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The Kinetics and Analysis of Very Fast Chemical Reactions

R. G. W. Norrish

The reactions about which I propose to speak are considered fast because they take place in times measured by microseconds and milliseconds. They comprise adiabatic processes such as explosive and pyrolytic reactions which themselves are made up of intermediate reactions involving transients of very short life, and also the isothermal reactions of atoms and radicals in both gaseous and liquid media. Reactions in this category, whose half-lives vary between 10^{-6} and 10^{-2} seconds, are not the fastest known processes: they are exceeded by ionic processes in solution, by the reactions of many electronically excited species and by the relaxation of rotational energy of molecules. They comprise, however, a very large class which until recently it had not been possible to follow kinetically or to analyse objectively. Very much had indeed been achieved by the study of the overall kinetics and stoichiometry of explosive and photochemical processes, and the various patterns of chain reactions and radical reactions which have emerged constitute an impressive inductive achievement. That the new methods of kinetic spectroscopy have confirmed in no small measure the modern deductions from reaction theory is satisfactory, but I hope to show here that they have also contributed much in their own right, and have elucidated mechanisms of chain reactions, radical processes and relaxation phenomena which were hitherto obscure.

The methods of flash photolysis and kinetic spectroscopy which were discovered in our laboratory at Cambridge and developed in the beginning by Porter are well known (*1, 2*), so I shall refer only to the general principles involved. When a powerful flash created by a discharge of 2000–4000 joules through an inert gas is applied to a photochemically responsive system, very high momentary concentrations of atoms and free radicals are produced. The concentrations produced are in certain cases so high that radical-radical reactions are more important than radical-molecule reactions. They are also so high as to make possible the photography of their absorption spectra by a second flash-lamp triggered electronically by the first flash at specific intervals of 0–10^4 microseconds after the first. Thus by a series of experiments the growth and decay of transient species in the reacting system may be observed. The first flash is called the photoflash; the second, which is of much lower intensity and results from a discharge of about 100 joules through inert gas, is called the specflash. The general plan of the apparatus is shown in Fig. 1. The success of the method depends upon making the duration of the photoflash and specflash for a given output of

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energy as short as possible, and this is achieved by making the capacity of the condensers as low as possible, and the potential difference as high as possible. The energy output, E, in joules is given by $E = \frac{1}{2} CV^2$, where C is the capacity in microfarads and V is the potential in kilovolts. Inevitably a compromise has to be achieved. The voltage cannot be made too high, otherwise the electrical system is unstable. We generally use for the photoflash a capacity of 40–50 μfarad and a voltage of 10 kilovolts; if the self-induction of the circuit is brought as low as possible this gives a flash with a half-life of about 8–10 μsec. Similarly the specflash can be limited to 1–2 μsec duration. Considerations of this kind limit the time-scale of the instrument to microseconds, and though it is possible that in the future improvement in electrical technique may give still shorter flashes and a corresponding improvement in time resolution, we have felt justified in calling a halt to development in order to exploit as far as possible the great potentialities of the existing instrument. With this in mind I will now endeavour to describe some typical results, together with some new ideas arising therefrom, which demonstrate the flexibility and power of the techniques of flash photolysis and kinetic spectroscopy. I must limit myself to gaseous reactions, though many reactions in solution have been successfully studied.

Adiabatic and Isothermal Processes

It early became apparent that when gaseous photochemical systems such as halogens, nitrogen peroxide and ketones are submitted to the photoflash, virtually complete dissociation occurs. The light flux is such that during the period of the flash each molecule probably suffers many dissociations and recombinations. Thus the light energy of the flash which was absorbed by the system is very rapidly degraded to heat, either by chemical reaction or collisional relaxation, and it can be very readily calculated from a knowledge of the magnitude of the absorbed light flux that very high temperatures amounting to 2000°–3000°C are instantaneously produced in the reactant. Unless precautions are taken, the system is thus subjected to a considerable adiabatic shock, and the reactions observed are pyrolytic rather than photochemical in character. This forms the basis of the *adiabatic method.*

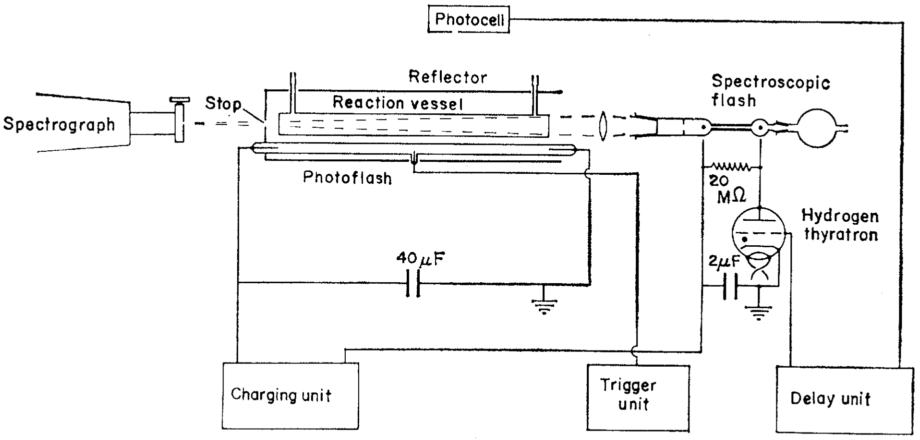


Fig. 1. Schematic diagram of apparatus for flash photolysis and kinetic spectroscopy.

By allowing the temperature to rise in a potentially reactant system, both pyrolyses and explosive processes can be studied, and since the temperature rise can be controlled by the addition of inert gas, explosive limits dependent on temperature (that is, flash energy) and pressure can be explored. If, however, the pressure of the reactant is kept low —usually less than 1 millimeter—and a high pressure (some 200- to 600-fold) of an inert diluent gas is added to increase the heat capacity of the system, the temperature rise can be kept below 10° C, and a wide range of photochemical reactions involving atoms and free radicals can be studied to advantage. For reactants in solution there is of course no problem, since the solvent is an effective diluent. We call this method of experimentation the *isothermal method;* it makes possible the study of the absorption spectra and reactions of free radicals and excited molecules, and the relaxation of vibrational energy in isothermal systems, where this was not possible before. I shall now give some examples of the results achieved, firstly by the adiabatic and secondly by the isothermal method.

The Adiabatic Method

Pyrolysis and combustion of gaseous hydrides. The hydrides of sulphur, nitrogen and phosphorus all absorb sufficiently strongly in the ultraviolet to give both photolytic and pyrolytic dissociation when subjected to flash photolysis under respectively isothermal or adiabatic conditions. The radicals HS, PH_2, PH, NH and NH_2 are observed in absorption immediately after flashing hydrogen sulphide (*3*), phosphine (*4*), ammonia and hydrazine (*5*). They are concluded to arise from two sources; the radicals SH, PH_2 and NH_2 are the result of primary dissociation

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

The radicals PH, NH and S result from secondary reactions such as

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

and

$$XH_{n-1} + H \quad = XH_{n-2} + H_2$$

it being remembered that under the conditions of flash pyrolysis radical-radical reactions become highly significant.

In the case of ammonia, the generation of NH_2 radicals is also confirmed by the recognition of small quantities of hydrazine, while in the case of hydrazine itself the spectroscopic observations are in agreement with the interpretation of Ramsay (*6*):

$$\begin{aligned} N_2H_4 + h\nu &= NH_2 + NH_2 \\ NH_2 + N_2H_4 &= NH_3 + N_2H_3 \\ N_2H_3 &= NH + NH_2 \end{aligned}$$

the last reaction taking place at high temperatures since the NH absorption is only observed under adiabatic conditions. In all cases, the radicals NH and PH, and probably S, are only produced as the result of secondary reactions under pyrolytic conditions.

When one of the above hydrides is mixed with oxygen, either explosive or slow reaction occurs in all cases. This arises from the generation of free radicals which initiate reaction chains of oxidation and from the rise of temperature due to flash-heating. Sharp limits of ignition are observed which, as may be expected, are conditioned by the intensity of the initiating photoflash. The most difficult case is that of phosphine, because of its spontaneous combustion with oxygen. However, with the help of inert gas, one can prepare mixtures above the upper limit and below the lower limit of ignition that are susceptible to flash photolytic ignition. Though the physical conditions of temperature and pressure vary from hydride to hydride, certain important general features emerge: firstly, an incubation or induction period of from half to one or two milliseconds during which the products of the pyrolysis of the hydride appear, accompanied usually by the absorption spectrum of the OH radical; secondly, the explosion, generally accompanied in oxygen-rich mixtures with a burst of hydroxyl; and the subsequent rapid appearance of the reaction products. Let me illustrate this by two cases—hydrogen sulphide and ammonia.

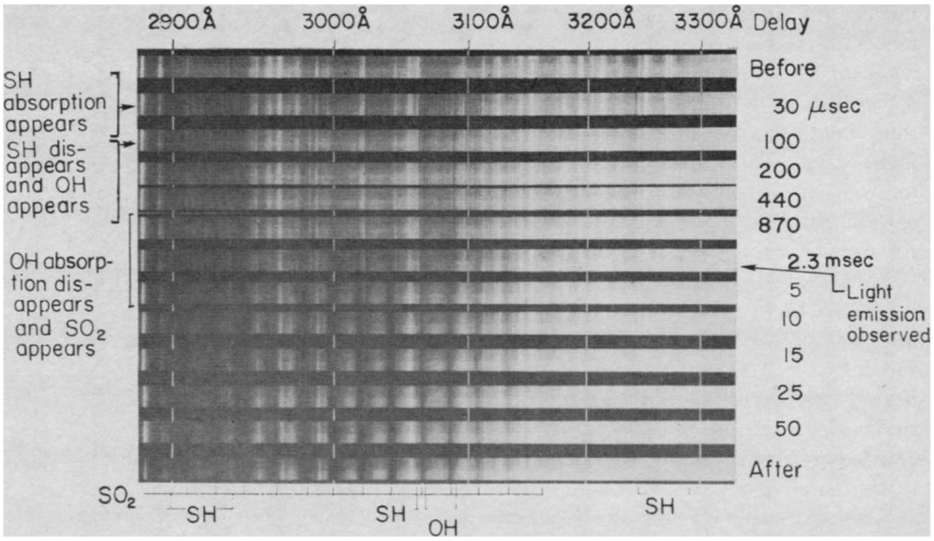


Fig. 2. Spectra against time. 1 mm H_2S + 3 mm O_2. Flash energy 1500 joules.

In Fig. 2 is shown the explosion of 1 mm of hydrogen sulphide with 3 mm of oxygen as observed by Dr. Zeelenberg (*3*). During an induction period of about 1 millisecond both the SH and OH radicals are visible. The explosion is accompanied by a sharp flash, followed by the appearance of sulphur dioxide. The reaction is complete. In the presence of sufficient inert gas as coolant, no explosion occurs, and though the same initiating radicals are observed, no sulphur dioxide is produced, the final products being characterized by the strong absorption spectrum of S_2O_2. Under these conditions the reaction is far from complete (see Fig. 3).

A full consideration of these and many other results led us to the following mechanism of reactions:

$H_2S + h\nu = SH + H$		Initiation
$H + H_2S = SH + H_2$	+ 19 kcal	
$SH + O_2 = SO + OH$	+ 16 kcal	Propagation
$OH + H_2S = H_2O + SH$	+ 22 kcal	
$SO + SO = S_2O_2$	+ 49 kcal	Chain termination (slow reaction)
$SO + O_2 = SO_2 + O$	+ 18 kcal	Chain branching (explosive reaction)
$O + H_2S = OH + SH$	+ 19 kcal	
$SO + O = SO_2^* = SO_2 + h\nu$		Chain termination and light emission in explosive reaction

When H_2S is in excess, and also in the pyrolytic reaction,

$$HS + HS = S_2 + H_2,$$

or

$$HS + H = H_2 + S,$$

occurs, giving rise to the absorption spectrum of S_2.

In the case of ammonia (*5*), studied by Dr. Husain, the results are typified by the appearance of NH and OH during the induction period, followed by the sudden appearance of the absorption spectrum of nitric oxide and a burst of hydroxyl at the instant of ignition (see Fig. 4). Coupled with the results of flash pyrolysis of ammonia, we deduce the following mechanism for the explosive oxidation of ammonia initiated by flash photolysis:

$NH_3 + h\nu = NH_2 + H$	Initiation
$NH_2 + O_2 = HNO + OH$	Propagation
$OH + NH_3 = NH_2 + H_2O$	
$HNO = H + NO$	Branching
$H + H + M = H_2$	Termination
$H + OH + M = H_2O$	

Small quantities of N_2O are also observed and probably arise from the reaction

$$HNO + HNO = H_2O + N_2O.$$

The oxidation of hydrocarbons such as methane, ethylene and acetylene follows the same pattern as that of other hydrides; it is characterized by induction periods of the order of a millisecond, and, in the case of oxygen-rich mixtures, a burst of hydroxyl at the point of ignition (*7*). For fuel-rich mixtures the hydroxyl spectrum is very faint, and at the point of ignition is replaced by a burst of hydrocarbon radicals (CH, C_2, C_3, etc.) seen in absorption for the first time. For such systems, as also for hydrogen and oxygen mixtures, which do not absorb the radiant energy emitted in the photoflash, a sensitizer is needed that will absorb sufficient energy to raise the temperature and also by photolysis furnish free radicals for initiation of reaction chains; both nitrogen peroxide and amyl nitrite are very efficient. Nitrogen peroxide, for example, is dissociated by ultraviolet light to give oxygen atoms

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

and these reacting with the fuel furnish hydroxyl and hydrocarbon or hydrogen radicals by which reaction chains may be initiated (*8*). For example,

$$H_2 + O = H + OH$$
$$CH_4 + O = CH_3 + OH$$

An example of the explosion of $2H_2 + O_2$ marked by the growth and decay of the OH radical is shown in Fig. 5.

The explosive combustion of such hydrocarbons as acetylene and ethylene is conditioned by the stoichiometric equations of Bone (*9*),

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

according to which there appears to be a preferential burning of carbon. If oxygen is in excess, water is produced; if on the other hand the mixture is fuel-rich, smoke is formed. This is to be correlated with the appearance of OH in oxygen-rich mixtures and carbon radicals when the fuel is in excess of the equimolecular mixture. By photometry the growth and decay of the free radicals can be followed. It is apparent that during the induction period a rise of temperature occurs as indicated by the rotational-vibrational structure of NO γ-bands derived from the sensitizer, and that the temperature after a slow start finally rises exponentially to the ignition temperature of the mixture. The hydrocarbon radicals observed are the result of after-cracking of the excess hydrocarbon and the burst of hydroxyl in oxygen-rich mixtures arises from the after-burning of the hydrogen. The only radical to be seen during the induction period, albeit faintly, is the hydroxyl radical, and this is the only radical indicated by flash photolysis as participating in the pre-flame chain reactions.

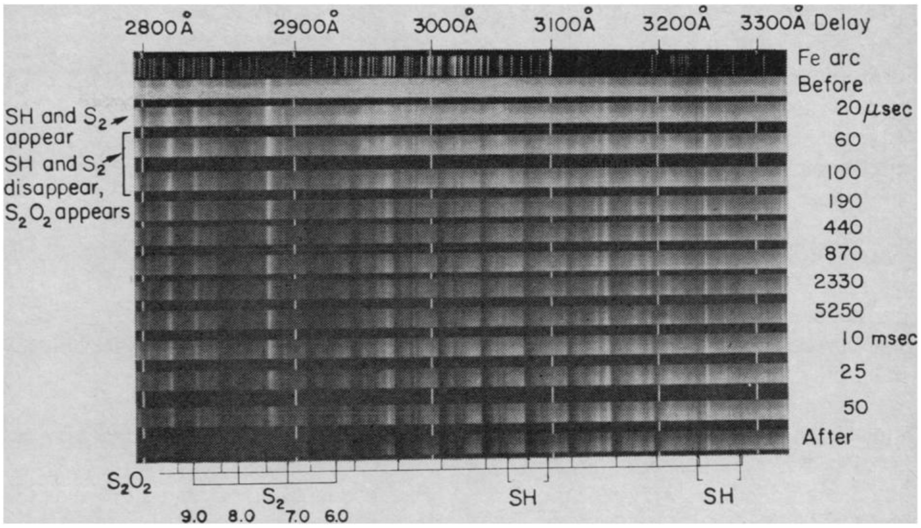


Fig. 3. Spectra against time. 1 mm H_2S + 3 mm O_2 + 40 mm N_2. Flash energy 1500 joules. (The S_2 bands unfortunately do not reproduce clearly on the plate.)

Knock and antiknock. The explosion produced in an explosive mixture by the photoflash is homogeneous and practically simultaneous throughout the whole of the irradiated reaction vessel, so that in a tube 0.5 meter long we virtually have a flame-front 0.5 meter thick. It is this which makes it possible to photograph the absorption spectra of transients (*10*). The conditions are similar to those in an internal combustion engine when the "rest gas" towards the end of the piston stroke ignites homogeneously—that is, detonates—giving rise to the damaging condition of "knock."

The action of antiknocks such as lead tetraethyl can be studied by kinetic spectroscopy. For example, when a small quantity of lead tetraethyl is added to the hydrocarbon-oxygen charge, the induction period is greatly lengthened and the absorption spectrum of gaseous lead oxide appears and increases in intensity up to the point of ignition, when it is instantaneously suppressed and replaced by the absorption spectrum of atomic lead. The evidence goes to show that atomic lead intervenes in the chain development by reacting with the hydroxyl radicals to produce gaseous lead oxide, which in its turn is reduced to lead by the hydrocarbon radicals, and also by reducing oxygenated intermediates responsible for chain branching. Thus the development of the pre-flame reaction and the release of energy is retarded and detonation prevented. To illustrate these points, in Figs. 6 and 7 the ignitions of hexane in the absence and presence of lead tetraethyl, with amyl nitrite as sensitizer, are compared. For antiknock action to occur it appears that the products derived from the lead tetraethyl must remain in the gaseous state. No heterogeneity in the form of "smoke" is observed. In contrast, tin tetraethyl, which has no antiknock action, forms copious smoke during the pre-flame period, and the spectrum of gaseous tin oxide is not observed until after the ignition. In other words, tin oxide is not sufficiently volatile to vaporize during the induction period, while the heterogeneous particles of tin oxide have no effect upon the development of the reaction.

This method of study of antiknock has been amplified by observing the rate of release of energy in terms of the light emission of the various radicals such as OH or CH with a photocell

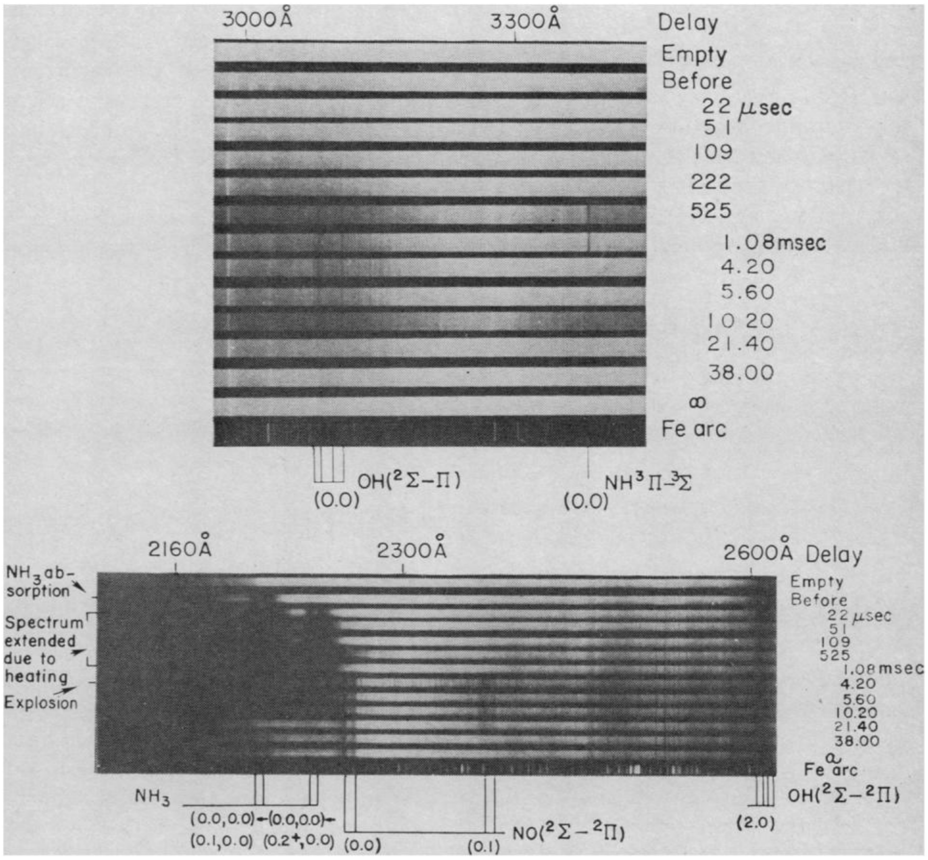


Fig. 4. (Top) The growth and decay of NH and OH resulting from the flash photolysis of ammonia and oxygen under adiabatic conditions. $p_{NH_3} = 10$ mm; $p_{O_2} = 10$ mm; flash energy 1280 joules. (Bottom) The production of NO, OH, and O_2 in vibrationally excited states resulting from the flash photolysis of ammonia and oxygen under adiabatic conditions. $p_{NH_3} = 1$ cm; $p_{O_2} = 1.5$ cm. Flash energy 1280 joules.

placed in the focal plane of the spectroscope and registering on an oscillograph (*10*). In Fig. 8, which refers to hexane-oxygen mixtures, the sharp peaks characteristic of detonation are suppressed by the antiknock, the induction period is lengthened and the rate of release of energy is seen to be decreased. Many other studies (*11*) of antiknock action have been made with other additives, but the matter cannot be pursued further here.

Combustion of gaseous hydrides in general. It will be appreciated from what has been said that we have concluded that the oxidation of all hydrides studied follows the same pattern. All the reaction chains are propagated by the OH radical. In all cases ignition is preceded by a period of incubation during which chain branching dependent on the generation of a moderately stable intermediate occurs, in accordance with the generalized scheme

$$\left.\begin{array}{l} OH + XH_n = XH_{n-1} + H_2O \\ XH_{n-1} + O_2 = XH_{n-2}O + OH \end{array}\right\}\begin{array}{l}\text{Straight-}\\ \text{chain}\\ \text{propaga-}\\ \text{tion}\end{array}$$

Branching is dependent on the intermediate $XH_{n-2}O$ and may take place variously by any one of the reactions

$$XH_{n-2}O + O_2 = XH_{n-2}O_2 + O \tag{1}$$

$$XH_{n-2}O + O_2 = XH_{n-3}O + HO_2 \tag{2}$$

$$XH_{n-2}O = XH_{n-3}O + H \tag{3}$$

The first is characterized by the hydrogen sulphide reaction (SO) (*3*), the second by methane (CH_2O) (*12*), and the third by ammonia (HNO) (*5*).

We may generalize by saying that all the hydrides examined are oxidized by a straight-chain reaction involving dehydrogenation by hydroxyl radicals with the production of a uniradical. The radical reacts with oxygen to regenerate a hydroxyl radical and a product which can give rise to branching or delayed branching according to its stability. Thus either degenerate explosions or true explosions can result according to the stability of the intermediate. All the uniradicals and the associated intermediates produced are isoelectronic (see Table 1).

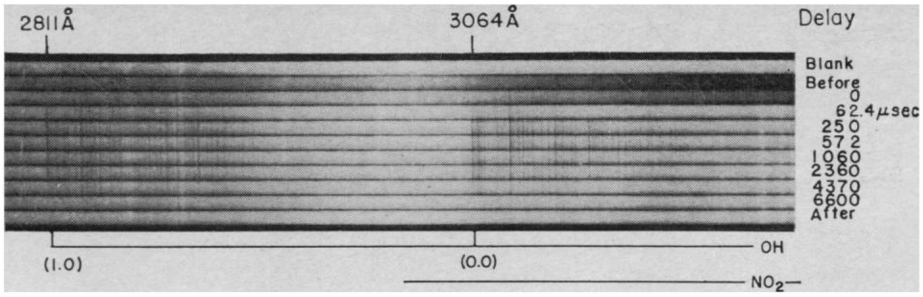


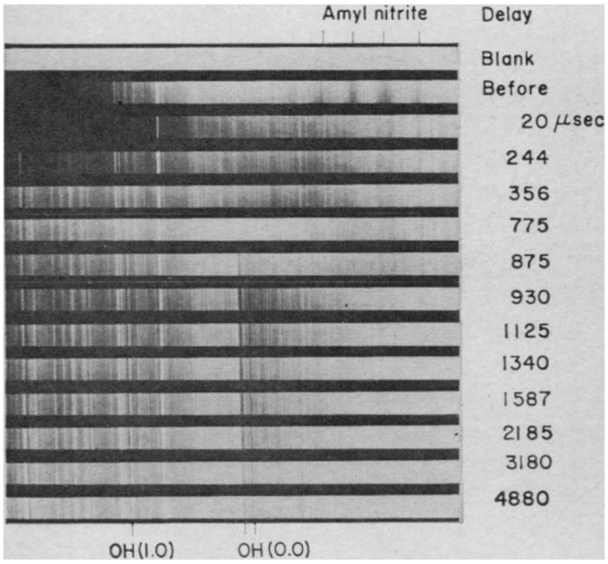
Fig. 5. Flash photolysis of NO_2 (2 mm) + H_2 (10 mm) + O_2 (5 mm) + N_2 (30 mm) showing the removal of the initial OH, and its regeneration on ignition after a typical induction period. Flash energy 3300 joules.

The pairs of propagating reactions associated with each hydride are simply an expression of the preference for uniradical chains where these are possible. More interesting is the nature of the intermediate. Not all of these are degenerate branching agents, nor are the modes of branching identical. The stability of the intermediates and their products of branching varies greatly; for example, H_2CO is much more stable than HNO, while HCO is less stable than NO; all, however, are molecular or quasi-molecular in character, and their varying stability is reflected in the overall kinetics of the particular reactions in which they are involved.

The Isothermal Method

Let us now consider some examples of isothermal reactions in gases studied by flash photolysis. These may result from either primary or secondary photochemical reactions and are in all cases maintained isothermal by the addition of inert gas at pressures some 200 to 600 times greater than the partial pressure of the reactant. We shall consider first the vibrational relaxation of nitric oxide, a process dependent on the primary excitation of nitric oxide by the photoflash.

Vibrational relaxation of nitric oxide. Until recently, kinetic measurement in gases was possible only in the case of the transfer of translational energy to low vibrational levels (*13*) and, in rare



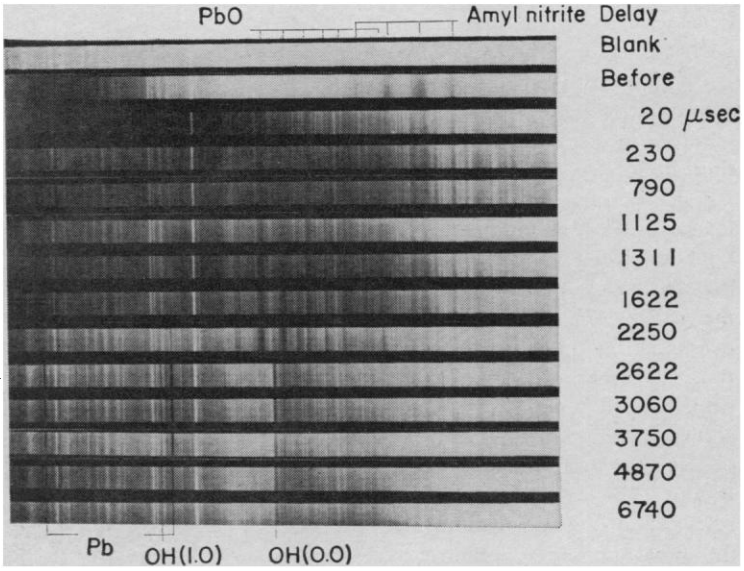
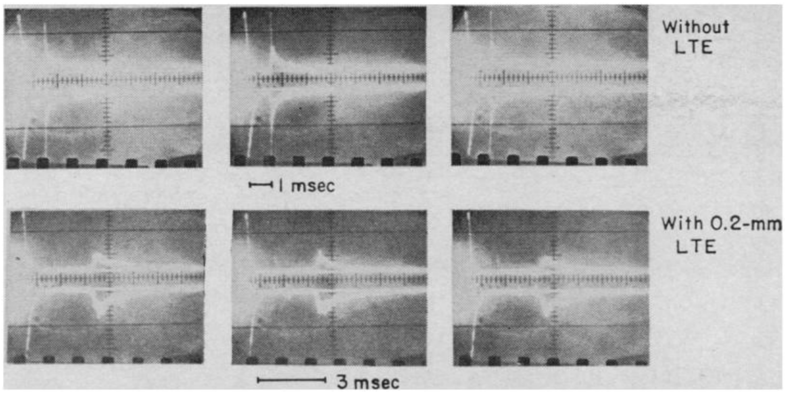


Fig. 6 (left). Spectra versus time. 2 mm $C_5H_{11}ONO$ + 2 mm C_6H_{14} + 32.5 mm O_2. Flash energy 2000 joules. Induction period about 875 μsec. Fig. 7 (right). Spectra versus time. 2 mm C_5H_{11} ONO + 2 mm C_6H_{14} + 32.5 mm O_2 + 0.2 mm lead tetraethyl. Flash energy 2000 joules. Induction period increased to about 2600 μsec. Gaseous PbO and Pb visible.



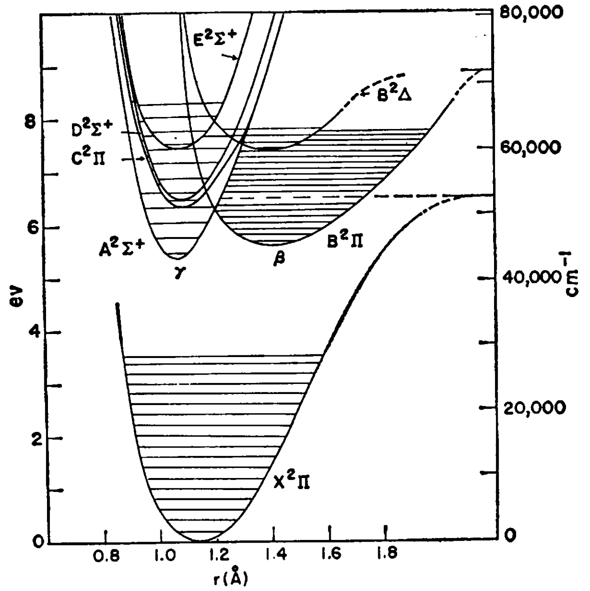


Fig. 8 (above). Light emission versus time. Comparison of ignition of hexane-amyl nitrite-oxygen mixtures in the absence (top row) and presence (bottom row) of lead tetraethyl, showing increase in induction period and suppression of detonation occasioned by additive. The induction period is measured from initial peak (initiating photo-flash) to second peak (ignition). 2 mm C_5H_{11} ONO + 2 mm C_6H_{14} + 32.5 mm O_2. Flash energy 200 joules. Fig. 9 (right). Potential curves of the NO molecule. [After Dr. H. P. Broida]

cases, rotational levels, by the study of the dispersion of a wide range of ultrasonic vibrations. Here the equilibrium of energy partition is suddenly disturbed by the rapid change of pressure in the wave front, and an evaluation of the probability of energy transfer on collision may be derived from the velocity of ultrasonic propagation. Methods of this kind have been amplified and extended by the application of shock-wave technique (*14*), but in all cases the measurements of vibration-translation transitions are restricted to the first few quantized levels. The higher vibrational levels are excluded because the temperatures necessary for their generation lie beyond the resources of the observational techniques available. By means of flash photolysis, however, considerable concentrations of vibrating molecules at high quantized levels may be generated at normal temperatures—that is, without any corresponding rise in rotational or translational temperatures —and their relaxational decay may then be followed.

The fluorescence and vibrational relaxation of nitric oxide can be studied by contrasting the reaction of NO, on the one hand, and NOCl and NOBr on the other. The various electronically excited levels of NO which give rise to the *β*-, *γ*- and other similar spectra by transition to the $X^2\Pi$ ground state are shown in Fig. 9. In the direct excitation of NO by flash irradiation studied by Basco, Callear and Norrish (*15*), the relevant absorption was limited to the 0,0 band of the *γ*-system at 2270 Å, and very faintly to the 0,1 band at 2365 Å. There is no appreciable absorption at longer wavelengths and absorption at shorter wavelengths is effectively limited by the cut-off at 2000 Å by quartz. Thus the excitation was by approximately monochromatic light. As seen from Fig. 9, the $A^2\Sigma^+$ curve which gives rise to the *γ*-spectrum lies vertically above the $X^2\Pi$ ground state: it gives rise to the fluorescence spectrum measured by Pearse and Gaydon (*16*).

On flashing a charge of 5 mm of NO, diluted with 600 mm of N_2 as coolant, the result shown in Fig. 10 was obtained, in which there is a high transient intensity of the 0,1 band and (less easily seen) the 1,1 band of the *γ*-spectrum in absorption. The origin of this vibrational excitation in the ground state is fluorescent or collisional transition from the upper state as shown in Fig. 11, and the momentary over-population of the ($v'' = 1$) level can be measured and its decay followed quantitatively by plate photometry. This is possible because the 0,1 band is visible spectroscopically in absorption with nitric oxide at 1 atmosphere pressure, and since under these conditions its concentration at equilibrium [NO*] is given by

$$[\mathrm{NO}^*] = [\mathrm{NO}]e^{-\frac{h\nu}{kt}}$$

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. 12 were obtained, with varying pressures of NO and N_2.

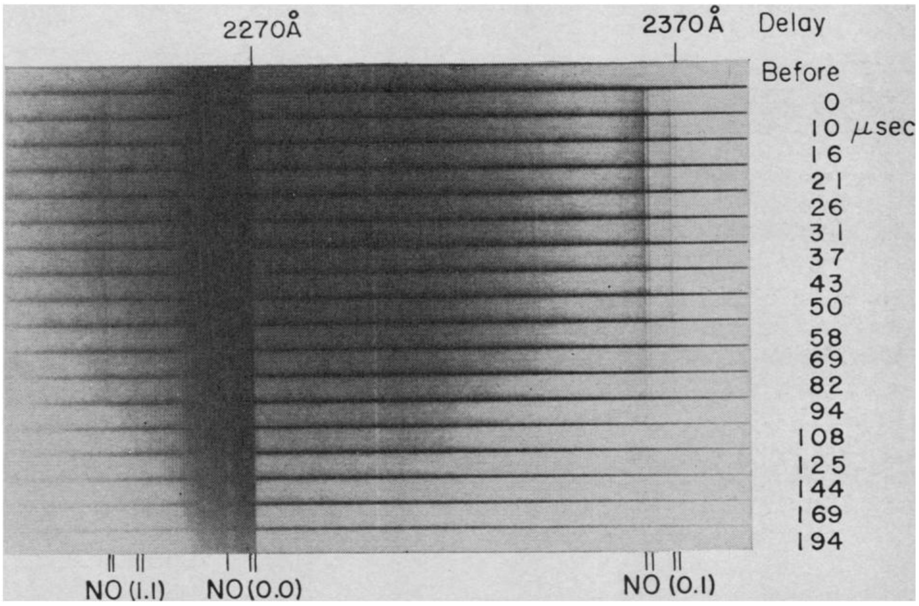


Fig. 10. Decay of NO ($^2\Pi$) ($v = 1$) with time. $p_{NO} = 5$ mm; $p_{N_2} = 600$ mm. Flash energy 1600 joules.

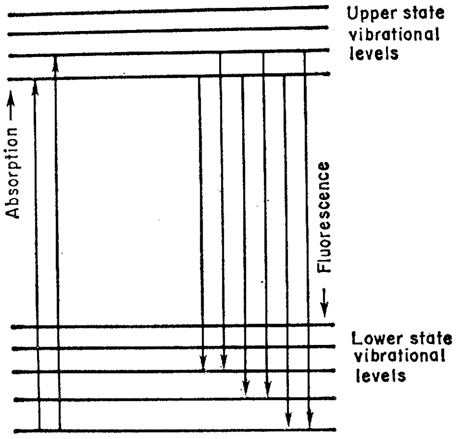


Fig. 11. Diagrammatic excitation of lower levels by fluorescence.

When plotted logarithmically they give good straight lines showing unimolecular decay from which the unimolecular constant, k_3, for the reaction

$$NO_{v=1} \rightarrow NO_{v=0}$$

can be obtained.

The reciprocal of k_3 is the mean lifetime, τ. If the excited species suffers Z collisions per second, then $P_{1\text{-}0}$, the probability of energy transfer at one collision, is given by

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

Now k_3 can be split into two terms depending on relaxation by NO and N_2 respectively. Thus

$$k_3 = k_4\,[NO] + k_5\,[N_2]$$

and so k_4 and k_5 may be calculated from the various values of k_3 derived from the curves of Fig. 12. Thus it is found that the value of $P_{1\text{-}0}$ for NO is $3.6 \pm 0.4 \times 10^{-4}$ at 300°K, in good agreement with the sound-propagation results of Bauer *et al.* (*17*) and the extrapolated shock-wave results of Robben (*18*):

	P_{1-0}
Sound absorption	10^{-3} — 10^{-4}
Shock wave	3.8×10^{-4}

The value of $P_{1\text{-}0}$ for nitrogen is very small; it is calculated as 4×10^{-7} within an order of magnitude. Data for other gases, such as CO_2, CO and Kr, as quenching agents have been obtained by using them as coolant additives in a similar way; CO and CO_2 give $P_{1\text{-}0}$ values of 0.25×10^{-4} and 1.7×10^{-4} respectively but krypton is totally without effect in quenching.

By flashing with the photoflash alone it is possible to photograph the fluorescent emission progressions from $v' = 0$ and $v' = 1$; they are visible to $v'' = 5$ in the latter case; but if the fluorescence is completely quenched by sufficient additive the ($v = 1$) level is still observed to be over-populated in the ground state. This leads to the conclusion that the vibrational levels of the ground state may be populated not only by fluorescent emission but also by collisional deactivation:

$$[NO]^2\Sigma^+ \ (v = 0,1,2..) + M = [NO]^2\Pi \ (v = 0,1,2..) + M$$

It is significant, however, that by whichever process the vibrational levels of the ground state are populated, only the level $v = 1$ (and at times $v = 2$ *very* faintly) can be seen by kinetic spectroscopy. Thus, since the fluorescence spectrum indicates that the higher v-levels of the ground state are initially populated, it must be concluded that the relaxation of the higher levels is extremely rapid and too fast to be seen by kinetic spectroscopy. We shall return to this point.

Photolyses of NOCl and of NOBr. The flash photolyses of NOCl and NOBr have been examined by Basco and Norrish (*19*). They have shown, by means of suitable light filters surrounding the reaction vessel, that strong photolysis takes place in the region 2500 Å with the production of highly vibrating NO molecules in the ground state. All levels from $v = 11$ to $v = 0$ were observed in absorption in the β, γ, δ and ε systems (see for example Fig. 13), and all vibrational states with the exception of $v = 1$ were short-lived and did not survive the period of the flash. By employing nitric oxide as a light filter it was shown that these excited species did not have their origin in the secondary excitation of NO molecules; they are the product of the primary reaction of the halide, NOX:

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

The rapidity of decay of NO* was found to be greater the higher the pressure of NOX, and the lower level $v = 1$ accumulates as the upper levels fade out. It would appear that "near-resonance" transfer processes are operating on its relaxation. Thus for the range $v'' = 11$ to $v'' = 0$, the vibration frequencies of NO lie between 1900 and 1600 cm^{-1}, while for NOCl and NOBr the frequency associated with the N—O bond by Burns and Bernstein (*20*) is 1800 cm^{-1}. These effects, and the almost complete absence of quenching by nitrogen and krypton, give us a qualitative picture, but an anomaly at once appears when the behaviour of NO* produced from NO is compared with that derived from nitrosyl halides. In the former case, as we have seen, the vibrational levels (except $v'' = 1$) disappear too quickly for them to be observed by kinetic spectroscopy; if their disappearance is by resonant transfer to lower vibrational levels of NO, why is it so much quicker than the disappearance of NO* produced from the nitrosyl halides?

Self-relaxation by resonant transfer. This dilemma may be resolved in the present case by two hypotheses, the first of which suggests a generalization applicable to all vibrationally relaxing systems.

I. The most favourable resonant col-

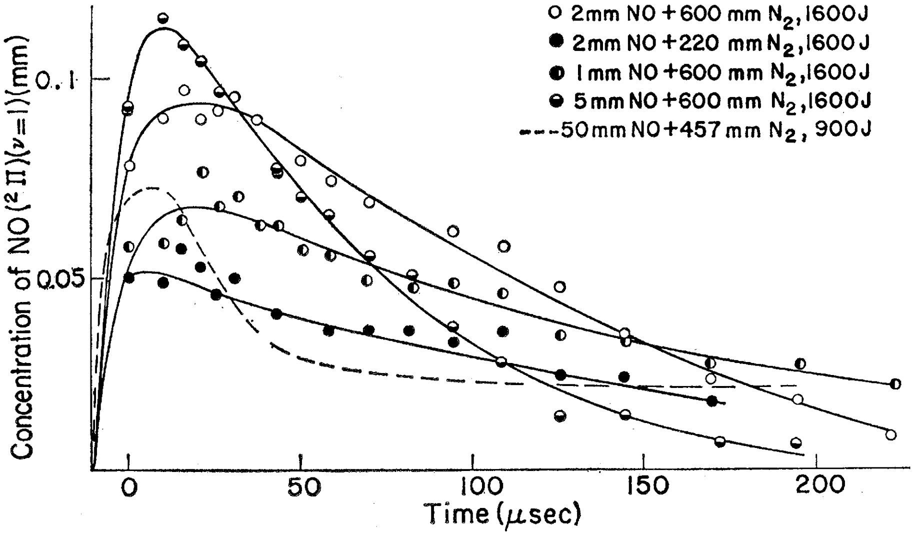


Fig. 12. Rise and decay of NO($^2\Pi$) ($v = 1$) measured by plate photometry.

Table 1.

Hydride	Uniradical	Associated intermediate
SH_2	SH	SO
NH_3	NH_2	HNO
PH_3	PH_2	HPO
CH_4	CH_3	H_2CO
C_2H_6	C_2H_5	CH_3CHO
N_2H_4	N_2H_3	NH_2NO

lisions are between closely associated levels of the vibrating species, for example

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

and, owing to change in frequency due to unharmonicity, the most favourable of all are derived from frequency levels which differ by 2 as above.

II. At the instant of production from the nitrosyl halide, the NO* is formed in very highly vibrating states—say $v =$ 12, 11, or 10. In consequence there is a gap between $v = 10$ and $v = 0$ and, remembering hypothesis I, in the absence of any other deactivating gases the higher vibrational levels are relaxed comparatively slowly by reaction between widely separated vibrational levels of NO.

First let us say that the energy relationships involved are in order. For example, the vibrational energy of $v =$ 11 is 55 kcal, and the bond strength of NO—Cl is 38 kcal; thus the energy available from the light quantum (98 kcal for 2800 Å) is adequate. The same is true for NOBr.

In fact, however, other deactivating species besides $NO_{v=0}$ are present: as we have seen, NOCl and NOBr are shown by experiment to be efficient; thus lower levels will be built up by collisional deactivation but the process will be comparatively slow compared with that envisaged in hypothesis I. As the lower levels are populated in this way, so will resonant self-quenching increase, but there will always be an irregular distribution of lower levels compared with the higher, since high levels are continually fed in during the flash. There is thus created a "bottleneck" in self-relaxation and during the flash all levels will be observed.

Contrast now the case of NO* produced from nitric oxide by fluorescence from the $A^2\Sigma^+$ to the $^2\Pi$ ground state. The intensities of the $v' = 0$ progression in emission were found by Pearse and Gaydon (*16*) (Table 2) and it is considered that the 0—0 intensity is weakened by self-reversal. Therefore all ground states are populated evenly by fluorescence. Thus, if there is no "gap" and each vibrational level is populated slightly less than the one below, its rapid resonant deactivation is possible by the mechanism of hypothesis I, repeated progressively. The consequence of this is that all levels are rapidly deactivated to $v = 1$ by self-quenching, at which point the resonant process must of necessity stop. Hence only the $v = 1$ level is seen to be over-populated, with the $v = 2$ level appearing very faintly and representing the last stage of the collapse of the vibrational pattern. With a smooth distribution we get very rapid relaxation, too rapid to be observed; with a gap in the distribution or a series of irregularities on the vibrational pattern, resonant deactivation is slowed down sufficiently to be observed by kinetic spectroscopy. Idealized diagrams illustrating the two cases are shown in Fig. 14.

Table 2.

Transition	0–0	0–1	0–2	0–3	0–4	0–5
Intensity	8	10	10	9	8	7

Further studies extending this work and also the relaxation of vibrational levels of the cyanogen radical derived from cyanogen or cyanogen halides have been made (*21*).

The reactions described above are dependent, one way or another, upon primary photochemical processes; we shall now briefly refer to phenomena originating from secondary photochemical processes, newly exposed by kinetic spectroscopy and derived mainly from the reactions of oxygen atoms.

The flash photolysis of nitrogen dioxide, of chlorine dioxide (*22*) and of ozone (*23*) by suitable ultraviolet light under isothermal conditions has been shown to yield highly vibrating mole-

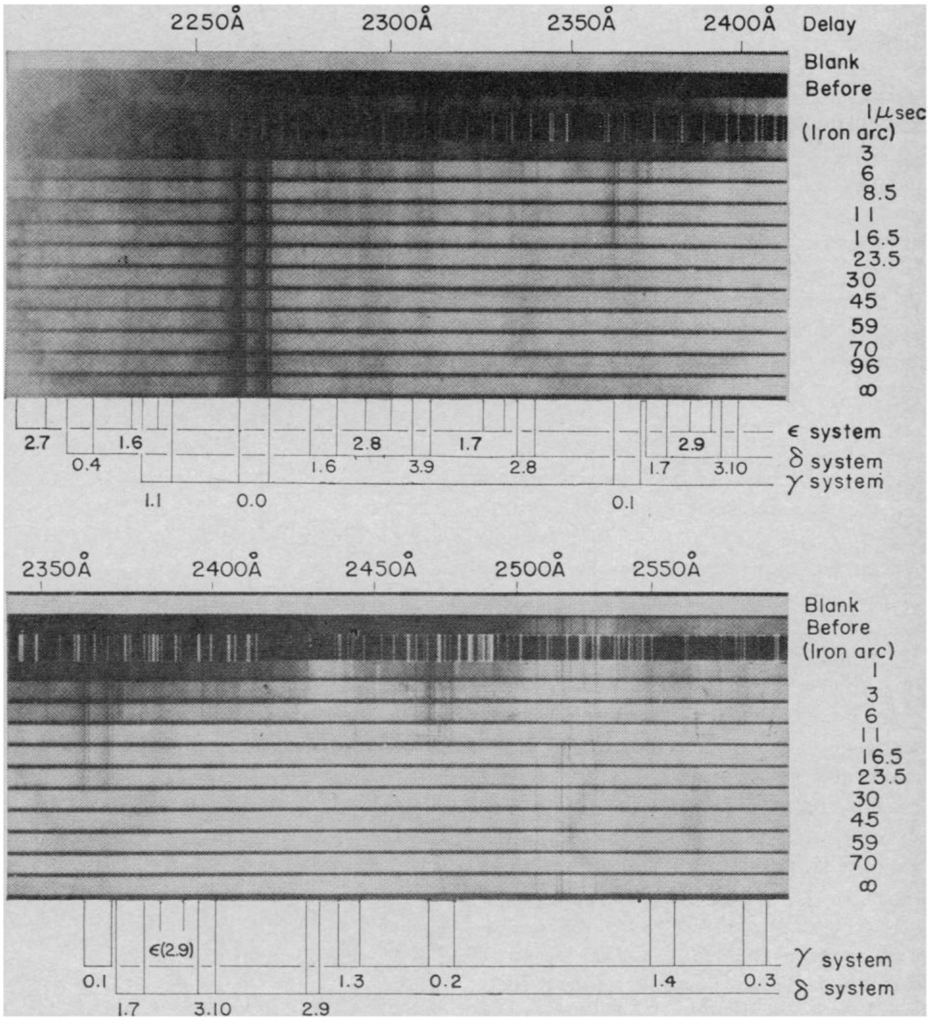


Fig. 13. Vibrationally excited NO produced in the flash photolysis of NOCl. p_{NOCl} = 1 mm; p_{N_2} = 375 mm. Flash energy 1600 joules. p_{NOC} = 2 mm; p_{N_2} = 420 mm. Flash energy 1600 joules.

cules in the ground state, whose presence is betrayed by their absorption bands observed in the quartz ultraviolet as an extension of the Schumann-Runge spectrum. An example is shown in Fig. 15.

For nitrogen dioxide and chlorine dioxide, the quantum yield is 2 (*24*); in the case of ozone it may be as high as 8 (*25*), indicating a chain reaction. Coupled with the results of classical photochemical studies, it is clear that the vibrating oxygen must result from the secondary reactions of oxygen atoms (*26*), according to the following reaction schemes:

$NO_2 + h\nu = NO + O$ (1)
$O + NO_2 = NO + O_2^* + 46\ \text{kcal}$ (2)
$ClO_2 + h\nu = ClO + O$ (3)
$O + ClO_2 = ClO + O_2^* + 61\ \text{kcal}$ (4)
$2ClO = Cl_2 + O_2$ (5)
$O_3 + h\nu = O_2 + O$ (6)
$O + O_3 = O_2 + O_2^*$ (7)

In the case of ClO_2 the transient spectrum of ClO, lasting about 0.5 millisecond, can be readily observed (see Fig. 20).

The degree of vibration in the oxygen molecules is high: maxima of v'' with ClO_2 of 8, with NO_2 of 11 and with O_3 of 17 (see Fig. 16), corresponding to considerably more than half the energy of the exothermic reactions, were indicated. This non-equilibration of the energy of reaction under isothermal conditions is a matter of considerable importance: it affords a second method for studying the relaxation of highly vibrating species by observing the rate of decay in the presence of various inert species, and forms the basis of a generalization concerning the energetics of atomic reactions to which we shall refer later. Preliminary work has indicated (*22*) that the efficiency of various molecular species in deactivating by transfer on collision depends on the degree of resonance between the two colliding molecules, which is the greater the closer their vibrational frequencies approximate to each other.

Photolysis of ozone. Ozone is photolysed both by orange light and by ultraviolet light below 2500 Å. In the former region the quantum yield is 2 (*24*), while, as stated, in the ultraviolet a short chain with quantum yield up to 8 is observed (*25*). The simplicity of the system uniquely requires a formal scheme involving chain propagation by excited oxygen molecules, which previous workers had always assumed to be electronic in character: on the basis of flash photolysis, the chain carrier is now revealed as a vibrationally excited oxygen molecule containing more than 17 quanta according to the reaction scheme (*28, 31*)

$O_3 + h\nu = O_2 + O$ (6) Initiation
$O + O_3 = O_2^* + O_2$ (7) Propagation
$O_2^* + O_3 = O_2 + O_2 + O$ (8) Propagation
$O_2^* + M = O_2 + M$ (9) Termination
$O_2 + O + M = O_3 + M$ (10) Termination

This conclusion is based upon the deduction that the oxygen atoms generated in reaction 6 must be in the ^1D state—the first excited state 45 kcal above the ^3P ground state—and also that the chain reaction in the ultraviolet is propagated by ^1D oxygen atoms, because no chain reaction occurs in the photolysis by orange light, where the magnitude of the light quantum is only sufficient for the generation of ^3P atoms. Reaction 8, involving ^1D oxygen atoms, is 69 kcal endothermic so that the excited oxygen molecule must bring 69 kcal or more to the reaction. More recent work of Basco and Norrish (*27*) has shown that the vibrationally excited O_2^* molecules may be faintly seen in absorption up to 20 quanta, corresponding to 73 kcal. The agreement is sufficiently close; we should expect all oxygen molecules with 17 quanta or less of vibration to be ineffective in energizing reaction 8: they must therefore decay by normal relaxation processes and they are visible by kinetic spectroscopy. Higher vibrational levels, however, which carry sufficient energy for reaction 8, react so rapidly that they are not seen except in that the threshold between the 17th and 20th vibrational levels is diffuse as the probability of reaction 8 rises from zero towards unity. Reaction 9, in which M is oxygen or an inert additive, is unimolecular and may therefore be considered the most probable termination reaction. Chainlengths of up to eight may then be achieved if there are on average up to six propagations to one termination, according to experimental conditions. It may be readily calculated that this involves up to 75 percent of the O_2^* produced, functioning in chain propagation—that is, with more than half the energy of reaction 7 which, involving ^1D oxygen atoms, is 138 kcal exothermic. It may well be that the vibrating molecules seen with less than 17 quanta are produced both directly by reaction 7 and also by collisional relaxation by reaction 9.

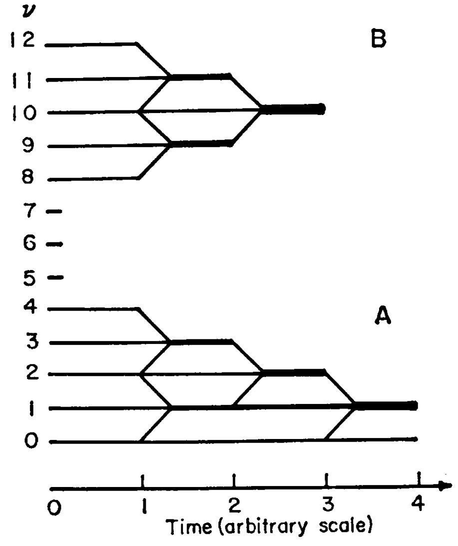


Fig. 14. Ideal diagrammatic schemes for selfrelaxation: (*A*) unhindered; (*B*) hindered.

The chemical proof that the oxygen atom in the above reactions is in the ^1D state lies in the fact when ozone is flash-photolysed in the presence of increasing quantities of water vapour, the spectrum of the vibrating oxygen molecules is progressively suppressed and

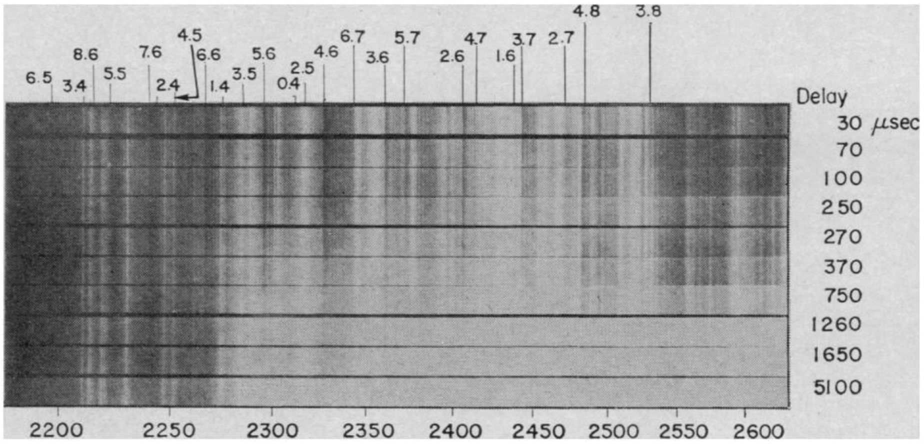
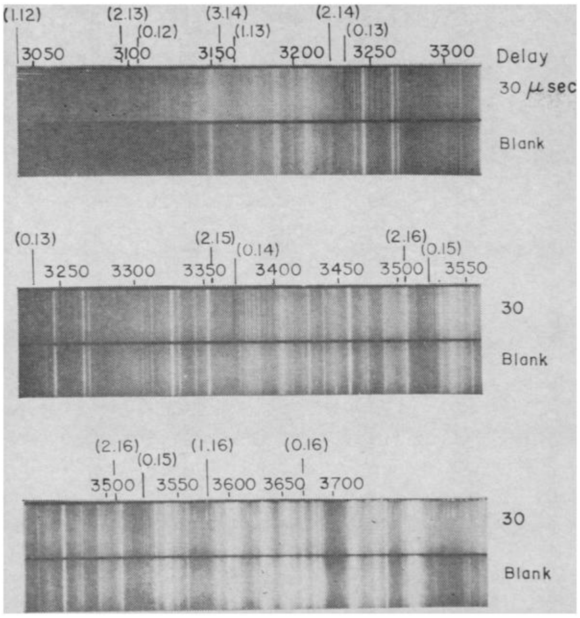


Fig. 15. Formation and decay of vibrationally excited oxygen by photolysis of ClO_2, shown in absorption by Schumann-Runge bands. $p_{ClO_2} = 0.5$ mm; $p_{N_2} = 150$ mm.



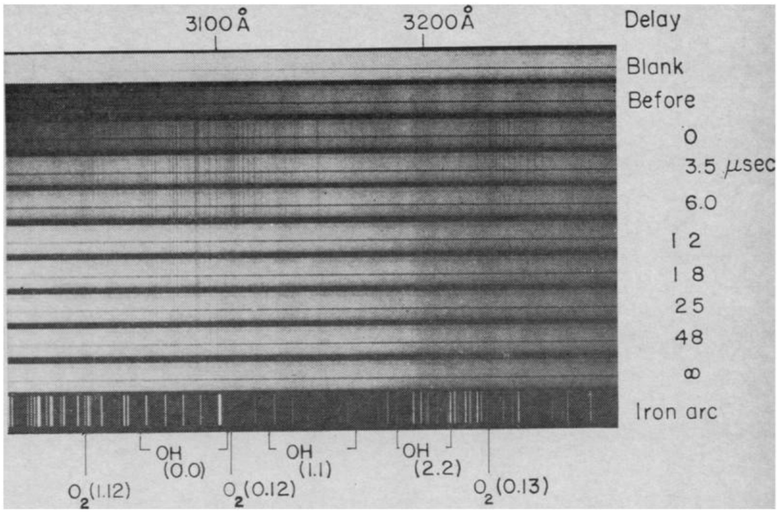
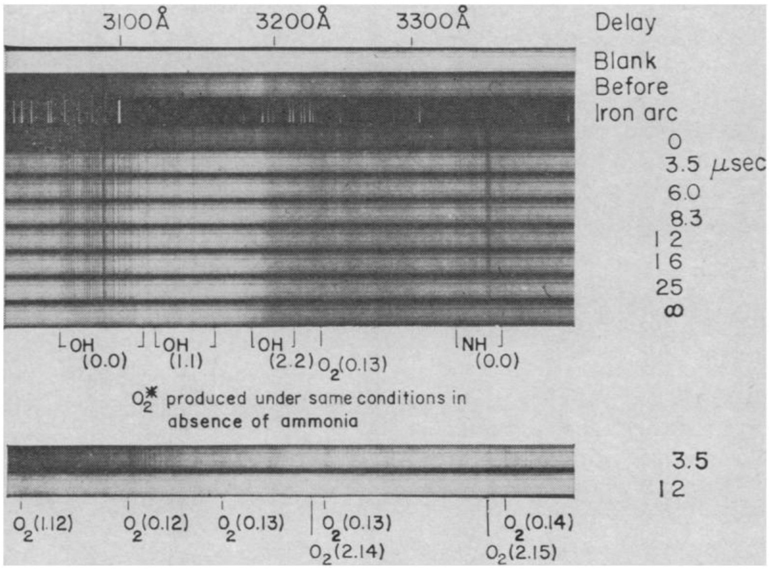


Fig. 16 (left). Vibrationally excited oxygen produced by the photolysis of ozone. $p_{O_3} = 20$ mm; $p_{N_2} = 800$ mm. Flash energy 2000 joules. Fig. 17 (above). Production of excited hydroxyl by reaction of O(^1D) with water. $p_{O_3} = 6$ mm; $p_{H_2O} = 4$ mm; $p_{N_2} = 200$ mm. Flash energy 1600 joules.



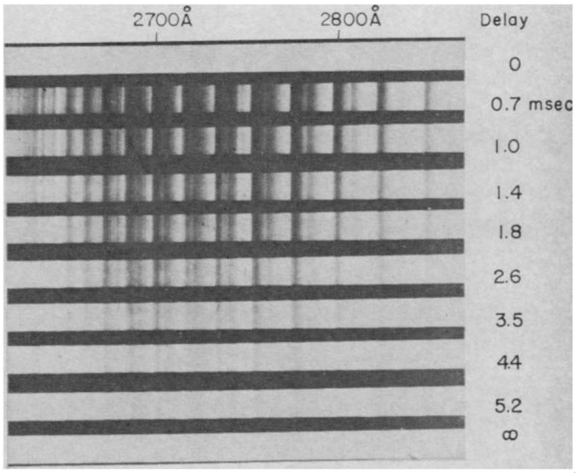


Fig. 18 (left). Production of excited hydroxyl by reaction of O(^1D) with ammonia. $p_{O_3} = 6$ mm; $p_{NH_3} = 4$ mm; $p_{N_2} = 200$ mm. Flash energy 1600 joules. Fig. 19 (above). ClO bimolecular decay.

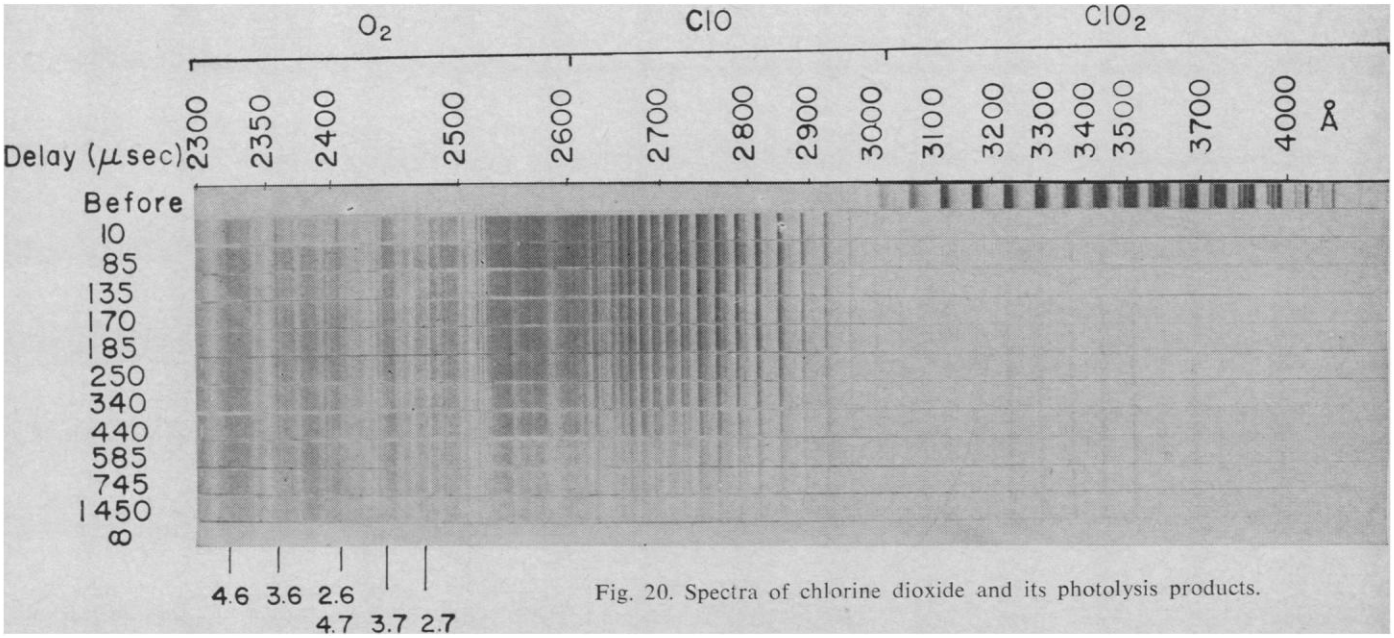


Fig. 20. Spectra of chlorine dioxide and its photolysis products.

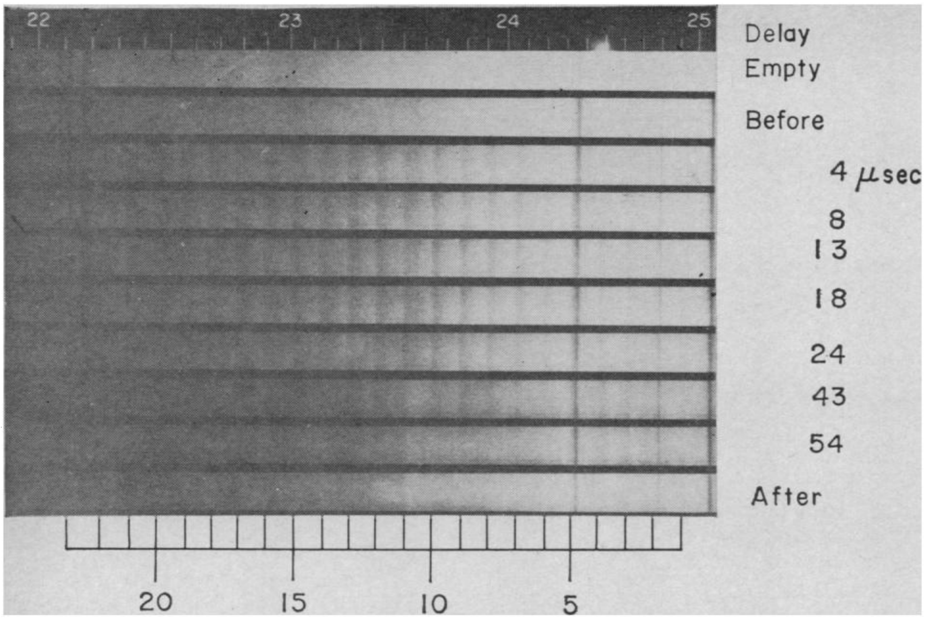


Fig. 21. Decay of the chlorine spectrum. $p_{\mathrm{Cl}_2} = 400$ mm; $p_{\mathrm{N}_2} = 350$ mm. Flash energy 980 joules.

replaced by the absorption spectrum of OH (Fig. 17). Forbes and Heidt (*29*) had shown by classical methods that the quantum yield for the photolysis of ozone in the presence of water could be as high as 130, compared with the maximum of 8 for dry ozone. Clearly the mechanism of chain propagation is altered and on the basis of the observation of the OH radical in our experiments we may postulate the chain mechanism

$$\begin{array}{lll} \mathrm{O_3} + h\nu = \mathrm{O_2} + \mathrm{O} & (6) & \multirow{2}{*}{\}\ \text{Initiation}} \\ \mathrm{O} + \mathrm{H_2O} = \mathrm{OH} + \mathrm{OH} & (11) & \\ \mathrm{OH} + \mathrm{O_3} = \mathrm{HO_2} + \mathrm{O_2} & (12) & \}\ \text{Propaga-} \\ \mathrm{HO_2} + \mathrm{O_3} = \mathrm{OH} + 2\mathrm{O_2} & (13) & \ \ \text{tion} \end{array}$$

followed most probably by chain-ending at the surface. This scheme satisfies the kinetic findings of Forbes and Heidt, but if reaction 11 is to take place it must be exothermic and this is only possible if the oxygen atom is in the ^1D state. We have indeed

$$\mathrm{O}(^3P) + \mathrm{H_2O} = 2\mathrm{OH} - 11\ \text{kcal} \qquad (11a)$$
$$\mathrm{O}(^1D) + \mathrm{H_2O} = 2\mathrm{OH} + 34\ \text{kcal} \qquad (11b)$$

The appearance of OH thus clearly proves the excited character of the oxygen atom and shows the reaction with water to involve a competition between reactions 7 and 11*b*. It is significant that water has no effect on the ozone photolysis in orange light where only ^3P oxygen atoms can be generated; the quantum yield remains unchanged at 2.

Addition of hydrides other than water similarly shows generation of OH radicals. Basco and Norrish (*30*) demonstrated the following reactions of O(^1D) (see Fig. 18).

$$\mathrm{O} + \mathrm{H_2} = \mathrm{OH} + \mathrm{H} \quad + 44\ \text{kcal}$$
$$\mathrm{O} + \mathrm{HCl} = \mathrm{OH} + \mathrm{Cl} \quad + 45\ \text{kcal}$$
$$\mathrm{O} + \mathrm{NH_3} = \mathrm{OH} + \mathrm{NH_2} + 45\ \text{kcal}$$
$$\mathrm{O} + \mathrm{CH_4} = \mathrm{OH} + \mathrm{CH_3} + 46\ \text{kcal}$$

and found that in all cases, as with the reaction between $\mathrm{O_3}$ and $\mathrm{H_2O}$, the OH radicals are maximally excited to the extent of two vibrational quanta.

These results make it clear that in certain cases chain reactions may be propagated by vibrationally hot molecules.

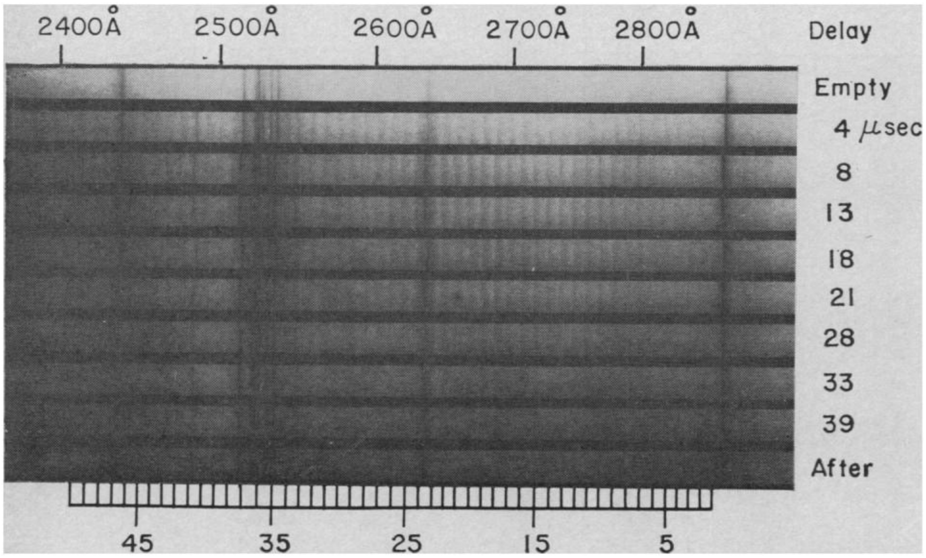


Fig. 22. Decay of the bromine spectrum. $p_{\mathrm{Br}_2} = 100$ mm; $p_{\mathrm{N}_2} = 600$ mm. Flash energy 980 joules.

Atom-Molecule Reactions

A + BCD = AB + CD

The reactions of atomic oxygen described above all result in the formation of excited oxygen molecules, or hydroxyl radicals. They may be compared with the reactions of halogen atoms with ozone, studied by McGrath and Norrish (*31*) by flash spectroscopy with a glass filter

$$\mathrm{Cl} + \mathrm{O_3} = \mathrm{ClO^*} + \mathrm{O_2}$$
$$\mathrm{Br} + \mathrm{O_3} = \mathrm{BrO^*} + \mathrm{O_2}$$

The ClO radical is maximally excited to the fifth vibrational level and the BrO radical to the fourth. Taken together with the reaction of hydrogen atoms with ozone

$$\mathrm{H} + \mathrm{O_3} = \mathrm{O_2} + \mathrm{OH^*}$$

in which the hydroxyl radical was demonstrated by McKinley, Garvin and Boudart (*32*) to be highly vibrationally excited, they form a series of exothermic atomic reactions which prompted the following generalization by McGrath and Norrish (*31*):

"When an exothermic atomic reaction of the general form

$$\mathrm{A} + \mathrm{BCD} = \mathrm{AB} + \mathrm{CD}$$

occurs, the molecule AB with the newly formed bond takes a high proportion of the exothermic energy of the reaction in the form of unequilibrated vibrational energy."

To this may be added reactions of the form

$$\mathrm{A} + \mathrm{BC} = \mathrm{AB^*} + \mathrm{C}$$

such as

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

described by J. C. Polanyi (*33*) in which six quantized levels of the HCl molecule are revealed by the emission of infrared radiation. Table 3 shows the collated results.

Table 3.

Reaction	Q (kcal)	Highest level observed, and energy (kcal/mole)	Reference
$O + ClO_2 \rightarrow O_2^* + ClO$	61	8; 34	(*22, 27*)
$O + NO_2 \rightarrow O_2^* + NO$	46 (48?)	8; 34 11; 45½ (12; 49?)	(*22, 27*) (*34*) (*34*)
$O + O_2 \rightarrow O_2^* + O_2$	138 O(^1D) 93 O(^3P)	17; 66½ 19(20?); 73	(*23, 31*) (*34*)
$Br + O_2 \rightarrow BrO^* + O_2$	19 Br($P_{3/2}$) 29½ Br($P_{1/2}$)	4; 8	(*23, 35*)
$Cl + O_3 \rightarrow ClO^* + O_2$	40 Cl($P_{3/2}$) 42½ Cl($P_{1/2}$)	5?; 11	(*23, 35*)
$O + H_2 \rightarrow OH^* + H$ $O + HCl \rightarrow OH^* + Cl$ $O + H_2O \rightarrow OH^* + OH$ $O + NH_3 \rightarrow OH^* + NH_2$ $O + CH_4 \rightarrow OH^* + CH_3$	43 44 29 O(^1D) 45 45	2; 19.8	(*34*)
$H + O_3 \rightarrow OH^* + O_2$	80	9; 75	(*32, 36–39*)
$H + Cl_2 \rightarrow HCl^* + Cl$	45	6; 45	(*40, 41*)
$H + Br_2 \rightarrow HBr^* + Br$	41	5; 34	(*33*)
$H + HO_2 \rightarrow OH^* + OH$	38	1; 9.9	(*42*)
$N + NO \rightarrow N_2^* + O$	70	1; 6.6	(*43, 44*)
$H + F_2 \rightarrow HF^* + F$	98	9; 86	(*45*)
$X + Na_2 \rightarrow NaX^* + Na$	81 (X = Cl) 71 (X = Br) 54 (X = I)	?; ca. 48.5	(*46*)
$Na + ClX \rightarrow NaX^* + Cl$	52? (X = Cl) 39? (X = Br) 53? (X = I)		
$Na + HgX \rightarrow NaX^* + Hg$	75 (X = Cl) 71? (X = Br)		

These generalizations present an invitation to the theoretical chemist to provide an acceptable model for the reaction, but while suggestive hypotheses have been made by J. C. Polanyi (*33*) and Smith (*47*), a fully satisfactory solution has not yet appeared, and this may well have to wait for further and more accurate work. In particular, much greater time-resolution is required before we can decide whether the excited molecule AB* is initially produced over a wide range of vibrational levels, or whether it is first formed in the highest vibrational state and subsequently degraded.

Further Reactions of the Halogens

The examples which we have so far considered have been dealt with in some detail in order to show the power and the varied applications of kinetic spectroscopy in gaseous systems. I will conclude by making brief mention of two further examples which are well worthy of consideration.

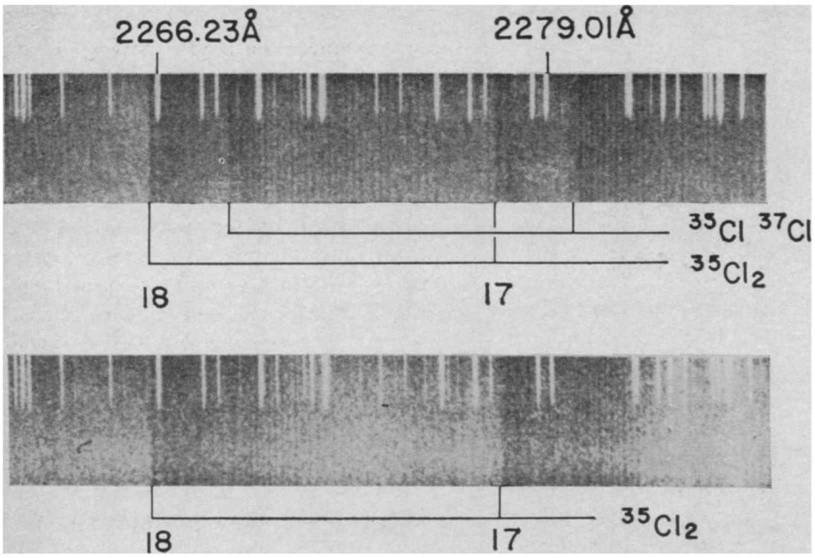
The ClO Radical. The ClO radical was discovered in absorption in the early days of this work when Norrish and Porter were searching for the HO_2 radical by flashing a mixture of $H_2 + Cl_2 + O_2$. A transient spectrum of duration of about a millisecond was observed (Fig. 19) which was equally well obtained isothermally from a mixture of $Cl_2 + O_2 + N_2$, and which was identified as due to the radical ClO. Remembering that under conditions of flash photolysis, radical-radical reactions become predominant, its origin was traced to the following sequence of reactions

$Cl_2 + h\nu = Cl + Cl$
$Cl + O_2 = ClOO$ (sticky collision)
$Cl + ClOO = ClO + ClO$
$ClO + ClO = Cl_2 + O_2$

Its decay to $Cl_2 + O_2$ as measured by Porter and Wright (*48*) by photometry was unimolecular, and practically independent of temperature, but the absolute value of the bimolecular coefficient could not be obtained until its extinction coefficient (for which a knowledge of its absolute concentration was required) was derived by Lipscomb, Norrish and Porter (*49*) by studying the photolysis of chlorine dioxide. Figure 20 shows that ClO_2 is converted quantitatively to ClO on flash photolysis, so that its absolute concentration can be assumed equal to that of the ClO_2 from which it was produced. ClO is also produced as we have shown by the reaction of chlorine atoms and ozone, and also by the photolysis of chlorine monoxide. It is a free radical whose moderate stability makes it of considerable importance to photochemical chlorination reactions occurring in the presence of oxygen. By a partial analysis of its band spectrum, Porter (*1*) measured the strength of the Cl—O bond in the radical as 63 kcal.

Transient spectra of chlorine and bromine. In studying the chlorine-photosensitized decomposition of nitrogen trichloride, new absorption spectra of transient bimolecular species of chlorine and bromine were recently observed in the regions 2500–2100 Å and 2900–2400 Å, respectively (*50*). These arise as a fairly regular series of vibrational bands of which about 30 can be seen in the case of chlorine and 40 or more in the case of bromine when the two halogens, with colour filters round the reaction vessels, are flashed by light of 3000–4000 Å and 4000–5000 Å respectively. Their duration was about 50 μsec and their intensities waxed and waned in phase with the photolysis flash of about 1000 joules. High pressures of halogen (mixed with inert gas) were required, so the systems cannot be said to be maintained isothermal: in the case of bromine the best results were obtained with 100 mm Br_2 and about 600 mm N_2. The bands were the more intense the greater the amount of inert gas present and depended on its nature, increasing in the order argon, nitrogen, carbon dioxide. In the presence of oxygen, the chlorine bands were completely eliminated. Examples of these spectra are shown in Figs. 21 and 22. The chlorine bands were double-headed and degraded towards the red; when viewed in the third order of a 3-meter concave grating, they showed reasonable fine structure of rotation. That the double-headed character was due to the chlorine isotopes ^{35}Cl and ^{37}Cl is seen in Fig. 23; with pure $^{35}Cl_2$ the head due to $^{35}Cl^{37}Cl$ disappears. With normal chlorine the heads gradually approach one another until they reach the first band of the series, when they coalesce. Thus by a short extrapolation the correct numbering of the chlorine bands could be determined.

The vibrational-rotational structure of the chlorine spectrum and the vibrational structure of the bromine spectrum were analysed by Dr. Briggs and he was able to establish that in the case of chlorine the spectrum is derived from transitions from the $^3\Pi_{0^+,u}$ state, to an upper state which may be designated as O_g+. The $^3\Pi$ has a measure of metastability since it is formed from the $^1\Sigma^+$ ground state, a theoretically prohibited transition, and this gives it an abnormally long life. It is possible to popu-



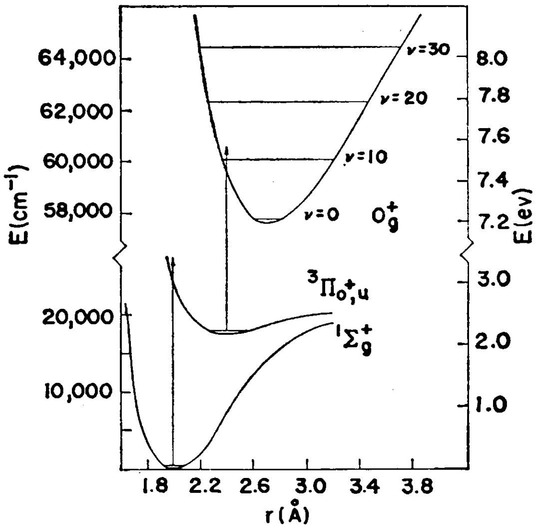


Fig. 23 (left). Some bands of the chlorine spectrum obtained with a grating spectrograph in the third order. A mixture of 400 mm Cl_2 + 350 mm N_2 was flash-photolysed (980 joules) at a delay of 10 μsec. Upper spectrum: ordinary chlorine. Lower spectrum: chlorine containing 96 percent $^{35}Cl_2$. The references spectrum is an iron arc in the second order. Fig. 24 (right). Morse potential-energy curves for the transitions involved in the production of the chlorine transient spectrum. The $^1\Sigma_g^+$ and $^3\Pi_{0^+,u}$ curves were constructed from the constants of Barrow (1962), and the O_g^+ curve from the constants determined from the analysis of the new spectrum.

late the $^3\Pi$ state to a significant degree both by absorption from the ground state and by recombination of chlorine atoms in the $^2P_{1/2}$ and $^2P_{3/2}$ states. It is to be noted that the addition of inert gases will facilitate this recombination and hence the population of the $^3\Pi$ state and increase the intensity of the transient spectrum as observed.

Figure 24 shows the calculated O_g+ level which was calculated by Dr. Briggs from his analysis of the chlorine spectrum. His results agree well with the analysis by Barrow (*51*) for the normal chlorine spectrum. We have thus been able to characterize a well-defined upper state of chlorine and bromine above the well known $^3\Pi_{0^+,u}$ and to indicate the possibility of a photochemistry of the halogens appertaining to and corresponding to absorption in the far-ultraviolet at wavelengths which may be calculated to be of the order of 1800 Å.

I have limited my discussion to reactions in the gas phase. This has precluded mention of the extensive and important study of the triplet state in organic compounds by Porter and his colleagues, an authoritative account of which was given by him in his Tilden Lecture to the Chemical Society in 1959 (*52*). It has also precluded the mention of other reactions in solution involving the reactions of complex halogen ions, of alkali and alkaline-earth salts (*53*), and of the reactions of polymerization (*54, 55*). There is indeed wide scope for the examination of reactions in solution by the technique of kinetic spectroscopy, and it seems likely that new avenues will soon be opened up.

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