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Some fast reactions in gases studied by flash photolysis and kinetic spectroscopy

Nobel Lecture, December 11, 1967

Realisation that free radicals and atoms take part in chemical reactions has focussed attention on the processes of photo-chemistry which are not only paramount in the geochemistry of the upper atomosphere but are also basic to many reactions of organic chemistry involving free radicals and the triplet state; this realisation also has led to the development of gas lasers, and to the esploration in detail of the intimate anatomy of reactions of pyrolysis, combustion and explosion.

Classical photochemistry emerged in 1908 with the understanding by Stark of the distinction between the primary and secondary photochemical processes, of which the former is the immediate result of the absorption of a light quantum by a molecule or atom and the latter the subsequent "dark" reactions initiated by the products of the former[1]. Into this simple pattern it has been possible to fit the whole gamut of photochemical phenomena-fluorescence, phosphorescence, photolytic and photosynthetic processes, photocatalytic and photosensitised reactions. Determination of quantum yields led to the distinction of endoactinic and exoactinic reactions; the former being endothermic in character draw their energy requirement from the absorbed quantum and rarely exceed an overall quantum yield of 2, the latter, being exothermic release their "pent up" energy by photochemical initiation and are usually of the nature of chain reactions, with high quantum-yields, and sometimes explosive characteristics. For example, the dissociation of hydrogen iodide into its elements is 2200 cal endothermic and its quantum yield is limited to two[2] while the synthesis of hydrogen chloride from its elements is exothermic to the extent of 22,000 cal and may have a quantum yields as high as 10^6.

It was indeed the study of these two reactions that first led to the conclusion that the primary reaction may involve photolysis of the reactant into atoms (and later free radicals). In the former case we have

$$HI + h\nu = H + I$$

in the latter

$$Cl_2 + h\nu = Cl + Cl$$

followed by the well known H_2-Cl_2 chain reaction. We owe much to Bodenstein, Warburg and Nernst[4] by whose early work the reality of the participation of atoms in chemical reactions was made apparent and the concept of the chain reaction established. Following this, the reactions of H atoms generated by an electric discharge through hydrogen gas were established by R.W.Wood[5] and by Bonhoeffer[6], and the production of free alkyl radicals by the pyrolysis of metal alkyls proved unequivocably by Paneth[7].

Simultaneously the growth of the study of the band spectra of gaseous molecular species in particular by Frank* and V. Henri[9] clarified the quantum mechanisms of the processes of thermal dissociation, photo dissociation and predissociation, indicating the production of free radicals and atoms in both ground and electronically excited states. It may justly be claimed that from the marriage of photokinetics with spectroscopy there resulted a new insight into the mechanism of chemical reactions; the part played by atoms, free radicals and excited species as transient intermediates became abundantly apparent. The reactions of these transients however, which together make up the overall process of conversion of reactants to final products are so fast that they can neither be observed nor isolated by classical means, and their nature and participation could until recently only be deduced from the circumstantial evidence ofreaction kinetics, quantum yields, and the spectroscopic characteristics of the reactants.

It therefore became of importance if further progress was to be made, to endeavour to obtain objective evidence of the presence of short lived transients both in thermal and photochemical reactions. Using continuous sources of the highest attainable intensity (e.g. a 10 kW high pressure mercury arc) the author and his collaborators in 1946 attempted to obtain evidence by spectroscopic means of a stationary concentration of intermediates in such reactions as the photolysis and photo oxidation of ketene without success. In no case could any absorption spectrum which could be attributed to reacting transients be observed in the reacting system and it became apparent that their reactivity was so great that no sufficient stationary concentration for detection by the means then available could be achieved.

It was the realisation that enormously greater "instantancous" light intensities could be obtained from a powerful light flash than from a conventional light source, and that such a flash need not be of greater duration than the half life of the elusive transients that led Porter and me to study the results of applying such flashes to suitable responsive photochemical systems[10]. Using an electric discharge from a condenser bank through inert gas, dissipating about 10 000 joules it was immediately found that the resulting light flashes of about 2-3 milliseconds duration were able to create large measures of photodecomposition in reactants such as nitrogen peroxide, chlorine, ketene, acetone and diacetyl, amounting to 100% in some cases. It was obvious that momentarily there must be very high concentrations of free radicals or atoms in such reacting systems which by suitable means should be detectable by absorption spectroscopy. This was first achieved by Porter[11] who using a second less powerful flash triggered mechanically by the method of Oldenberg[12] at specific short intervals after the first was able to observe the complete dissociation of chlorine by the disappearance of the Cl_2 absorption spectrum and its return over a period of milliseconds as the atoms recombined.

The modern method of flash photolysis developed from this uses an electronic technique by which the first flash (photoflash) is caused photo-electrically to trigger the second flash (specflash) at specific short intervals measured in microseconds and milliseconds[13]. The photoflash is generated by discharging a capacity of the order of 40 μF at 10 kV through an inert gas such as krypton or xenon contained in a quartz tube generally 50 cm in length and 1 cm in diameter. The reaction vessel is a quartz tube of similar dimension with plane quartz end plates, lying close to and parallel to the photoflash tube. The specflash lamp consisting of a quartz capillary tube about 10 cm in length is placed "end on" to the reaction vessel, and has a plane quartz end plate so that by means of a lens and limiting stop, a beam of light can pass longitudinally through the reaction vessel to a suitable spectrometer to register the absorption spectrum of the reacting system at any specific interval after the photoflash (see Fig. 1). The discharge is made as before through inert gas.

The energy dissipated by the discharge of a condenser is given in joules by the relationship, $E = 1/2\ C\ V^2$, where the capacity is measured in microfarads, and the potential difference in kilovolts. For a given energy the duration of the flash is the shorter the smaller C and the greater *V*; the self inductance of the circuit must be kept as low as possible. For the photoflash, a convenient energy

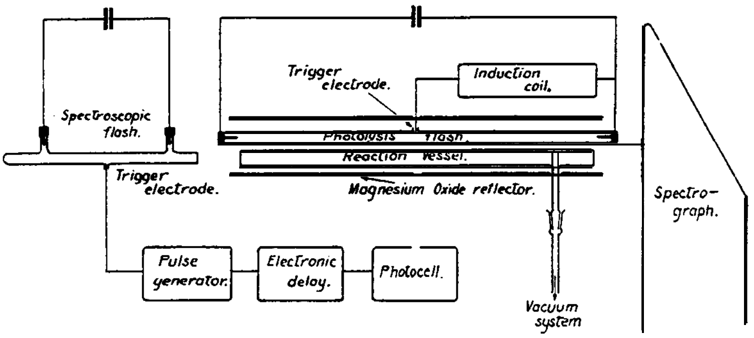


Fig. 1. Diagram of flash photolysis apparatus.

dissipation is 2000 J derived from the discharge of 40 F at 10 kV. The halflife of the light flash is about 10 μsec. For the specflash a discharge of 100 J is generally used, obtained by discharging 2 μF at 10 kV; its half life is of the order of 2μsec. The pressure of gas in both lamps is of the order 5-10 cm Hg. The reaction vessel may be double walled for the introduction of gaseous or liquid colour filters in the annular space. Both it and the photolysis lamp are surrounded by a tubular reflector coated on the inside with magnesium oxide, and when necessary the whole can be mounted in a tubular electric furnace. A general description of the apparatus which throughout our work has had several minor modifications is given in detail by Norrish, Porter and Thrush (ref. 13); the technique at present in use, represents a compromise between all the factors affecting its operation. Improvements have been effected by using highly transparent "spectrosil" quartz which transmits down to 1 600 Å, end plates of lithium fluoride, and vacuum spectrographs for detection of transients whose absorption spectra lie in the far ultraviolet. Of great importance for the future is the reduction in the periods of the photoflash and specflash to achieve greater time resolution, and the development of highly transparent materials for construction of apparatus suitable for shorter wave photolysis than is at present available.

It may readily be calculated that the "instantaneous" dissipation of only 1 joule of energy *(i.e.* about 0.05% of the total output of the photoflash) by 150 ml of gas at 1.0 mm pressure will raise the temperature of the reactant by about 5 000°C for there is no time for cooling during the short period of the flash. Thus the early results of flash decomposition are more properly regarded as flash pyrolysis than flash photolysis, and unless steps are taken to neutralise this rise in temperature by the dilution of the system by the addition of a large excess of inert gas, we cannot expect to study the photochemical effects divorced from thermal complications. This however is readily done: by the introduction of inert gas at pressures of 100 to 500 times that of the reactant. the temperature rise can be kept below 10°C, which for practical purposes may be regarded as isothermal, while for reactions in solution of course, there is no problem. On the other hand we may take advantage of flash heating in undiluted systems to administer an adiabatic shock which for many purposes is superior and certainly simpler than the technique of shock wave kinetics. This arises from the fact that by flash heating the whole system is instantaueously and nearly homogeneously heated to high temperatures, making possible the detection of the transient products of pyrolysis and growth and decay of intermediates in chain reactions leading to explosion in suitable systems. Indeed, it is the homogeneity of the explosive processes which makes it possible to observe in absorption the unexcited radicals taking part; we have in fact in a reaction vessel 0.5 m in length a "flame front" virtually 0.5 m thick which is very different from the thin element propagating an-explosive wave. This is important because it makes possible for the first time the observation of the reactions of unexcited species leading to and taking part in explosion as well as the electronically excited species to which we were limited in the past.

Thus there are two ways in which we can employ the techniques of kinetic spectroscopy and flash photolysis, the *isothermal* method and the *adiabatic*. The field of their application is almost unlimited; I must content myself with general remarks, and three specific examples.

The first objective of flash photolysis, namely to observe the growth and decay of radical species by kinetic spectroscopy has been achieved; following the first demonstration of the dissociation of chlorine, the spectrum of the ClO radical was first seen in absorption on flashing a mixture of chlorine and oxygen. Its origin was ascribed to the almost complete dissociation ofchlorine, and to the reaction to be expected from the chlorine atom in an atmosphere of oxygen. It was possible to show that the sequence of reactions

$$Cl_2 + h\nu = Cl + Cl$$

$$Cl + O_2 = ClOO$$

$$ClOO + Cl = ClO + ClO$$

$$ClO + ClO = Cl_2 + O_2$$

in which the final state of the system is the same as the first provides a complete basis for explaining the reaction.

The study of this reaction[14] constituted an early success in the application of flash photolysis to chemical kinetics and will be described in some detail today by my colleague Professor Porter.

Dr. Husain. has collected references to some sixty simple free radicals and atoms whichhave been discerned and characterised in absorption, either by isothermal flash photolysis or by adiabatic flash pyrolysis and explosion. Prominent among them are CH, CH_2, CH_3, NH, NH_2, OH, HCO, HNO, CN, CS, ClO, BrO, IO, NCl, NCl_2, PH, PH_2, PO, PN, SH, SO, SiO, TeO, TeH, W, Te, Sn, Hg, Fe, Mn and also highly vibrating states of several molecular species, such as O_2. The collection of this information is the first step towards identifying the nature of radical reactions observed by kinetic spectroscopy. To illustrate this we shall now consider two examples of the application of the isothermal technique, the first involving the primary photolysis of nitrosyl halides, the second the secondary reactions associated with the photolysis of nitrogen dioxide, chlorine dioxide and ozone.

Vibrational Excitation by Primary Reaction

The flash photolysis of nitrosyl halides – Vibrational relaxation

The sequence of spectra shown in Fig. 2 show the course of the photolytic dissociation of nitrosyl chloride, typical also of nitrosyl bromide, which takes place in the region of 2 600 Å (Basco and Norrish[15]). A study of a large number of plates showed that the primary product, NO is highly vibrationally excited in the ground state comprising all levels from $v'' = 11$ to $v'' = 0$. All these were observed in absorption in the β, γ, δ and ε spectra of NO; the rotational temperature of the molecule was, however, unaffected. By using NO as a light filter surrounding the reaction vessel it was proved that these excited species do not have their origin in the secondary excitation of NO molecules and after consideration of all possibilities it was concluded that they are in fact the product of the primary photolysis of the halide, NOX:

$$NOX + h\nu = NO^{*} + X$$

It was found that the relative "instantaneous" population of the higher levels of nitric oxide increased as the halide pressure decreased and that *at first* the level $v'' = 1$ was barely detectable. The decay of the higher excited levels was however extremely rapid and increased with the pressure of the halide yielding ultimately the level $v'' = 1$ which accumulated and was virtually the only excited level detectable after the photoflash. It was in fact established that

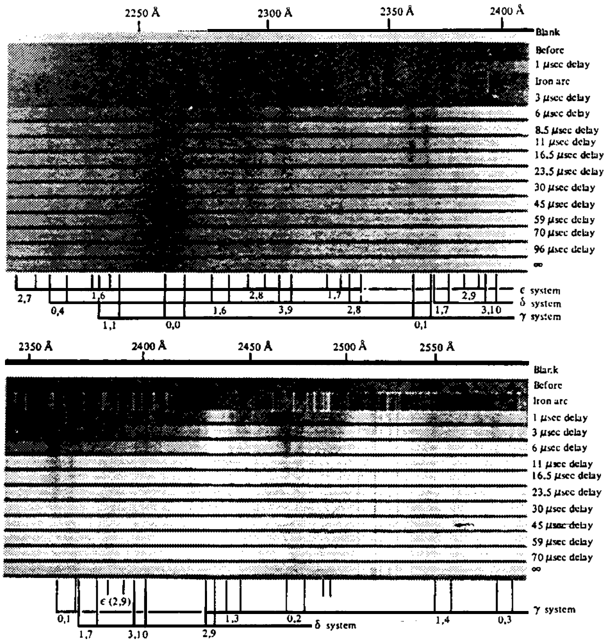


Fig.2. Vibrationally excited NO produced in the flash photolysis of NOCl. Upper picture: pressure of NOC1, 1.0 mm Hg; pressure of N_2, 372 mm Hg. Lower picture: pressure of NOCl, 2.0 mm Hg; pressure of N_2, 40 mm Hg. Flash energy, 1600 J. (Basco and Norrish[15])

the rate of decay is determined by the pressure of the unchanged nitrosyl halide, and that on the other hand, the effect of inert gases was not detectable.

The rapidity of decay of NO* and the specific effect of the parent NOX suggests that near-resonance transfer processes are operating in deactivation as indeed is confirmed by the fact that the vibration frequencies of NO in the range of levels $v = 11$ to $v = 1$ lie between 1 900 and 1 600 cm^{-1} while for both NOCl and NOBr the frequency associated with the NO bond was found by Burns and Bernstein[16] to be 1 800 cm^{-1}.

At this point, however, there arises an apparent anomaly. The observation of Pearse and Gaydon[17] showed that the first levels in the ground state of NO can be populated by fluorescence as shown diagrammatically in Fig. 3. This fluorescence which consists of the banded $v = 0$ progression $A^2\Sigma^+ \leftarrow X^2\Pi$ of NO was also seen by Basco, Callear and Norrish[18] using the flash technique; yet by the same means they were unable to observe levels higher than $v = 1$ in absorption, with the exception of $v = 2$ *very* faintly, Fig.4. It might be postulated that the higher levels are populated very weakly relatively to the first,

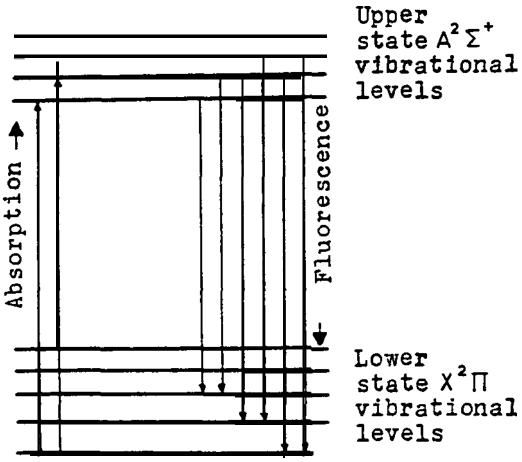


Fig. 3. Diagrammatic representation of population of vibration levels of NO in the ground state by fluorescence.

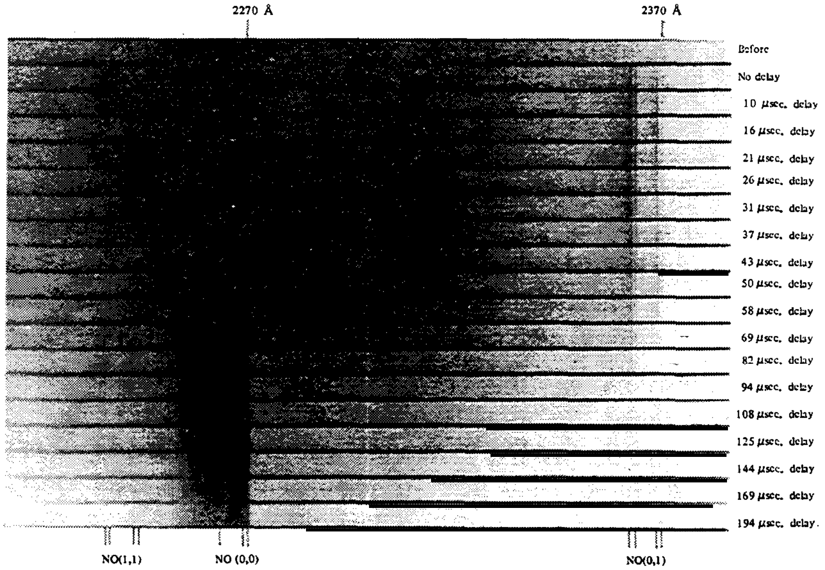


Fig. 4. NO $^2\Pi(v=1)$ produced by flash fluorescence of NO, showing decay. Pressure of NO, 5 mm Hg; pressure of N_2, 600 mm Hg; flash energy, 1600 J. (Basco, Callear and Norrish[18])

but this is not so; Pearse and Gaydon from a measurement of the intensities of the fluorescent bands found the first five levels to be populated almost equally. Herein lies the problem: why is only the level v = 1 seen by kinetic spectroscopy and why do the higher levels v = 2,3,4 and 5 decay too rapidly to be observed in absorption when the same and higher levels derived from the photolysis of the nitrosyl halides are readily detected and their decay, albeit rapid, easily followed in times measured in microseconds?

The solution to this apparent anomaly may be achieved by means of the two following hypotheses[19]:

(1) The most favourable resonant collisions are between closely associated levels of the vibrating species, e.g.

$$NO_{v=n} + NO_{v=(n-2)} \rightarrow 2NO_{v=(n-1)}$$

and owing to change in frequency of levels due to anharmonicity, the most favourable of all will be obtained when the frequency levels differ by 2 as above.

(2) At the instant of production from the nitrosyl halide the NO* is formed in very highvibrating states-say v = 12, 11, or 10.

The vibrational energy of v = 11 is 55 kcal, and since the bond strength of NO-Cl is 38 kcal there is plenty of energy available from the light quantum (say 98 kcal for 2 800 Å) for this to occur. The same applies for NOBr. In consequence there is a gap between v = 10 (say) and v = 0 and in the absence of other deactivating species (inert gases ineffective) the high vibrational levels cannot be relaxed. This of course is an ideal conception; lower levels will be built up by collisional deactivation by species such as the nitrosyl halides as we have seen, but it will be a relatively slow process compared with self deactivation. As the lower levels are populated so will resonant self-quenching increase, but there will always be an irregular distribution which will cause a retardation, and further, since high levels are continually fed in by the flash, the irregular distribution will be preserved and all levels will be observed during its operation.

In contrast, when the first five vibrational levels of the ground state of NO are populated by fluorescence they are populated as we have seen above, nearly equally; thus the highly efficient process of self-quenching described in hypothesis (1) can take place as shown in Fig. 5, and all levels are deactivated to v = 1 when the resonant process must of necessity stop. The collapse of the pattern is so rapid that only the first level is seen to be overpopulated, and this can only be deactivated slowly by the inefficient process of collisional con-

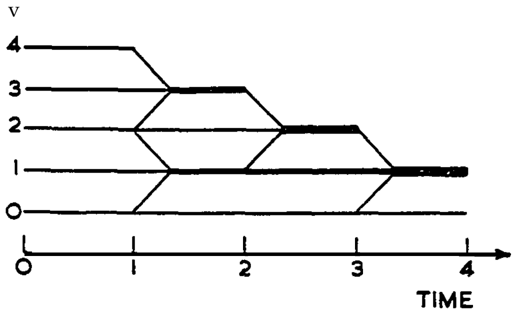


Fig. 5. Diagrammatic representation of relaxation of vibrational energy of NO by self quenching.

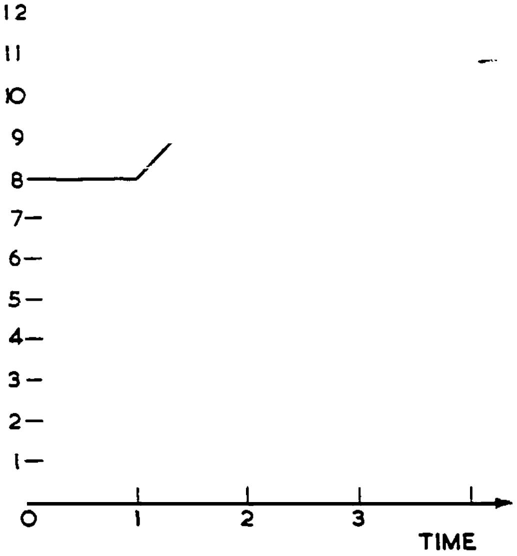


Fig. 6. Diagrammatic representation of relaxation of high levels of vibrational energy of NO, restricted by isolation. (Ideal)

version to translational energy. If, however, we have a gap in the vibrational distribution or a series of irregularities in the sequence of population of the pattern of vibrational levels as with NO* derived from nitrosyl halides the resonant deactivation must be brought to a halt, or slowed down, shown for an ideal case in Fig.6. Overpopulation of all higher levels is observed.

The overpopulation of the NO $_{v=1}$, level in the ground state by fluorescence (Fig. 4) makes possible the quantitative study of the relaxation reaction[18]

$$NO_{v=1} + M = NO_{v=0} + M'$$

This arises from the fact that the absolute concentration of $NO_{v=1}$ can be measured by plate photometry because the (0,1) band is visible spectroscopically in absorption with nitric oxide at atmospheric pressure, and since its concentration at equilibrium is given by

$$[NO^*] = [NO]\, e^{-h\nu/kT}$$

the photometric curves can be calibrated to give absolute concentrations by choosing one particular line in the band for measurement. In this way the curves shown in Fig.7 were obtained; when plotted logarithmically they give good straight lines indicating first order decay from which the unimolecular constant k_3 can be obtained. I/k_3 is the mean life time τ of the excited species, and if this suffers Z collisions per second then $P_{1\text{-}0}$ the probability of energy transfer at one collision is given by

$$P_{1-0} = \frac{1}{\tau Z} = \frac{k_3}{Z}$$

k_3 can be split into two terms depending on relaxation by NO, and by any added gas M. Thus

$$k_3 = k_4(NO) + k_5(M)$$

and k_4 and k_5 may be calculated from the various values of k_3 derived from the curves of the type shown in Fig. 7 for nitrogen. The data shown in Table 1 show preliminary figures for the quencing probabilities of various added gases, the high value for water being probably due to chemical reaction.

Table 1

Molecule	NO	CO	H_2O	CO_2	N_2	Kr
P_{1-0}	$3.55 \cdot 10^{-4}$	$0.25 \cdot 10^{-4}$	$7 \cdot 10^{-3}$	$1.7 \cdot 10^{-4}$	$4 \cdot 10^{-7}$	zero

Further studies[18] ofrelaxation by CO indicated unmistakably that the process occurs by resonant transfer of vibration

$$NO_{v=1} + CO_{v=0} = NO_{v=0} + CO_{v=1}$$

The concentration of CO* was measured by photometering the unresolved band of the fourth positive $A^1\Pi \rightarrow X^1\Sigma^+$ system which is visible in the spectrum of CO at atmospheric pressure and so can be used to measure in absolute terms the vibrational exchange between NO and CO shown in Fig. 8.

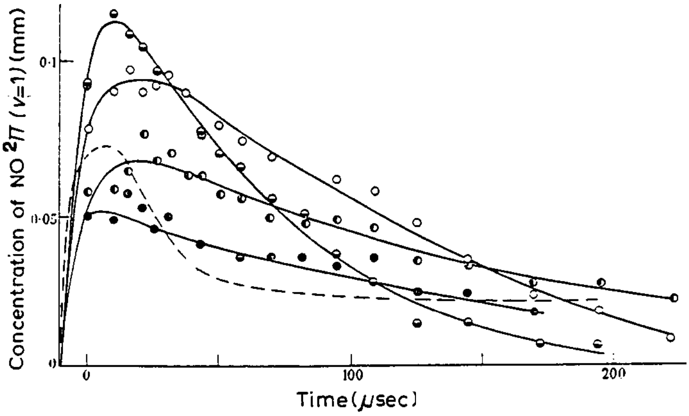


Fig. 7. Rise and decay of NO $^2\Pi$ ($v = 1$) measured by plate photometry. ○, 2 mm NO + 600 mm N_2·(1600 J). ●, 2 mm NO + 220 mm N_2·(1600 J). ◐, 1 mm NO + 600 mm N_2·(1600 J). ⊖, 5 mm NO + 600 mm N_2·(1600 J). --, 50 mm NO + 467 mm N_2·(900 J). (Basco, Callear and Norrish[18])

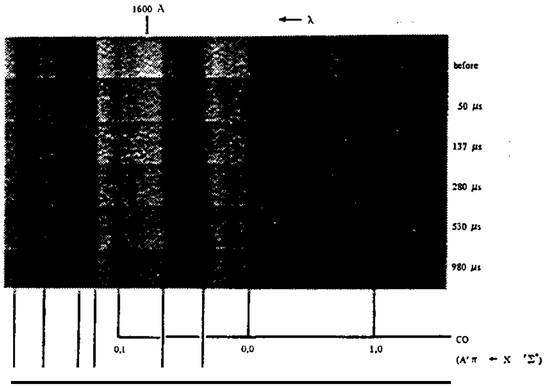


Fig. 8. Production of CO ($v = 1$), ground state, by resonance with NO ($v = 1$), ground state. NO pressure, 5 mm; CO pressure, 100 mm; N_2 pressure, 650 mm. (Basco, Callear and Norrish[20])

Studies of the photolysis of $(CN)_2$, CNBr and CNI generically represented as C N R by kinetic spectroscopy yield results similar to those described for NOBr and NOCl (Basco *et al* [20]). These substances absorb at the short end of the quartz ultraviolet below 2 300 Å and on flashing in the presence of inert gas yield vibrationally excited CN radicals up to v = 6 which are observed spectroscopically in absorption in the $\Delta v = 0 \pm 1$ and - 2 sequences of the violet ($B^2\Sigma - X^2\Sigma$) system at 3590, 3883, 4216 and 4660 Å. Decay sequences with time of C N* indicated the preferential production of C N* in the higher excited vibrational states and their decay by collision with CNR as with the analogous nitrosyl halide reactions, but owing to the very high extinction coefficient of the C N radical itself there was also detected, using colour filters, a high secondary population of C N* resulting from absorption of light in the region 3500-4500 Å by CN far outside the photolytic wave lengths of CNR. The process

$$\mathrm{CN}\cdot X^2\Sigma(v=0,1,2\ldots) \rightleftharpoons \mathrm{CN}\cdot B^2\Sigma(v=0,1,2\ldots)$$

is indicated involving many reversible excitations during the flash, the reverse reaction raking place either by fluorescence or collision; but in the end only $v = 1$ persists as before.

Vibrational Excitation by Secondary Reactions

The reactions of oxygen atoms

The photolysis of nitrogen dioxide, chlorine dioxide and ozone studied by the techniques of classical photochemistry were all concluded to proceed by similar mechanisms, involving the primary generation of oxygen atoms, as follows[21] :

Nitrogen dioside:

$$NO_2 + h\nu = NO + O$$
$$O + NO_2 = NO + O_2$$

Chlorine dioxide:

$$ClO_2 + h\nu = ClO + O$$
$$ClO_2 + O = ClO + O_2$$
$$ClO + ClO = Cl_2 + O_2$$

Ozone:

$$O_3 + h\nu = O_2 + O$$
$$O + O_3 = O_2 + O_2^*$$
$$O_2^* + O_3 = O_2 + O_2 + O$$
$$O_2^* + M = O_2 + M'$$

The quantum yield of the first two reactions in the near ultraviolet is of the order 2. In the case of O_3 it was measured as up to 8 in the region of 2000-

2500 Å, but limited to 2 when photolysis occurs at the red end of the spectrum. Thus a chain reaction is indicated in the former case, which owing to the inherent simplicity of the system must be propagated as shown by excited oxygen molecules, considered by the earlier workers to be an electronically excited species. On studying these reactions by isothermal kinetic spectroscopy, we found that not only is the kinetic scheme of reactions shown above confirmed, but that in addition highly vibrating oxygen molecules in the ground state, cold rotationally and translationally, are produced in each case. Thus the reactions

$$NO_2 + O = NO + O_2^*$$
$$ClO_2 + O = ClO + O_2^*$$
$$O_3 + O = O_2 + O_2^*$$

were indicated[22,23]. With NO, vibrational levels up to v = 11 were observed; with ClO_2 levels up to v = 8, and with O_3 levels up to v = 17-20. In each case more than half the exothermic energy of reaction appeared unequilibrated as vibrational energy of the oxygen molecule observed in absorption in the Schumann-Runge spectrum. Fig.9 shows the flash photolysis of ClO_2 in which after flashing, the transient spectrum of the ClO radical is seen together with the absorption by highly vibrating oxygen molecules. The production of excited O_2^* is seen more clearly in Figs. 10 and 11 resulting from the photolysis of NO_2 and O_3 respectively.

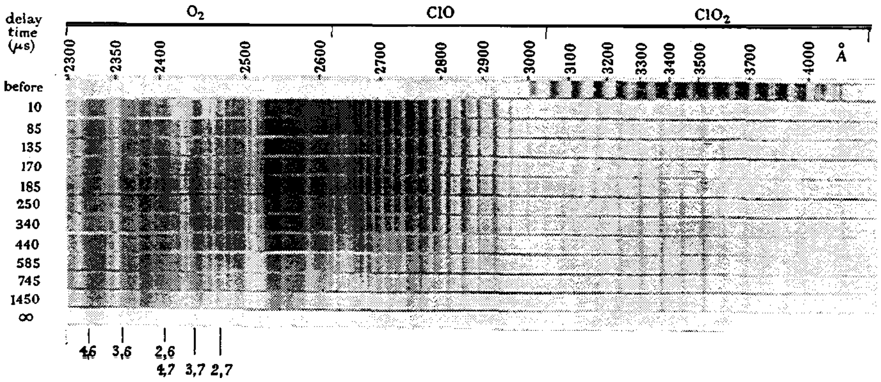


Fig. 9. Flash photolysis of ClO_2 ClO_2 pressure, 0.5 mm Hg; N_2 pressure, 580 mm Hg. Flash energy, 320 J, showing ClO and vibrationally excited O_2 (latter seen with difficulty owing to low dispersion). (Lipscomb, Norrish and Thrush[22])

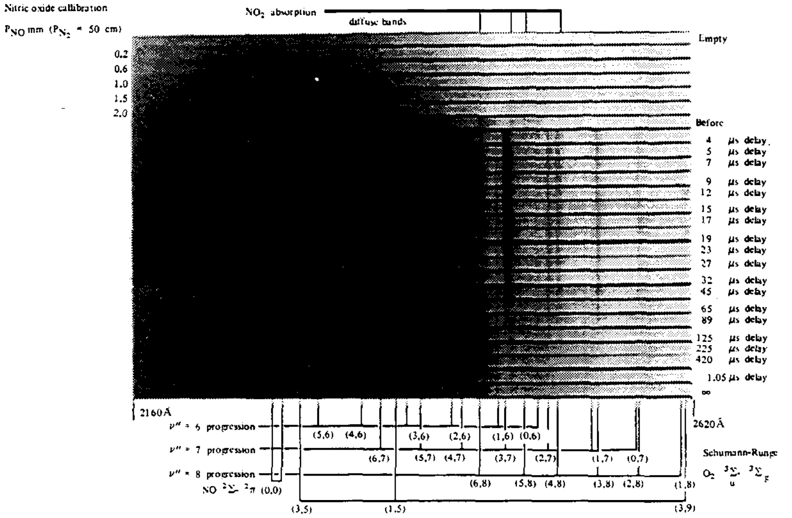


Fig. 10. Decay of vibrationally excited O_2 resulting from the flash photolysis of NO_2 under isothermal conditions. NO_2 pressure, 2 mm Hg; N_2 pressure, 500 mm Hg. Flash energy, 2025 J. (Husain and Norrish[34])

These results led McGrath and Norrish[24] to the tentative generalisation that when an atom reacts with a polyatomic molecule, a large proportion of the exothermic energy of reaction is preferentially located initially as vibration in the newly formed bond, *i.e.*

$$A + BCD = AB^* + CD$$

Qualitatively this seems reasonable since the main interaction must be visualised as between A and B, while the elimination of CD could well occur without much appreciable change in the interatomic distance between the parts C and D. The generalisation has now been widely confirmed. McGrath and Norrish[24] have shown by flash photolysis that the reactions

$$Cl + O_3 = ClO^* + O_2$$
$$Br + O_3 = BrO^* + O_2$$

yield highly vibrating ClO and BrO with up to six quanta of vibration, while likewise, the reactions of ^1D oxygen atoms derived from ozone on reacting with a wide range of hydrides yield vibrationally excited OH[26], *e.g.*

$$O + H_2O = OH^* + OH$$
$$O + NH_3 = OH^* + NH_2$$
$$O + H_2 = OH^* + H$$

Other examples such as the reactions of hydrogen atoms observed by McKinley, Garvin and Boudart[27] and Cashion and Polyani[28],

$$H + O_3 = OH^* + O_2$$
$$H + Cl_2 = HCl^* + Cl$$
$$H + Br_2 = HBr^* + Br$$

further confirm the correctness of our generalisation which invites detailed quantitative study, and must probably await greater time resolution in our technique before it can be achieved. For example, we cannot yet be sure whether the vibrationally excited products are produced *ab initio* in their highest vibrating state and relax subsequently, or whether a complete spectrum of vibrating states results directly as part of the reaction mechanism.

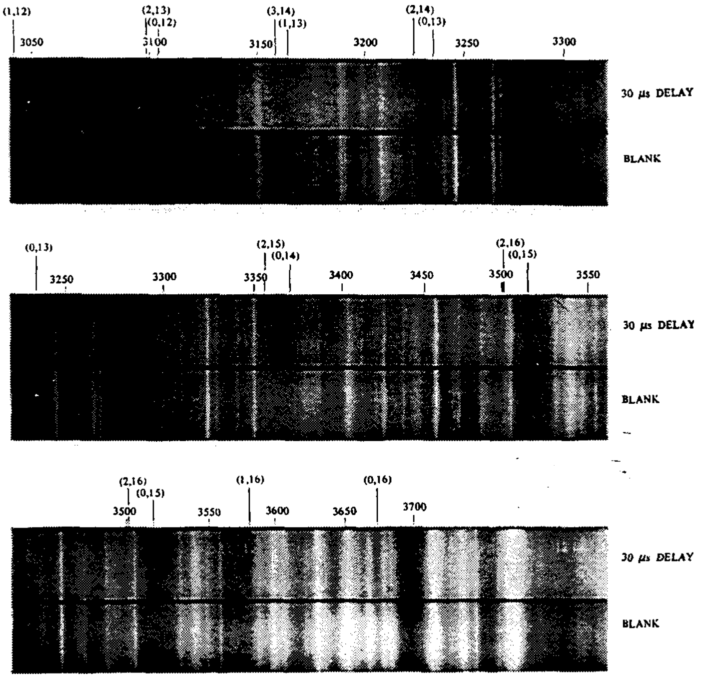


Fig. 11. Schumann-Runge absorption spectrum of vibrationally excited O_2 produced by flash photolysis of ozone. O_3 pressure, 20 mm Hg; N_2 pressure, 800 mm Hg. O_3/N_2 ratio = 1/40. Flash energy, 2000 J. (McGrath and Norrish[23])

The Photolysis of Ozone

The photolysis of ozone was first discerned as a chain reaction by Heidt and Forbes[21] and confirmed for pure ozone by Norrish and Wayne[29] who observed quantum yields up to 16 in the ultraviolet. The nature of the excited oxygen functioning as chain carrier would now appear to be identified as the vibrating molecule with more than 17 quanta of vibration. For the propagation of the chain the endothermic reaction

$$O_3 + O_2^* = O_2 + O_2 + O$$

requires 69 kcal, and this is supplied precisely by a molecule vibrating with more than 17 quanta. All those vibrating with less are visible by flash photolysis and decay by normal relaxation processes. Those with more react so rapidly with ozone molecules that they are not seen, except that they may be faintly discerned up to $v = 30$ as a consequence of competition between reaction and collisional deactivation. This conclusion is based upon the deduction that the oxygen atom is generated in the first electronically excited state, ^1D, lying 45 kcal above the ground state and that the chain reaction is propagated uniquely by ^1D oxygen atoms, because no chain reaction follows photolysis

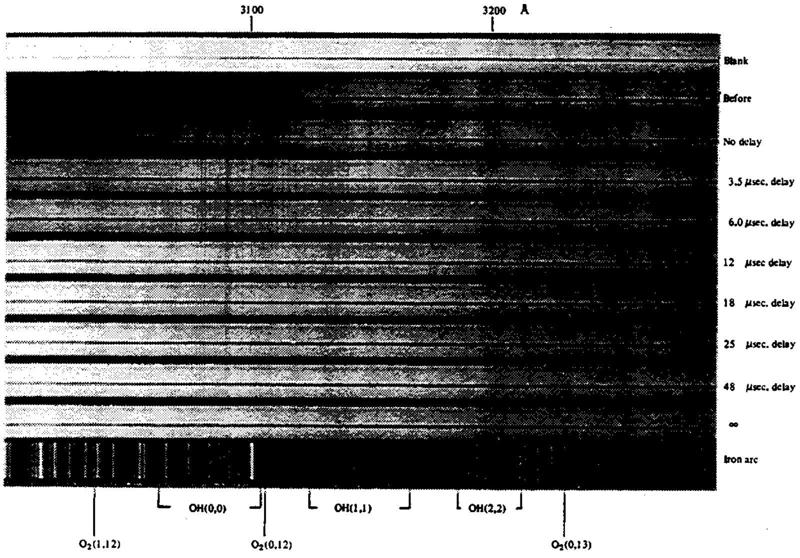
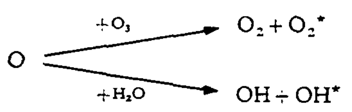


Fig. 11. The flash photolysis of water/ozone mixtures. Production of excited hydroxyl by reaction of O(^1D) with water vapour. Pressure of ozone, 6 mm Hg; pressure of water vapour, 4 mm Hg; pressure of nitrogen, 200 mm Hg. Flash energy, 1600 J. (Basco and Norrish[23])

by "orange" light where the magnitude of the quantum is only sufficient for the generation of ^3P oxygen atoms.

The chemical proof that the oxygen atoms generated by the photolysis of ozone in ultraviolet light are in the ^1D state lies in the fact that when small quantities of water vapour are added to the system the spectrum of vibrationally excited O_2 molecules is progressively suppressed and replaced by the absorption spectrum of OH as seen in Fig. 12. This is to be correlated with the observation-of Forbes and Heidt[39] that in "damp" ozone the quantum yield is increased to values as high as 130, as compared with their maximum value of 8 for dry ozone, and in the light of our observation it may be concluded that an entirely new mechanism of chain propagation is substituted as a consequence of the successful competition of water with ozone for the oxygen atom, *i.e.*:



This however can only take place if the 0 atom is excited to the ^1D state for the reaction of $O(^3P)$ with water is endothermic; we have

$$O(^3P) + H_2O = 2\,OH - 11\,\text{kcal}$$

$$O(^1D) + H_2O = 2\,OH + 34\,\text{kcal}$$

In the presence of water, the chain reaction may be written

$$O_3 + h\nu = O_2 + O(^1D)$$

$$O(^1D) + H_2O = OH + OH^*$$

$$\left.\begin{aligned} OH + O_3 &= HO_2 + O_2 \\ HO_2 + O_3 &= OH + 2\,O_2 \end{aligned}\right\}\ \text{propagation}$$

followed by chain ending by intercombination of radicals. This scheme satisfies the kinetic findings of Forbes and Heidt; it explains the appearance of the OH radical and demands the formation of the excited **O** atom. The reaction of 0 atoms with other hydrides referred to above is also equally dependent on the photolytic generation of $O(^1D)$ in the ultraviolet. It is significant that water has no effect on ozone photolysis in "orange" light where only ^3P oxygen atoms can be generated. The quantum yield remains unchanged at 2 in accord with the simple scheme[31]

$$O_3 + h\nu = O_2 + O(^3P)$$
$$O(^3P) + O_3 = O_2 + O_2$$

analogous to the photolysis of NO_2 and ClO_2.

It was shown by McGrath and Norrish[22] that the rate of decomposition of ozone by the secondary reactions subsequent to the flash is strongly affected by the addition of inert gases. Starting with 2.94 mm of O_3 and diluting with added gas to give a mixture ratio of O_3/M=1:163, the rate of disappearance of O_2 was determined by photometering the O_2 absorption in a series of spectra such as those shown in Fig. 13. In Fig. 14 are seen three typical curves showing ozone decay. From these curves could be measured the efficiences of third bodies M in the back reaction

$$O(^1D) + O_2 + M = O_3 + M'$$

When M is O_2 the ratio of O_2 to O_2 is 163:1 so it is hardly surprising that the above reaction predominates over the reaction

$$O(^1D) + O_3 = O_2 + O_2^*$$

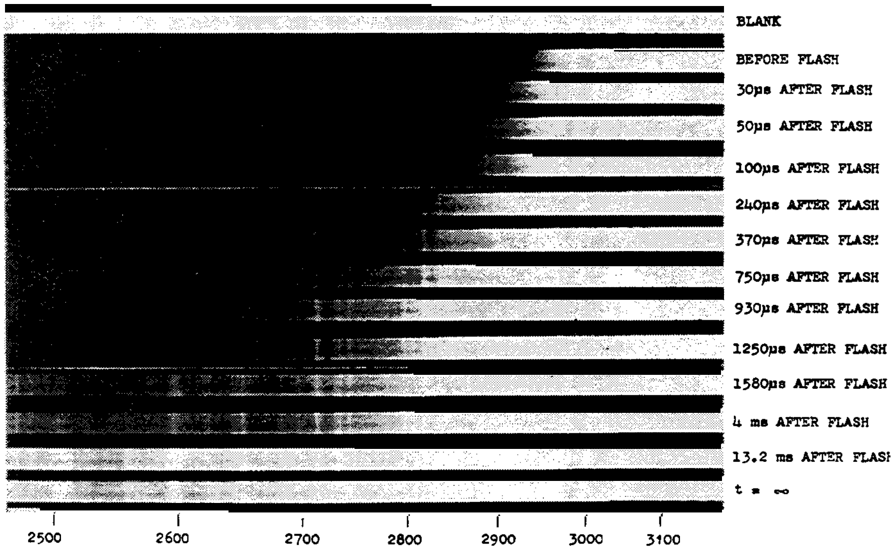


Fig. 13. Disappearance of ozone spectrum in time after flash. Flash energy, 1280 J. O_3/N_2 mixture, ratio 1 : 163. Ozone pressure, 2.93 mm Hg.

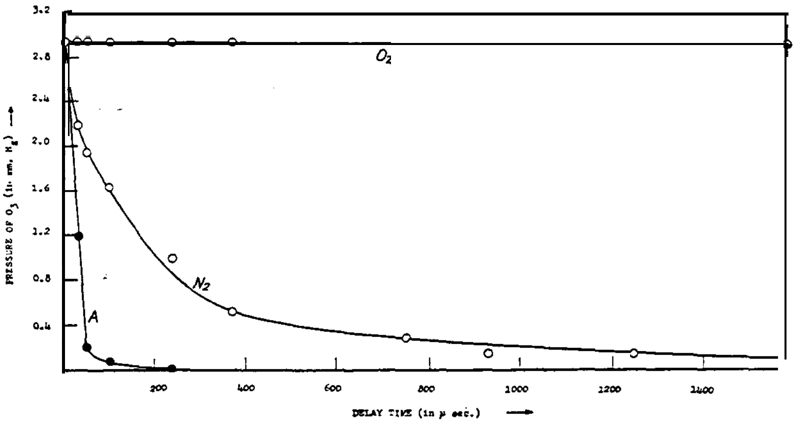


Fig. 14. Typical ozone decay curves for O_3/N_2, O_3/A and O_3/O_2 mixtures. Mixture ratio in all cases 1:163.

to such an extent as to reverse all O_2 decomposition. With other added gases the relative efficiences of the molecules M for the three body recombination were determined as He=1, A=1, SF_6=1.5, CO_2=14, N_2=16, N_2O=17.

The gases divide into two groups : (1) the inert gases and SF_6 and (2) N_2, CO_2 and N_2O. Group (1) exhibiting low efficiency are spherically symmetrical and chemically inert. Group (2) are much more efficient. It is possible with group (2) that some form of chemical affinity is operative in forming intermediate transition species, and that a more facile energy transfer is possible due to readily stimulated vibrational modes. Further work along these lines may well prove rewarding.

Application of the Adiabatic Method

The study of explosive processes exemplified by the oxidation of hydrides

The gaseous oxidation of hydrides, including hydrocarbons occurs by exothermic processes which have the characteristics of chain reactions, that is to say they proceed by initiation, propagation, multiplication and extinction of reacting centres. The reactions are said to be autocatalytic and if the conditions are such that multiplication of propagating centres exceeds extinction, the process may develop to explosion. These conditions depend on the parameters of temperature, total pressure, relative concentrations of reactants, catalytic activity of the surface in initiating or terminating reaction chains, the geometry of the reaction vessel, and the activity of added catalysts and inhibitors. The variation of these parameters gives rise to sharp limits of explosion, and by judicious kinetic experiment the separate effect of each can be isolated and defined by keeping all but the one under examination constant.

The development of the slow reaction and the incidence of ignition arc subject to an induction or incubation period during which autocatalysis occurs (initially exponentially) to a steady state or to explosive reaction. This autocatalysis is dependent on the magnitude of the "net branching factor", which is the result of the interplay of the physical parameters leading to multiplication and extinction of reaction centres. If in the notation of Semenov, f represents the sum of the reactions leading to multiplication and g the sum of those leading to extinction

$$(f-g) = \Phi$$

the net branching factor, which may obviously be positive or negative and the development of the reaction velocity *(v)* in time *(t)* is given by

$$v = A\,e^{\Phi t}$$

where the pre-exponential term A varies only slowly and in a much less dramatic way then Φ, with changing kinetic conditions. When Φ is negative from the beginning a finite and small stationary reaction velocity is imposed. When Φ is positive, rapid and exponential development of velocity to explosion may occur. This is the case with the reaction of hydrogen with oxygen which shows sharp explosive limits dependent on the parameters listed above. There exist cases, however, where Φ starting positive, may give rise to exponential development of the reaction in a big way, but owing to consumption of reactants or varying catalytic factors may become negative during the course of reaction which, as it were, starting hopefully towards explosive build up is finally quenched to a stationary state and subsequent decline, by the failure of the net branching factor to remain positive. Such reactions are termed degenerate explosions by Semenov. They are distinguished by having a small but positive initial value of Φ and depend for branching on the reaction of a "precariously stable" intermediate which builds up as the reaction proceeds and which can be detected by kinetic and analytical observation. The recognition of degenerately branched-chain reactions represents the culminating triumph in Semenov's interpretation of branching-chain reactions and in particular provides a pattern for the understanding of hydrocarbon oxidation[33].

But while giving us the overall pattern of reaction, neither the experimental methods nor the mathematical conceptions were capable of exposing the intimate nature of the precise reactions involved. These were deduced in some instances from circumstantial evidence, with the gradual realisation that atoms and free radicals are more often than not concerned in the chain processes.

It has remained for flash photolysis and kinetic spectroscopy not only to confirm and amplify the general conclusions of the classical studies of chain reactions, but also to provide objective proof of the nature and reactions of the transient participating species. For this purpose we use the *adiabatic* method taking advantage of the free radicals produced by pyrolysis and photolysis for initiation, and flash heating to generate temperatures suitable to sustain the propagation and branching reactions upon which the autocatalytic chain reaction depends. We take for example the case ofhydrides.

Since oxygen does not absorb energy from the photolytic flash under the condition imposed by the limitations of the transparency of quartz, it is fortunate therefore that many hydrides absorb sufficiently to provide the necessary pyrolysis for initiation. This is true for hydrogen sulphide, hydrogen telluride, ammonia, hydrazine, and phosphine, all of which photolyse isothermally and pyrolyse adiabatically by eliminating a hydrogen atom:

$$XH_n + h\nu = XH_{n-1} + H$$

The growth and decay of the free radical XH_{n-1} so generated can be followed by kinetic spectroscopy. Under pyrolytic conditions however when the concentration of free radicals generated may be high, the above reactions may be followed by further elimination of hydrogen from the free radical, e.g.

$$XH_{n-1} + XH_{n-1} = XH_n + XH_{n-2}$$

This is true for example for ammonia (Husain and Norrish[34]), which under isothermal conditions gives only NH, but under adiabatic conditions yields NH radicals as well. We observe the same result with PH_3 (Norrish and Oldershaw[35]), H_2S (Norrish and Zeelenburg[36]), and H_2Te (Norrish and Osborne[37]), the last two yielding HS and S, and HTe and Te respectively even under isothermal conditions as shown for example in Fig. 15.

The pyrolytic reactions under our conditions are generally limited in extent, but on the addition of oxygen in sufficient quantity oxidation proceeds to explosion, unless the system is partially cooled by the addition of an inert diluent. Sufficient excess fuel or oxygen has the same effect. Under such conditions the oxidation proceeds by a quenched-chain reaction, and is much more limited in extent.

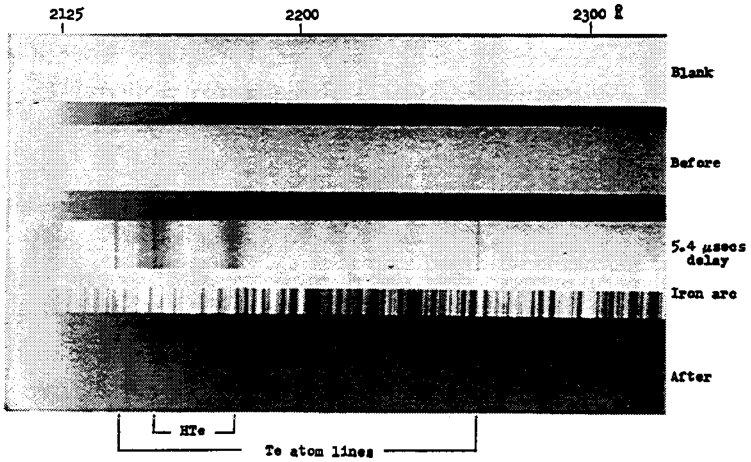


Fig. 15. Flash photolysis of tellerium hydride. Pressure of TeH_2, 0.25 mm Hg; pressure of N_2, 350 mm Hg. Flash energy, 2 500 J. (Norrish and Osborne[37])

The development of reaction from initiation to explosion involves an incubation period of less than a millisecond, and in oxygen rich mixtures the onset of ignition is marked by a copious burst of hydroxyl radicals. It is clear that in all cases studied the hydroxyl radical acts as a chain carrier.

Hydrocarbons on the other hand do not in general absorb light transmitted by quartz (with the exception of highly unsaturated compounds) and the fuel oxygen mixture therefore does not respond to the flash. To initiate explosive reaction it is necessary to add a small quantity of sensitizer such as chlorine, nitrogen peroxide or alkyl nitrite. These, by absorbing strongly, raise the temperature of the system, and simultaneously photolyse and pyrolyse to give free atoms or radicals which act as initiators. Nitrogen peroxide for example absorbs strongly throughout the spectrum and yields oxygen atoms which give ready initiations*

$$NO_2 \rightarrow NO + O$$

In Fig. 16 is shown a sequence of absorption spectra illustrating the explosion of a mixture of $2\ H_2 + O_2$ sensitized by nitrogen peroxide[39]. The growth and decay of the OH radical is seen in the (0,0) and (0, 1) bands of the transition $^2\Sigma^+ - ^2\Pi$. This and the earlier study of the reaction of oxygen atoms with hydrogen by Norrish and Porter[38] go far to confirming the scheme of oxidation of hydrogen proposed by Lewis and Von Elbe[40] of which the following are some constituent reactions

$$\left.\begin{aligned} OH + H_2 &= H_2O + H \\ H + O_2 &= OH + O \\ O + H_2 &= OH + H \end{aligned}\right\} \text{Propagation and branching}$$

$$\left.\begin{aligned} OH + \text{surface} &= \text{products} \\ H + O_2 + M &= HO_2 + M' \end{aligned}\right\} \text{termination}$$

The explosion of hydrocarbons sensitized by amyl nitrate was studied by Erhardt and Norrish[41] and is illustrated in Figs. 17 and 18 which show the effect of adding tetraethyl lead to a mixture of hexane and oxygen. The first shows the ignition in the absence of the addendum with the rapid disappearance of the spectrum of the sensitizer on flashing, followed by an incubation period of 875 μsec to the onset of explosion as marked by the sudden growth of the OH radical. The second shows the ignition under identical conditions in the presence of the addendum. It is seen that the incubation. period is increased some three-fold to *ca.*2600 μsec, while during the growth to explosion the spectrum of gaseous lead oxide is strongly developed. At the point of ignition the PbO spectrum disappears completely and is replaced by the

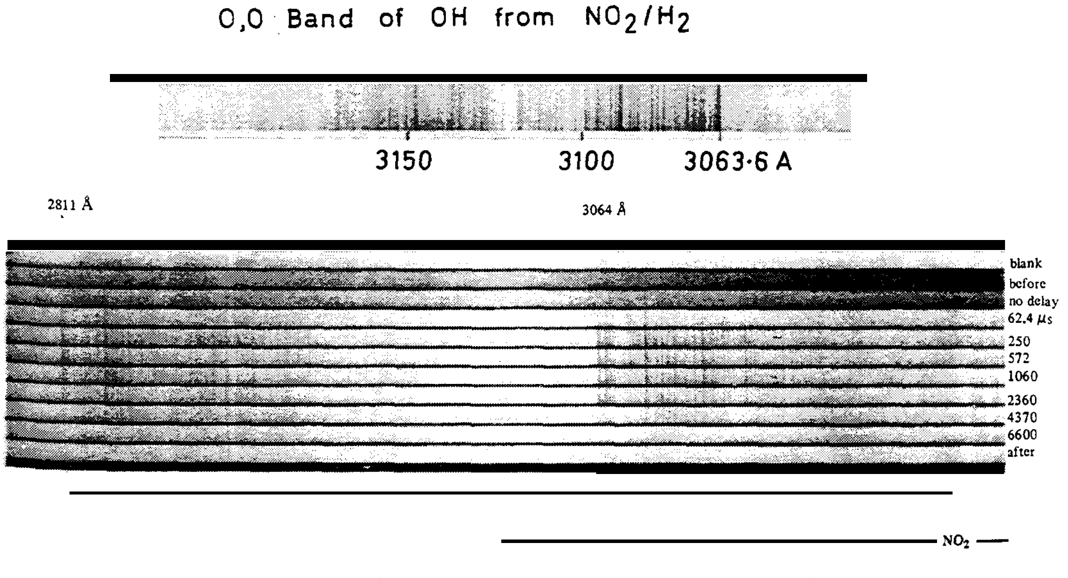


Fig. 16. (a) Photo-reaction of NO$_2$+ H$_2$giving OH radical. Pressure of H$_2$, 2 mm Hg; pressure of NO$_2$, 2 mm Hg. No delay. (Norrish and Porter[38]) (b) Flash photolysis of NO, (2 mm) + H$_2$(20 mm) + O^2(10 mm) + N$_2$(15 mm) showing the formation and decay of OH during a typical explosion. Flash energy, 3 300 J.

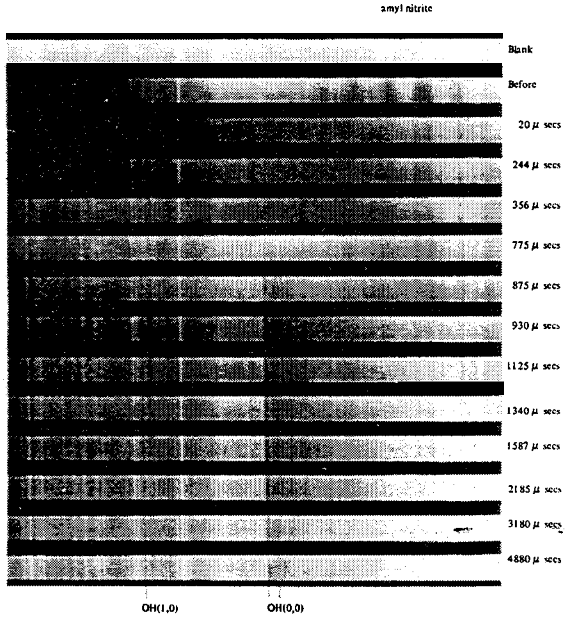


Fig. 17. Spectra vs. time. Explosion of hexane and oxygen sensitized by amyl nitrite. Pressure of C_6H_{14}, 2 mm Hg; pressure of $C_5H_{11}ONO$, 2 mm Hg; pressure of O_2, 32.5 mm Hg. Flash energy, 2000 J. (Erhard and Norrish[41])

resonance spectrum of lead. Both the OH and the Pb spectra are very faintly visible before ignition. These and other experiments in which ignition was observed photoelectrically by the sudden growth of OH emission, throw light upon the mechanism of antiknock in the internal combustion engine which we conclude to be dependent on the moderating effect of Pb and PbO on the development of the autocatalytic growth to explosion.

Knock has been proved by Miller[42] and Male[43] to be due to the homogeneous detonation of the residual charge in the cylinder at the end of the ignition stroke. It is believed to be due to the generation of centers of autoignition (peroxides, aldehydes, etc.) due to adiabatic rise of temperature, which replaces the smooth explosion wave generated by the spark ignition. We have concluded that the tetraethyl lead clearly must operate in the gas phase and suggest that (1) it may remove the centers of autoignition by reduction - e.g. peroxides may be removed by

$$\mathrm{R{\cdot}OOH + Pb(C_2H_5)_4 \rightarrow PbO + products}$$

and (2) moderate the liberation of energy as the reaction develops to explosion by the following reactions

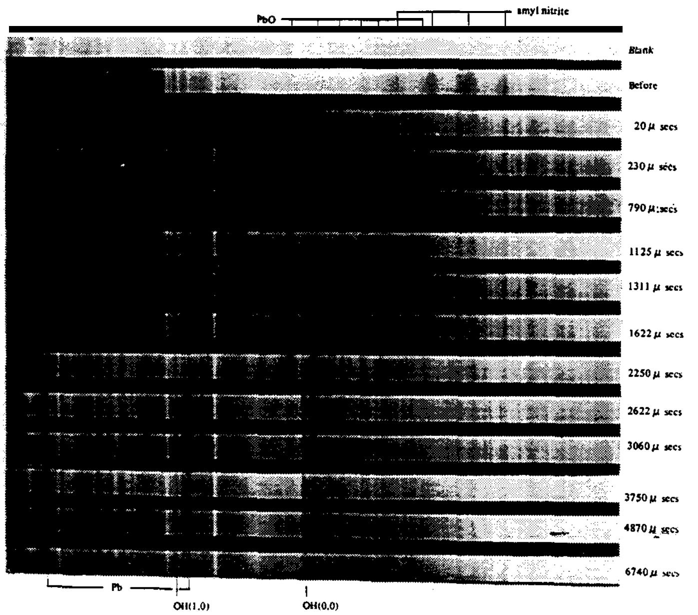


Fig.18. Spectra vs. time. Effect of tetraethyl lead on the hexane explosion. Pressure of C_6H_{14}, 2 mm Hg; pressure of $C_5H_{11}ONO$, 2 mm Hg; pressure of O_2, 32.5 mm Hg; pressure of tetraethyl lead, 0.2 mm Hg. Flash energy, 2 000 J. (Erhard and Norrish[41])

$$\mathrm{OH} + \mathrm{Pb} \rightarrow \mathrm{PbOH} \xrightarrow{+\mathrm{OH}} \mathrm{Pb(OH)_2} \xrightarrow{-\mathrm{H_2O}} \mathrm{PbO}$$

$$\mathrm{PbO} + \mathrm{R} \rightarrow \mathrm{RO} + \mathrm{Pb}$$

Thus by alternate oxidation and reduction from lead to lead oxide and back again the atomic lead and lead oxide can intervene in chain propagation by the removal of OH, and so by shortening the chains retard their development. With the onset ofexplosion, the PbO is instantaneously decomposed to atomic lead, which as the system cools is finally deposited on the surface of the reaction vessel.

The question as to whether moderation of the explosive process occurs in the gas phase, or by chain ending on heterogeneous particles of lead or lead oxide ("smoke") would appear to be answered by these results, since no "smoke" is observed during the course of the reaction, which is seen to be completely homogeneous. In contrast the addition of tetraethyl tin which has no anti-knock action is accompanied by the copious formation of smoke. There is no sign of the production of gaseous SnO during the incubation period and no effect whatsoever on the said incubation period and the reactions leading to ignition[44]. This is due to the lower volatility of SnO.

Many other studies of the affects ofaddenda on explosive reactions of hydrocarbons have been made by Callear and Norrish[44] with interesting results which cannot be discussed here. Reactions of this kind provide a plentiful source of free radicals and atoms derived from the addenda in high temperature reactions.

The growth and decay of free radicals as we pass through ignition is shown for the combustion of acetylene sensitized by NO, in Figs. 19 and 20 (Norrish, Porter and Thrush[45]). The curves were obtained by plate photometry of the various radical spectra seen in absorption at increasing intervals after initiation.

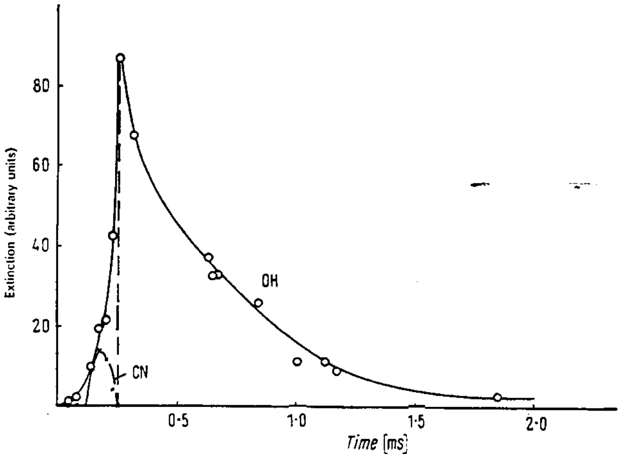


Fig. 19. Growth and decay of OH and CN radicals in oxygen-rich mixture of acetylene and oxygen (NO_2 counting as O_2). Pressure of C_2H_2, 10 mm Hg; pressure of O_2, 10 mm Hg; pressure of NO_2, 1.5 mm Hgl (Norrish, Porter and Thrush[45])

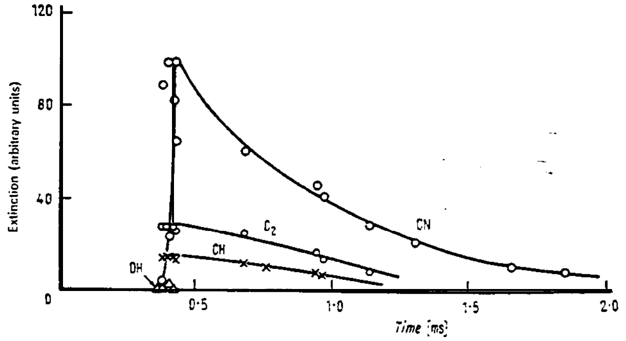


Fig. 20. Growth and decay of radicals in fuel-rich mixture of acetylene and oxygen. Ordinates of curves not comparable since extinction coefficients of radicals unknown. Pressure of C_2H_2, 13 mm Hg; pressure of O_2, 10 mm Hg; pressure of NO_2, 1.5 mm Hg. (Norrish, Porter and Thrush[45])

They are also typical of curves obtained for ethylene and methane[46] and indicate the growth and decay of the observed radicals with time, though they cannot be compared in terms of absolute concentration since the extinction coefficients of the radicals are at present unknown. The combustion of acetylene and ethylene were shown by Bone[47] to depend on the stoichiometric equations

$$C_2H_2 + O_2 = 2CO + H_2$$
$$C_2H_4 + O_2 = 2CO + 2H_2$$

according to which there is an apparent preferential burning of carbon. With oxygen in excess, water is formed, while in fuel-rich mixtures free carbon in the form of smoke is produced. These two conditions are very sharply distinguished on either side of the fuel-oxygen ratio of 1:1. This classical result is very clearly confirmed by the curves shown in Figs. 19 and 20. In the former we have an oxygen-rich system and the formation of water is indicated by the copious display of OH, in the latter - the fuel-richsystem - the OH is barely in evidence and the precursors of free carbon arc observed in the CH, C_2, and C_3 radicals. The change from one type of display to the other takes place extremely sharply at the fuel : oxygen ratio of 1:1, nitrogen peroxide for this purpose being counted as oxygen.

The CN radical which is strongly in evidence in fuel-richsystems is derived from the sensitizer. It has been shown[48] that during the induction period of about 0.5 msec the temperature rises exponentially, slowly at first and very sharply at the end. With the sudden appearance of the free radicals the explosive reaction is complete: we are witnessing in fact the afterburning of hydrogen in oxygen-rich mixtures, and the after-cracking of the fuel in fuel-rich mixtures. The only radical which can be seen during the induction period before ignition is the OH radical which grows in concentration as the reaction develops.

Further experiments with fuel-rich mixtures[46] indicated the growth and decay of a precursor of free carbon which followed closely the growth and decay of the carbon radicals C_2, C_3 and CH. It was possible to deduce the extinction coefficient of this carbon precursor at 3 700 Å and to show that its high value is characteristic of aromatic polynuclear hydrocarbons. It may be suggested49 that in the high temperature of the flame (> 3 000°C) cracking of some of the excess fuel occurs to yield free carbon atoms, which progressively "crystallise" through C_2 and C_3 to the "aromatic" structure of graphite. The confirmation or otherwise of this view must await further studies of the products of explosion by means of the vacuum spectrograph when we may hope to see the resonance line of carbon in absorption.

A General Mechanism for the Combustion of Hydrides

As I have mentioned above we have noted that the hydroxyl radical is common to the ignition processes of all the hydrides so far examined. Where initiation occurs by the direct photolysis of the hydride yielding an H atom, it may be generated by the reaction

$$\mathrm{H} + \mathrm{O_2} = \mathrm{OH} + \mathrm{O}$$

When initiation is by the photolysis of a sensitizer yielding oxygen atoms as with NO_2, OH may be derived from the reaction.

$$\mathrm{O} + \mathrm{XH}_n = \mathrm{OH} + \mathrm{XH}_{n-1}$$

During the incubation period the OH is observed gradually to increase, and the instant of ignition is marked in oxygen-rich mixtures by a very sudden and enormous increase in its concentration. By detailed comparison of the oxidation reactions of H_2S, NH_3, PH3 and hydrocarbons it may be concluded that the pattern of chain propagation is the same in all cases, and represented by the general scheme

$$\left.\begin{aligned} \mathrm{OH} + \mathrm{XH}_n &= \mathrm{H_2O} + \mathrm{XH}_{n-1} \\ \mathrm{XH}_{n-1} + \mathrm{O_2} &= \mathrm{XH}\ \mathrm{O} + \mathrm{OH} \end{aligned}\right\} \text{propagation}$$

Branching is dependent on the intermediate and may take place variously by any one of the following reactions

$$\begin{aligned} \mathrm{XH}_{n-2}\mathrm{O} + \mathrm{O_2} &= \mathrm{XH}_{n-2}\mathrm{O_2} + \mathrm{O} \\ \mathrm{XH}_{n-2}\mathrm{O} + \mathrm{O_2} &= \mathrm{XH}_{n-3}\mathrm{O} + \mathrm{HO_2} \\ \mathrm{XH}_{n-2}\mathrm{O} &= \mathrm{XH}_{n-3}\mathrm{O} + \mathrm{H} \end{aligned}$$

The first reaction takes place in the autocatalysis of H_2S oxidation, in which SO (seen by kinetic spectroscopy) is the intermediate. The second occurs in the oxidation of methane which yields formaldehyde (readily detectable during the reaction by conventional methods of analysis). The third is exemplified by the oxidation of ammonia in which HNO is concluded to be the origin of chain branching.

Table 2

Hydride	*Uniradical*	*Associated intermediate*	*Reference*
SH_2	SH	SO	36
TeH_2	TeH	TeO	37
NH_3	NH_2	HNO	34
PH_3	PH_2	HPO	35
N_2H_4	N_2H_3	NH_2NO	34
CH_4	CH_3	H_2CO	50
C_2H_4	CH_3	H_2CO	51
B_2H_6	BH_2	HBO	52

Table 2 shows the uniradical and the associated intermediate derived from a series of hydrides which take part in chain propagation and branching, in accordance with our conclusions based on comparative study both by classical kinetic methods and flash photolysis. In cases where the intermediate is moderately stable, as with SO from H_2S and H_2CO from CH_4 the overall oxidation exhibits the slow autocatalysis associated with degenerate branching. In other cases, with extremely unstable intermediates the branching factor may be high, and is reflected in kinetics which show very short incubation periods and sharp transition from very slow reaction to explosion.

All the uniradicals and associated intermediates are seen to be isoelectronic or electronically structurally similar. This and the uniform participation of the OH radical in all the chain-propagation reactions would seem to provide a generalizing hypothesis of value and one which invites further experimental examination.

In connexion with the continued study of the reactions of the OH radical, Home and Norrish[53] have recently been able to measure quantitatively the kinetics of the reactions

$$OH + C_2H_6 \xrightarrow{k_4} C_2H_5 + H_2O$$
$$(\log_{10}k_4 = (11.1 \pm 0.7) - (3600 \pm 600)/2.303\,RT \text{ l mol}^{-1}\text{ sec}^{-1})$$

and

$$OH + CH_4 \xrightarrow{k_5} CH_3 + H_2O$$
$$(\log_{10}k_5 = 10.7 - 5000/2.303\,RT \text{ l mol}^{-1}\text{ sec}^{-1} \text{ approximately})$$

by kinetic spectroscopy.

The OH radicals were generated by flashing water vapour in highly transparent quartz and comparing their rates of decay in the presence of inert gases and hydrocarbons. Further measurements of this kind with other hydrides will be of value to the continued study of the combustion of hydrocarbons along the lines indicated above. They are also of course of importance in consideration of the reactions involved in the evolution of planetary atmospheres, as are many other reactions studied by kinetic spectroscopy such as the photochemistry of NO, and of ozone and the reactions of the oxygen atom described above.

The examples which I have cited give, I hope, some indication of the breadth of application of methods based on flash photolysis in the study of gas reactions. Other results of importance involve the discovery of new absorption spectra of chlorine and bromine by Briggs and Norrish[54], and the detection of population inversion such as is observed in the study by Donovan and Husain (ref. 55) of spin orbit relaxation of the metastable iodine atom I $(5^2P_{1/2})$ produced in the photolysis of CF_3I

$$\mathrm{I}\,(5^2P_{1/2}) \rightleftharpoons \mathrm{I}\,(5^2P_{3/2})$$

Population inversion in favour of high vibrational levels is as we have seen also observed in NO and CN, and has also been studied effectively by Polanyi and his co-workers[56] for atomic reactions such as

$$\mathrm{H} + \mathrm{Cl_2} = \mathrm{HCl^*} + \mathrm{Cl}$$

$$\mathrm{Cl} + \mathrm{HI} = \mathrm{HCl^*} + \mathrm{I}$$

All these reactions form the basis of potential gas laser action and are being effectively studied in this connexion.

The opportunity for the application of the methods of flash photolysis to chemical kinetics, not only in the gas phase, but also to the study of photochemical reactions in solution is very great, and is increasing steadily as improvement in technique gives greater time resolution, and ever increasing accessibility to reactions of the "vacuum ultraviolet".

In conclusion I give thanks to those who have collaborated and contributed to the work described in this lecture, many of whom are continuing to direct and develop it with distinction.

Mr. Chairman, ladies and gentlemen, thank you for your interest and attention.

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