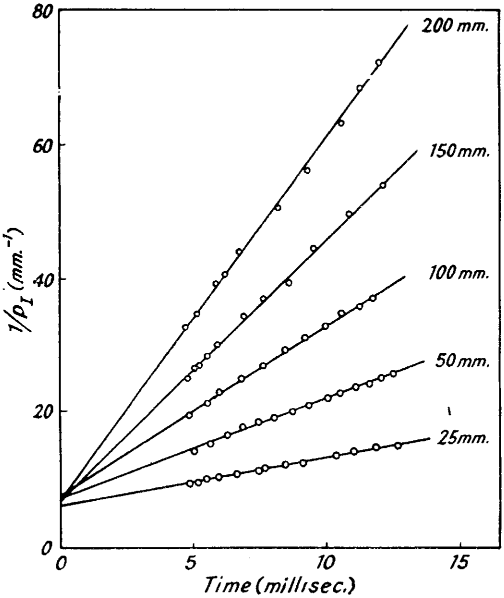


FIG. 4

Bimolecular plots of iodine recombination in argon.
[Reproduced, by permission, from *Proc. Roy. Soc.*, 1953, *A*, **216,** 158.]

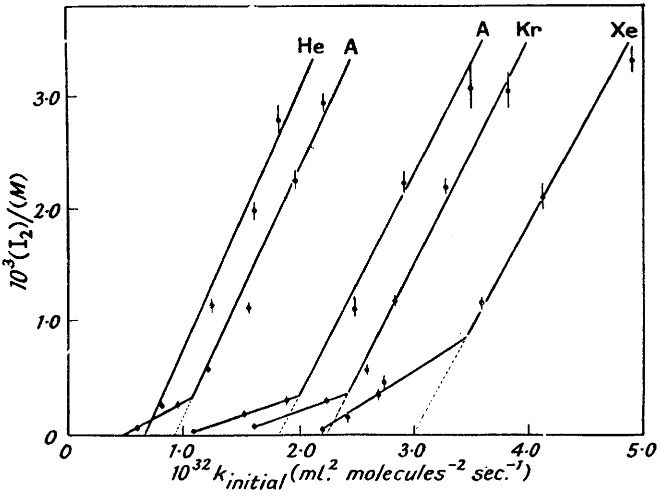


FIG. 5

Variation of iodine recombination rate constant with $[I_2]/[M]$.
[Reproduced, by permission, from *Proc. Roy. Soc.*, 1955, *A*, **231,** 449.]

gases, agree moderately well both with the simple Bodenstein expression [36] and with Wigner's [37] more elaborate theory. The apparent fall in the rate at low iodine pressures is not so easily explained, and it has been suggested that a metastable iodine molecule with a different absorption spectrum is formed in the three-body collision involving an inert-gas molecule, and that this is only deactivated by collision with another iodine molecule.

TABLE 2

M	He	Ne	A	Kr	Xe	I_2
$10^{32}k_m$(ml.^{2} mol.$^{-2}$ sec.$^{-1}$)	0·67	0·92	1·82	2·25	2·99	470

The effectiveness as third bodies of a wider range of other gases has been studied by Russell and Simons,[33] who also showed that for a range of substances the rate constant at 127° was 0·4 times that at 20°. For a large number of molecules they showed that the logarithms of the third-order rate constants varied linearly with the boiling points, apparently owing to the importance of van der Waals forces in relation to both properties. For helium, hydrogen, and water this relation does not hold.

The Study of Combustion by Flash Photolysis

There are two desiderata concerning the initiation of an explosive reaction : the first that a sufficient temperature should be generated for the propagation of the reaction chains ; the second that an adequate concentration of atoms or free radicals should be formed to act as initiators of the chains. We have seen above that, unless suitable precautions are taken to keep the system isothermal by the addition of inert gas, flash photolysis leads to very high temperatures in the absorbing system, and it is just this possibility of administering a thermal shock that makes the method valuable as a tool in the study of ignition processes. The system, however, must be capable of absorbing the light energy of the flash—so that unless one of the reactants has a suitable chromophoric group within the range 2200—6000 Å, a sensitiser must be used. This is the case with mixtures of oxygen with hydrogen,[38] carbon monoxide, aliphatic paraffins,[39] and acetylene,[14] where nitrogen dioxide has proved to be an excellent initiator, though other substances such as chlorine are efficient.

Nitrogen dioxide has two advantages : it absorbs over the whole range of the available spectrum and this absorption contributes directly to a considerable temperature rise, while in the ultraviolet region direct dissociation occurs according to the equation :

$$NO_2 + h\nu = NO + O$$

giving rise to oxygen atoms which readily form initiating centres for the

---

[36] Bodenstein, *Z. phys. Chem.*, 1922, **100,** 118.
[37] Wigner, *J. Chem. Phys.*, 1937, **5,** 720.
[38] Norrish and Porter, *Proc. Roy. Soc.*, 1952, *A*, **210,** 439.
[39] Norrish, Porter, and Thrush, *ibid.*, 1955, *A*, **227,** 423.

reaction chains leading to ignition. With chlorine, initiation may be achieved by free radicals derived from Cl atoms generated by the flash, *e.g.* :

$$CH_4 + Cl = CH_3 + HCl$$

Pentyl nitrite has recently been used as a sensitiser by Erhard and Norrish in the study of knock and antiknock.[40]

Certain other combustible substances such as aromatic hydrocarbons, butadiene, aldehydes, and ketones are themselves sufficiently strong light-absorbers for explosions with oxygen to be produced directly without the use of a photosensitiser.

The great advantage of flash photolysis is that by its use it is possible to generate approximately *homogeneous* explosions. Thus, if the reaction tube is one metre long, we virtually have a " flame front " one metre thick and free radicals with suitable absorption spectra are readily visible spectroscopically by means of the spectroflash lamp triggered at suitable intervals after the initiating flash. In this way the waxing and waning of diatomic and triatomic radicals over a period of 1—3 milliseconds during and after the ignition can be followed and in some cases their reactions with each other can be deduced. Thus it has been possible to obtain in absorption the spectra of several radicals previously known only in emission, and by suitable methods of photometry to follow changes in their relative concentrations, though unfortunately their absolute concentrations cannot yet be deduced. A further limitation, which may well be overcome by the vacuum-spectrograph, is that the resonance lines of C, H, and O atoms cannot be observed owing to the limitation imposed by atmospheric transmission. Thus only a partial picture of the reactions constituting an explosion is at present objectively possible, but sufficient results have been obtained to provide considerable support for the belief that our intuitive deductions about the chain reactions of combustion and explosion are basically right.

The Explosion of Hydrogen and Oxygen.—Fig. 6 shows the decay of the OH spectrum in mixtures of different pressures of hydrogen with nitrogen dioxide observed by Norrish and Porter,[38] and since the stoicheiometric equation for the reaction is :

$$H_2 + NO_2 = H_2O + NO$$

it will be seen by inspection that the disappearance of OH is faster the greater the H_2 is in excess of the stoicheiometric ratio, evidence for the elementary reaction,

$$H_2 + OH = H_2O + H$$

postulated in the H_2–O_2 reaction.

A second elementary reaction of the hydrogen–oxygen reaction is proved by the initial generation of the OH spectra which can only arise from the oxygen atoms generated in the photolysis of NO_2 :

$$O + H_2 = OH + H$$

A third elementary process in the same reaction is displayed by the fact that the rate of disappearance of OH, when there is no excess of H_2 to remove

---

[40] Erhard and Norrish, *Proc. Roy. Soc.*, 1956, *A*, **234,** 178.

it, is greatly reduced by increasing pressure of inert gas (N_2), showing how its removal by diffusion to the wall is hindered by increase of pressure.

In Fig. 7 is shown a record of an explosion of $2H_2 + O_2$ sensitised by NO_2, in which the explosion as demonstrated by the growth and decay of OH can be clearly followed in both the 1,0 and 2,0 bands. An induction period of about 0·8 millisec. is seen while the disappearance of the radical takes about 7 millisec. This work on hydrogen and oxygen is to be regarded as only preliminary to much that can be done by studying the reaction in more detail by the more refined apparatus now available.

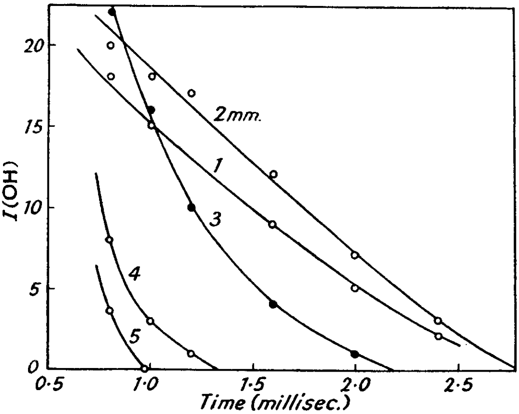


FIG. 6

OH *intensity against time : effect of* $P(H_2)$; $P(NO_2) = 2$ *mm. Figures on the curves show* $P(H_2)$ (*mm.*).

[Reproduced, by permission, from *Proc. Roy. Soc.*, 1952, *A*, **210**, 450.]

The Explosion of Acetylene and Oxygen.—Fig. 8 shows the absorption spectra of some of the diatomic radicals obtained when mixtures of acetylene are exploded with NO_2 as sensitiser. All the carbon radicals appear when the acetylene oxygen ratio is in excess of 1 : 1 and, with the exception of the weak appearance of CN, do not occur when the oxygen is in excess of this mixture ratio. Under these conditions, however, a strong generation of OH occurs. Figs. 9—11 show three sets of results obtained by the two-path method, Fig. 9 the variation of OH with time for various mixture strengths, Fig. 10 the carbon radicals with acetylene in slight excess, and Fig. 11 the OH radical with oxygen in slight excess. From curves such as these Fig. 12 has been constructed in which the maxima of the curves of the various radicals are plotted against mixture strengths. Counting the oxygen of the NO_2 as O_2 we see an almost exact switch from oxygen to carbon radicals at the ratio $C_2H_2 : O_2 = 1$. At this point the only radicals in evidence are OH, CN, and NH, and the last-named is confined closely to this specific mixture strength. It seems reasonable to ascribe its production to the reaction :

$$OH + CN = CO + NH$$

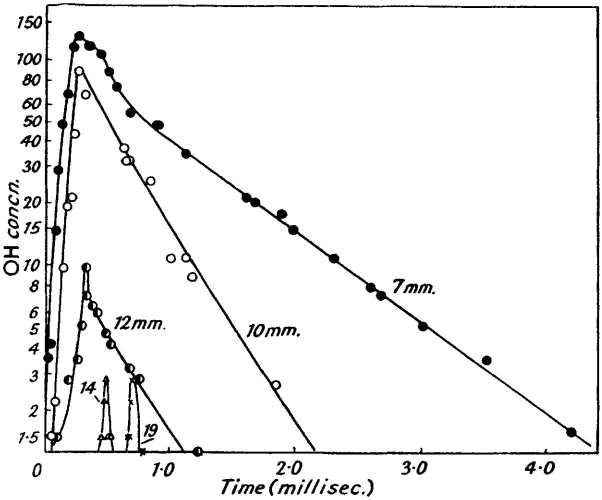


FIG. 9

OH *concentration (logarithmic scale) against time : effect of* $P(C_2H_2)$; $P(O_2) = 10$ *mm.,* $P(NO_2) = 1{\cdot}5$ *mm. Numbers on the curves are* $P(C_2H_2)$.

[Reproduced, by permission, from *Proc. Roy. Soc.*, 1953, *A*, **216**, 173.]

These results may be compared with those of Bone and Drugman [41] who noted the importance of the stoicheiometric equation,

$$C_2H_2 + O_2 = 2CO + H_2$$

according to which the carbon is burned preferentially to the hydrogen. With excess of acetylene they obtained carbon deposition in their explosions ; with excess of oxygen water was produced.

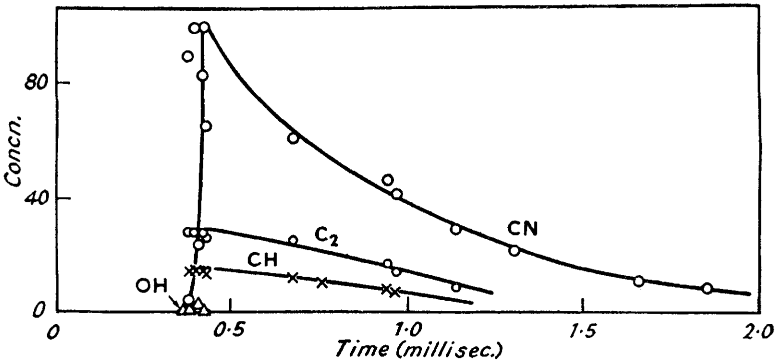


FIG. 10

Radical concentrations against time : $P(C_2H_2) = 13$ *mm.,* $P(O_2) = 10$ *mm.,* $P(NO_2) = 1{\cdot}5$ *mm.*

[Reproduced, by permission, from *Proc. Roy. Soc.*, 1953, *A*, **216**, 175.]

---

[41] Bone and Drugman, *J.*, 1906, **89**, 660.

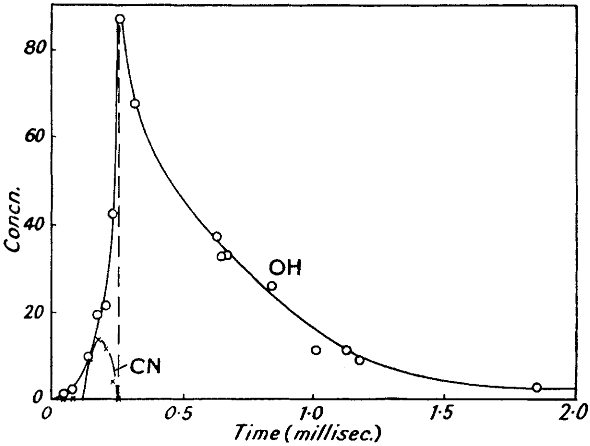


FIG. 11

OH *and* CN *concentrations against time :* $P(C_2H_2) = 10$ *mm.*, $P(O_2) = 10$ *mm.*, $P(NO_2) = 1{\cdot}5$ *mm.*

[Reproduced, by permission, from *Proc. Roy. Soc.*, 1953, *A*, **216**, 174.]

It may be concluded that the apparent induction period seen, for example, in Fig. 10 is really a period of developing reaction and that the carbon radicals seen to arise so suddenly at its end are really the product of after-cracking of the excess of acetylene, while in Fig. 11 the great development of OH is really the after-burning of hydrogen in excess of oxygen.

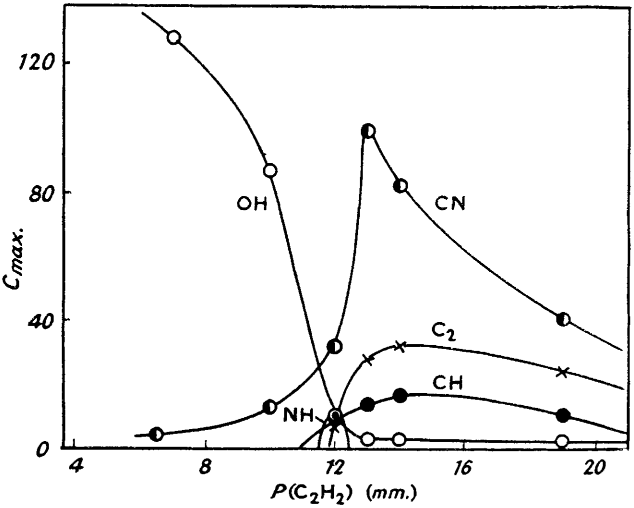


FIG. 12

Maximum radical concentrations against $P(C_2H_2)$; $P(O_2) = 10$ *mm.*, $P(NO_2) = 1{\cdot}5$ *mm.*

[Reproduced, by permission, from *Proc. Roy. Soc.*, 1953, *A*, **216**, 172.]

Certainly there is evidence that the temperature has risen to a high value near the end of the induction period for the vibrational temperature of the NO γ bands seen at the end is of the order of 2000° K.

While the carbon radicals all arise simultaneously, the appearance of OH both in carbon-rich and in oxygen-rich systems always precedes them. This seems to be the only radical which has so far been seen in the rapid chain reactions which culminate in ignition. At the same time, it will be seen that the peak of the OH curve in Fig. 11 definitely occurs at a later time than that of the CN, and thus, if the peak of the CN marks the explosion, the displaced peak of the OH must represent a later reaction—in accord with the hypothesis of the after-burning of hydrogen.

Other Hydrocarbons.—The explosions of ethylene, ethane, and methane have been studied by Norrish, Porter, and Thrush in a similar way.[39] The occurrence of the diatomic radicals is similar in all these cases to that of acetylene but there are quantitative differences in the stoicheiometry of the mixtures which give equivalent spectroscopic results. In this work continuous spectra and the spectrum of C_3 were studied in more detail. The continuum which is present at comparatively long times after the explosion is undoubtedly due to absorption by carbon particles, but a second continuum which has an intense maximum at 3900 Å and whose occurrence in time follows closely that of the carbon radicals is attributed to a carbon molecule in approximate thermal equilibrium with them and whose concentration must form a considerable fraction of the free carbon generated by the explosion. It seems probable that further evidence on the production of free carbon will be derived from experiments of this kind.

Photoelectric Recording of Emission and Absorption Spectra during Explosion.[15]—With the object of following continuously the kinetics of the approximately homogeneous explosions engendered by the photoflash, the photographic plate was replaced by two photomultiplier cells carried on a carriage interchangeable with the plate holder, and so mounted that they could be adjusted to receive any narrow wavelength region of the spectrum through narrow slits placed in front of them. The outputs of the photocells were fed through suitable amplifying circuits to a double-beam oscillograph and by this means the growth and decay of any suitable narrow part of the spectrum of OH, CN, CH, etc., could be recorded photographically. Changes in the absorption of a particular radical during explosion were observed by the light from a continuous-running xenon arc which was focused through the reaction mixture on to the slit of the spectrograph, the time base of the oscillograph being triggered by the scattered light of the initiating photoflash. Changes in light emission spectra of radicals could be observed directly, the time base being triggered by the photoflash as before.

Fig. 13 shows the OH emission from a $2H_2 + O_2$ explosion initiated by NO_2, for the wavelength range of the OH (0,0) band region. It is characterised by a remarkable peak, of not more than 2 or 3 μsec. duration. Similar peaks of short duration were observed in the acetylene–oxygen explosion for the C_2, CH, CN, and OH radicals. By observing the corresponding

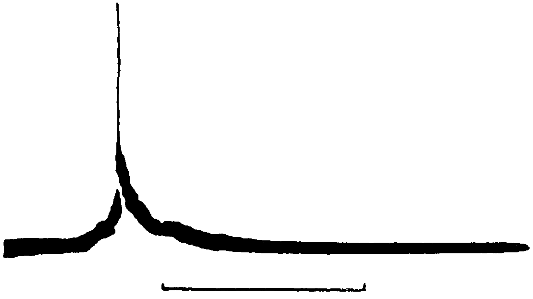


FIG. 13

OH *emission*: H_2–O_2–NO_2 = 8–2–0·8 *mm.*

[Reproduced, by permission, from *Fifth Symposium on Combustion*, Reinhold, New York, 1955, p. 655.]

changes in absorption, it was found that these peaks are superimposed as a strong emission which is not reversed by the xenon arc, and in Fig. 14 idealised pictures of the oscillograph records of absorption and emission are

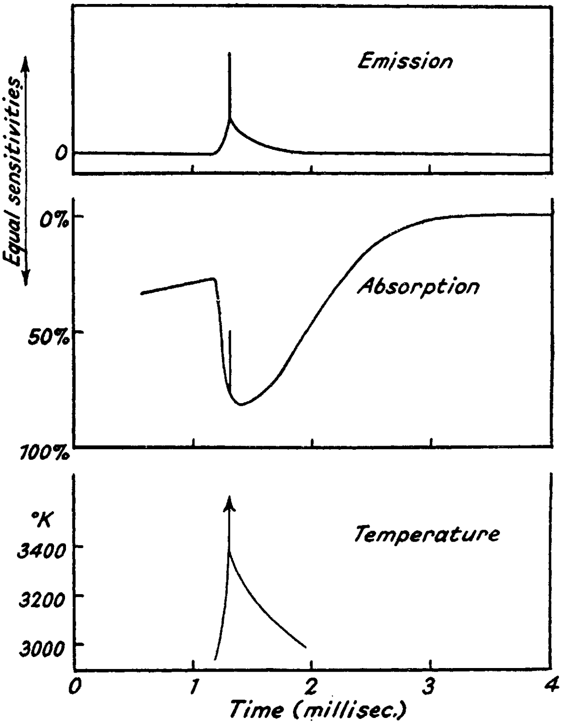


FIG. 14

Light emission and absorption with reversal temperatures: C_2H_2–O_2–NO_2 = 14–10–1·5 *mm.*

[Reproduced, by permission, from *Nature*, 1953, **172**, 71.]

given from which the temperature in different stages in the explosion can be calculated.[42] The temperature corresponding to the emission characterised by these short-lived peaks is some thousands of degrees greater than the thermodynamically expected temperatures of the explosions, and it has been proved by Thrush [43] that, while the main part of the explosion is homogeneous, detonation waves travel a short distance to the ends of the reaction vessel, the emission peak being caused by the impact of one of these on the vessel window nearest the spectrograph. In this way it has been shown conclusively that detonation waves, resulting from slight inhomogeneity in the extremely rapid energy release of the explosion, are readily betrayed by the oscillograph.

Knock and Antiknock.—By combining the photoelectric and the photographic techniques Erhard and Norrish [40] were able to study the role of tetraethyl-lead in its action as antiknock. Mixtures of acetylene and oxygen with pentyl nitrite as sensitiser in suitable mixture ratios were found to give strong indication of detonation when exploded by the photoflash : after an apparent induction period of 20—150 μsec. depending on the composition of the mixture and the energy of the initiating flash, the explosion was characterised by one or more sharp peaks of emission by the OH or CN radicals. With similar mixtures containing 0·5—1% of tetraethyl-lead the apparent induction periods were increased by some 200—300% while the incidence of detonation was greatly reduced or completely eliminated Fig. 15. Parallel with these observations photographic records of the absorption spectra showed that appearance of the OH and other radicals characteristic of ignition is delayed by the presence of tetraethyl-lead, the dominant intermediate species during the apparent induction period being PbO, which is rapidly reduced to atomic lead at the onset of the explosion. The sequence of events is shown photographically in Figs. 16 and 17, taken respectively with and without the addition of tetraethyl-lead. Taken in conjunction with previously existing evidence, it may be concluded that the role of tetraethyl-lead is to increase the delay before the second stage in the two-stage ignitions and that gaseous PbO is formed during the process by reaction with the oxygenated intermediates formed in the precombustion period and known to be conducive to knock. The PbO may be then further active in chain termination by reacting preferentially with the propagating radicals : in this way the rate of energy release is reduced, the PbO is converted into lead vapour, and conditions favourable to slow combustion and the absence of detonation are achieved. It is established that the seat of the reaction of tetraethyl-lead and its products is in the homogeneous gas phase.

Flash Photolysis coupled with Chemical Analysis

Most photochemical work in the past with concentrated light sources has been carried out with intensities of the order 10^{-10} einstein per cm.^{3} per second : by means of the high-powered flash lamps used in flash photolysis, intensities 10^7 times greater than this, lasting about 10^{-4} second,

---

[42] Norrish, Porter, and Thrush, *Nature*, 1953, **172**, 71.

[43] Thrush, *Proc. Roy. Soc.*, 1955, *A*, **233**, 147.

may be achieved. Under such conditions the final products may well be different from those resulting from the use of low conventional intensities. For in the latter case excited species or radicals are formed at a very low concentration, and in general their continuing reactions are with fresh molecules of reactant, while in the former the concentration of free radicals is so high that radical–radical reactions may become of predominant importance.

It thus becomes of interest to study the variation of final reaction products with intensity, by using ordinary methods of chemical analysis. For this purpose the lamp may be made of quartz tubing about 10 mm. in diameter, about 50 cm. long, wound in a spiral to fit closely round the reaction vessel, which is about 6—7 cm. in length and 2—2·5 cm. in diameter.

In the photolysis of acetaldehyde vapour the products at low intensity are methane and carbon monoxide, with very little hydrogen and practically no ethane. To account for this, Leermakers [44] postulated a chain mechanism involving the acetyl radical in which the chief operative reactions were :

$$\begin{array}{lrcll}
(1a) & CH_3{\cdot}CHO + h\nu & = & CH_4 + CO & k_{1a} \\
(1b) & CH_3{\cdot}CHO + h\nu & = & CH_3 + CHO & k_{1b} \\
(2) & CH_3 + CH_3{\cdot}CHO & = & CH_4 + CH_3{\cdot}CO & k_2 \\
(3) & CHO + CH_3{\cdot}CHO & = & CO + H_2 + CH_3{\cdot}CO & k_3 \\
(4) & CHO + CH_3{\cdot}CHO & = & CO + CH_4 + CHO & k_4 \\
(5) & CH_3{\cdot}CO & = & CH_3 + CO & k_5 \\
(6) & CH_3 + CH_3 & = & C_2H_6 & k_6 \\
(7) & CH_3 + CHO & = & CH_4 + CO & k_7 \\
(8) & CHO + CHO & = & 2CO + H_2 & k_8
\end{array}$$

Since ethane was absent from the products Blacet and Blaedel [45] replaced reaction 6 by a recombination of acetyl radicals to form diacetyl which was detected in roughly the expected amount. If, however, a sufficiently high concentration of methyl radicals could be generated by reaction 1*b* the incidence of reactions 6 and 7 should predominate over reaction 2, since the rates of the former are proportional to the second power of the concentration of radicals and that of the latter to the first power.

The consequence of this is that at very high intensity ethane should make its appearance and the above scheme leads under these conditions to the following limiting relationship between the products :

$$\frac{CH_4}{C_2H_6} = \frac{CH_4}{H_2} = \frac{2k_{1a}}{k_{1b}} + \frac{k_7}{\sqrt{k_6k_8}}\left(1 + \frac{k_{1a}}{k_{1b}}\right)$$

This was investigated by Khan, Norrish and Porter [46] using the flash discharge and a normal method of gas analysis and was found to be indeed very closely true. In this work the reaction was kept isothermal by the addition of excess of carbon dioxide. Similar studies with acetone and

---

[44] Leermakers, *J. Amer. Chem. Soc.*, 1934, **56,** 1537.

[45] Blacet and Blaedel, *ibid.*, 1940, **62,** 3374.

[46] Khan, Norrish, and Porter, *Proc. Roy. Soc.*, 1953, *A*, **219,** 312.

diacetyl showed but little change of product at high intensity, a result to be expected from the established mechanism of these processes, which are not chain reactions owing to the absence of the reactive aldehydic hydrogen atom and hence the impossibility of propagating reactions analogous to 2 above.

The decomposition of keten by light of very high intensity was studied in a similar way by Knox, Norrish, and Porter.[47] At low flash intensities in the presence of a large excess of inert gas the products are mainly carbon monoxide and ethylene, as found under normal photolysis conditions. As the intensity is increased or the inert-gas pressure decreased hydrogen and acetylene are formed in increasing amounts until eventually they with some carbon become the major products. The progressive change is caused by the increasing adiabatic nature of the photolysis. By analysis of the products formed under different conditions of reaction it is possible to follow the course of the reactions and to conclude that carbon formation takes place by successive dehydrogenation of C_2 hydrocarbons by Rice–Herzfeld mechanisms, and final polymerisation to graphite. It is of interest that in excess of methane the photolysis of keten at high light intensity leads almost exclusively to ethane and carbon monoxide.

One of the main limitations at the present stage of the work is that it is not possible to use monochromatic radiation while maintaining sufficiently high intensities, or to make direct measurements of quantum yield. There is, nevertheless, a wide field of reaction worthy of exploration by the analytical method from which we may hope to glean information about radical–radical reactions.

---

[47] Knox, Norrish, and Porter, *J.*, 1952, 1477.