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Flash photolysis and some of its applications

Nobel Lecture, December 11, 1967

One of the principal activities of man as scientist and technologist has been the extension of the very limited senses with which he is endowed so as to enable him to observe phenomena with dimensions very different from those he can normally experience. In the realm of the very small, microscopes and microbalances have permitted him to observe things which have smaller extension or mass than he can see or feel. In the dimension of time, without the aid of special techniques, he is limited in his perception to times between about one twentieth of a second (the response time of the eye) and about $2 \cdot 10^9$ seconds (his lifetime). Yet most of the fundamental processes and events, particularly those in the molecular world which we call chemistry, occur in milliseconds or less and it is therefore natural that the chemist should seek methods for the study of events in microtime.

My own work on "the study of extremely fast chemical reactions effected by disturbing the equilibrium by means of very short pulses of energy" was begun in Cambridge twenty years ago. In 1947 I attended a discussion of the Faraday Society on "The Labile Molecule". Although this meeting was entirely concerned with studies of short lived chemical substances, the four hundred pages of printed discussion contain little or no indication of the impending change in experimental approach which was to result from the introduction, during the next few years, of pulsed techniques and the direct spectroscopic observation of these substances. In his introduction to the meeting H. W. Melville referred to the low concentrations of radicals which were normally encountered and said "The direct physical methods of measurement simply cannot reach these magnitudes, far less make accurate measurements in a limited period of time, for example 10^{-3} sec."

Work on the flash photolysis technique had just begun at this time and details of the method were published two years later[1,2]. Subsequent developments were very rapid, not only in Cambridge but in many other laboratories. By 1954 it was possible for the Faraday Society to hold a discussion on "The study of fast reactions" which was almost entirely devoted to the new techniques introduced during the previous few years. They included, as well as flash photolysis, other new pulse techniques such as the shock wave, the stopped flow method, and the elegant pressure, electric field density and temperature pulse methods described by Manfred Eigen. Together with pulse radiolysis, a sister technique to flash photolysis which was developed around 1960, these methods have made possible the direct study of nearly all fast reactions and transient substances which are of interest in chemistry and, to a large extent, in biology as well.

The various pulse methods which have been developed are complementary to each other, each has its advantages and limitations, and the particular power of the flash photolysis method is the extreme perturbation which is produced, making possible the preparation of large amounts of the transient intermediates and their direct observation by relatively insensitive physical methods. Furthermore, the method is applicable to gases, liquids and solids and to systems of almost any geometry and size, from path lengths of many metres to those of microscopically small specimens.

My original conception of the flash photolysis technique was as follows: the transient intermediates, which were, in the first place, to be gaseous free radicals, would be produced by a flash of visible and ultraviolet light resulting from the discharge of a large condenser bank through an inert gas. The flash would be of energy sufficient to produce measurable overall change and of short duration compared with the lifetime of the intermediates. Calculation showed that an energy of 10 000 J dissipated in a millisecond or less, in lamps of the type which were being developed commercially at that time, would be adequate for most systems. The bank of condensers was given by my friends in the Navy, and, although I am grateful to them for saving us much expense, it consisted of a motley collection of capacitors which, owing to their high inductance, gave a flash of rather longer duration than was desirable. The detection system was to consist of a rapid-scanning spectrometer and much time was wasted in the development of this before I realised that to demand high spectral resolution, time resolution and sensitivity in a period of a few milliseconds was to disregard the principles ofinformation theory. Subsequent applications of flash photolysis, with a few exceptions, have been content to record, from a single flash, either a single spectrum at one time or a small wavelength range at all times. The use of a second flash, operating after a time delay, to record the absorption spectrum of the transients must now seem a very obvious procedure but it was many months before it became obvious to me. The double-flash procedure was an important step forward and is still, in principle, the most soundly based method for the rapid recording of information.

In the first apparatus the delay between the two flashes was introduced by a rotating sector, with two trigger contacts on its circumference, a photograph of which is shown in Fig. 1. The reason for using this, in preference to an electronic delay, was in anticipation of difficulties with scattered light from the high-energy photolysis flash, which could be eliminated by the shutter incorporated in the rotating wheel. As flash durations were reduced it became necessary to resort to purely electronic methods but the apparatus worked well for several years and provided, for the first time, the absorption spectra of many transient substances and a means for their kinetic study.

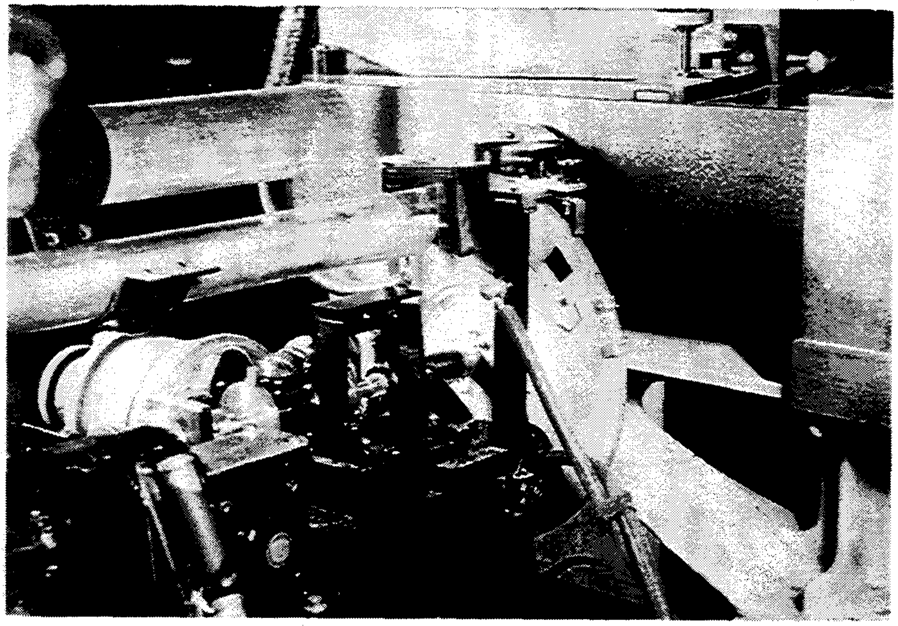


Fig. 1. Part of the original flash-photolysis apparatus showing the rotating sector with shutter and trigger contacts.

There have been many reviews of the flash-photolysis method[3-5] and in this lecture I should like to illustrate our work by describing four rather different problems: the first two are simple gas-phase reactions which were the earliest to be investigated in detail and which illustrate rather clearly the two principal variations of the flash photolysis technique; the second two examples are studies of the principal types of transient which appear in photochemical reactions, i.e. radicals and triplet states, with special reference to aromatic molecules.

The first free radical to be studied in detail by flash-photolysis methods, both spectroscopically and kinetically, was the diatomic radical ClO, and this study provided a proving exercise for the technique. The spectrum was discovered, somewhat accidentally, in the course of a study of the chlorine-carbon monoxide-oxygen system and provided one of the first of many lessons on the limitation ofpredictions based on conventional studies. This new spectrum, which is shown in Fig. 2, was produced by flash photolysis of mixtures of oxygen and chlorine, in which no photochemical reaction had previously been suspected. Indeed there is no reaction at all if one speaks of times of conventional experiments, since the system returns to its original state in a few milliseconds.

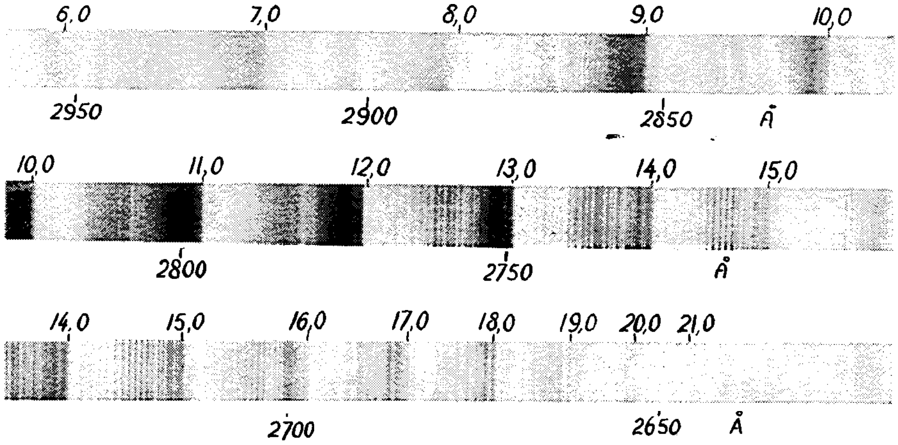


Fig. 2. Absorption spectrum of the ClO radical.

When a new transient species is detected in this way two kinds of information become available. First, analysis of the spectrum itself leads to structural and energetic data about the substance[6]; secondly, studies of the time-resolved spectra provide a measure of its concentration as a function of time and therefore provide kinetic data about the physical and chemical changes which it undergoes[7]. The information which resulted from the early studies of ClO is summarised in Table 1, the kinetic data being obtained from analysis of sequences of spectra of the type shown in Fig. 3.

Kinetic studies, even in this case, would have been more easily and accurately carried out by recording one wavelength only, so that a single flash can provide all the necessary kinetic information. Since flash photolysis of chlorine had already suggested that the amount of decomposition into atoms was very considerable, Norrish and I decided to study halogen atom recombi-

Table 1

Structural and kinetic information about the ClO radical obtained from Figs. 2 and 3

Spectroscopic

Ground state Dissociates to Cl ^2P and O ^3P

$D''_0 = 22{,}060\ \mathrm{cm^{-1}} = 63.0\ \mathrm{kcal/mole} \pm 0.3\ \%$

$\omega''_0 = 868\ \mathrm{cm^{-1}}$

Upper state Dissociates to Cl ^2P and O ^1D

$D'_0 = 7{,}010\ \mathrm{cm^{-1}} = 20.0\ \mathrm{kcal/mole} \pm 1\ \%$

$\omega'_e = 557\ \mathrm{cm^{-1}}$

$\nu_e = 31{,}080\ \mathrm{cm^{-1}}$

Kinetic

$$\left.\begin{aligned} 2\mathrm{Cl}+\mathrm{O}_2 &= 2\mathrm{ClO}\\ &= \mathrm{Cl}_2+\mathrm{O}_2\end{aligned}\right\} k_1$$

$2\mathrm{Cl}+\mathrm{N}_2 = \mathrm{Cl}_2+\mathrm{N}_2 \quad k_2$

$2\mathrm{ClO} = \mathrm{Cl}_2+\mathrm{O}_2 \quad k_3$

$k_1 = 46\,k_2$. $k_3 = 8.6\cdot 10^7 \exp(0 \pm 650/RT)\ \mathrm{l\ mole^{-1}\ sec^{-1}}$

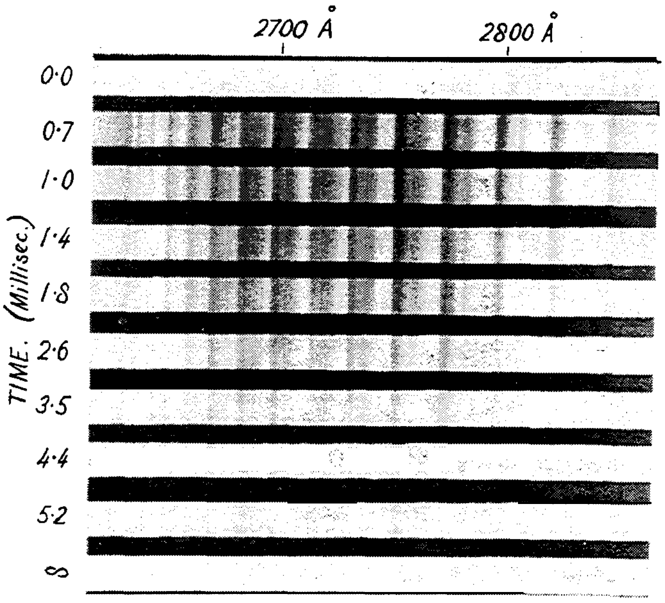


Fig. 3. Sequence of spectra of ClO after flash photolysis of a chlorine-oxygen mixture, showing bimolecular decay.

nation using, for monitoring, a continuous source, a monochromator and photoelectric detector. Iodine is the most convenient gas for these studies and the recombination of iodine atoms has been studied, in several laboratories, in more detail than perhaps any other gaseous reaction.

It was first necessary to show directly that the recombination of atoms, produced photolytically, was indeed a third-order reaction, as had been predicted theoretically for many years. It was satisfying, though not surprising, when this proved to be the case, at least to a first approximation. Oscilloscope traces and second-order plots of the decay of iodine atoms in argon are shown in Figs. 4 and 5, the gradients are proportional to the pressure of argon as they should be for a third-order reaction involving argon as the third body*.

Studies in a number of laboratories[9-12], revealed interesting complications and problems. There were complex concentration gradients across the reaction vessel, caused by the essentially adiabatic nature of the reaction. When these were eliminated, by working with a high excess of inert gas, further deviations from linearity appeared which were found to be caused by an unexpected very high efficiency of the iodine molecule as third body. There were striking differences in efficiency between different third body molecules and temperature coefficients were negative. Later work[13] showed that the negative temperature coefficients could be expressed in Arrhenius' form as "a negative activation energy" and that the more efficient the third body, the greater the value of this quantity. This is illustrated by the data in Table 2.

All these observations can be interpreted in terms of a mechanism involving intermediate formation of a complex between the iodine atom and a third body

$$\mathrm{I} + \mathrm{M} \rightleftharpoons \mathrm{IM}$$

$$\mathrm{IM} + \mathrm{I} \rightarrow \mathrm{I}_2 + \mathrm{M}$$
$$(k = k_3K)$$

the observed negative activation energy being nearly equal to the heat of formation of the complex. The nature of this complex is of interest. In extreme cases, such as that of NO as third body[14] the bonding is undoubtedly chemical. In the more general case of the molecules given in Fig. 2 we have suggested[13,15] that complexes are of the charge-transfer type and indeed, in solution, spectroscopic evidence for charge-transfer complexes of iodine atoms was obtained directly by flash-photolysis studies[16].

These studies of ClO and iodine atom reactions are representative of most of the work using flash photolysis which has followed, although there has

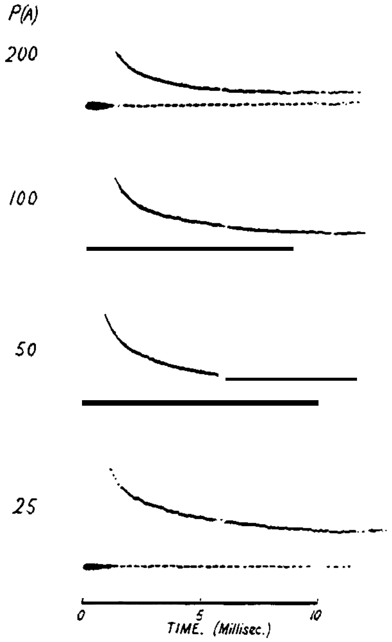


Fig.4. Oscillograph traces of I_2 absorption after flash photolysis of iodine in excess argon. P(A) is argon pressure in mm Hg.

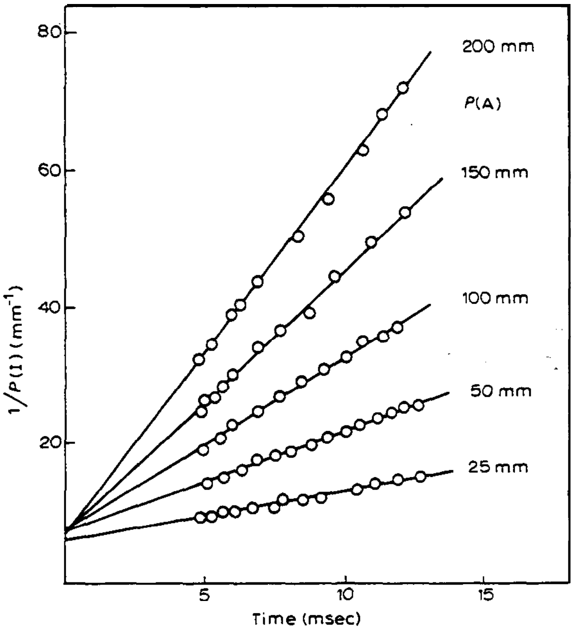


Fig. 5. Second-order plots of data from Fig.4. P(1) is iodine atom partial pressure.

Table *2*

Termolecular recombination constants *(k_{27})* at 27°C and temperature coefficients expressed as negative activation energies (E_a) for the recombination of iodine atoms in the presence of various chaperon molecules *M*

M	k_{27} (l^2 $mole^{-2}$ sec^{-1}) $\times 10^{-9}$	E_a (*kcal*)
He	1.5	0.4
A	3.0	1.3
H_2	5.7	1.22
O_2	6.8	1.5
CO_2	13.4	1.75
C_4H_{10}	36	1.65
C_6H_6	80	1.7
CH_3I	160	2.55
$C_6H_5CH_3$	194	2.7
C_2H_5I	262	2.4
$C_6H_3(CH_3)_3$	405	4.1
I_2	1600	4.4

naturally been a trend towards the study of more complex molecules. Some of the most significant spectroscopic work is that which has been carried out by Herzberg and his school on polyatomic radicals containing three or four atoms. When flash photolysis was first introduced, no absorption spectrum of a gaseous polyatomic radical was known and I think the first to be detected must have been that which has been assigned[2] to HS_2. One of our first interests had been the methylene radical, CH_2, and it was with this problem particularly in mind that the flash technique was conceived. It was very gratifying when, in 1959, Herzberg eventually brought methylene into the fold by extending flash spectroscopy into the vacuum ultraviolet region[17].

In addition to the increased complexity of the molecules investigated, the flash-photolysis technique has been increasingly applied. to solutions, solids and even to biological systems so that these applications are now more extensive than those in the gas phase. I have been particularly interested, for over ten years, in the transient species which appear upon excitation of larger organic molecules, many of them of interest in organic mechanisms and in biological processes. This will remain an active field for a long time, since it is as large as organic chemistry itself, and I shall devote the rest of this lecture to a brief description of two principal classes of these species, namely the aromatic free radicals and the triplet states of organic molecules.

The Aromatic Free Radicals

The first aromatic free radical, triphenyl methyl, was discovered, quite unexpectedly, by Gomberg[18] in 1900. Many similar resonance-stabilised free radicals, which are stable enough to exist in observable concentrations at equilibrium, were subsequently reported but the direct spectroscopic observation of reactive, shortlived, aromatic free radicals was only achieved relatively recently.

The first detection of the absorption spectra of these species was made possible by the development of low temperature trapping techniques by G.N. Lewis and his school[19] in the early 1940's. This important work attracted little attention, and the method was revived and extended by Norman and Porter[20] who, in 1954, were able to detect a number of simple aromatic free radicals in rigid media, radicals such as benzyl and anilino. This led us to search for similar spectra in flash-photolysis experiments, since the results-of low temperature trapping studies are very limited; the spectra are diffuse and no kinetic studies are possible.

Porter and F.J. Wright[21], in 1955, detected a series of aromatic free radicals in the gas phase by flash photolysis of aromatic vapours. For example, spectra in the region of 3 000 Å were attributed to benzyl (from toluene), anilino (from aniline) and phenoxyl (from phenol). These radicals are isoelectronic with each other, and form a type of seven π -electron system which, in aromatic free-radical chemistry, is of comparable importance with the six π-electron benzene ring in normal molecules. The spectra of radicals of this type, as has been shown by Dewar, Longuet-Higgins and Pople[22], result from the interaction of two degenerate configurations and consist of a weak forbidden transition at longer wavelengths and a strong allowed transition at shorter wavelengths. The transition observed near 3 000 Å is the strong, allowed one; the weaker longer wavelength transition has been observed by flash photolysis in the gas phase only relatively recently by Porter and Ward[23] (Fig. 6) though, being from the lowest excited state, it is relatively easily observed in emission[24].

The spectra of benzyl, anilino and phenoxyl in solution are diffuse, but quite characteristic as will be seen from the phenoxyl radical spectra, in various media, observed by Porter and Land[25] and shown in Fig.7. An interesting complication arises in the anilino radical, where two quite different spectra are observed[26] depending on solvent or, in aqueous solvents, on pH (Fig. 8). The two spectra correspond to the protonated and unprotonated forms, the radical

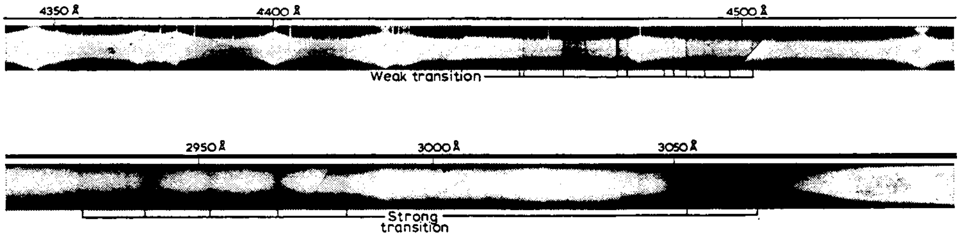


Fig.6. Absorption spectrum of the benzyl radical in the vapour phase after flash photolysis of toluene. Path length = 8 metres.

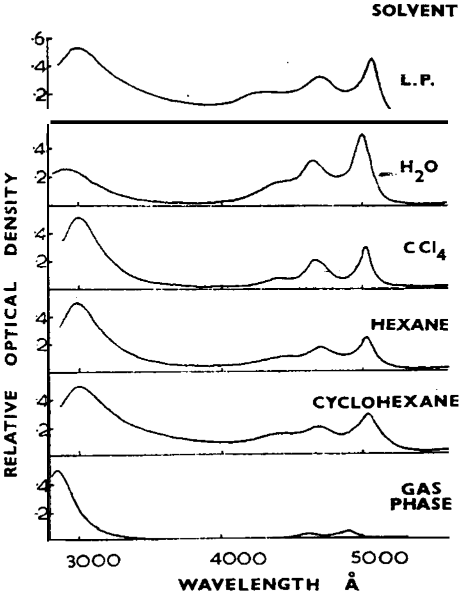


Fig.7. Absorption spectrum of the phenoxyl radical in the gas phase and in various solvents after flash photolysis of phenol.

ion and the radical, and the equilibrium can be established within the lifetime of the radical making it possible to determine the equilibrium constant of this acid-base equilibrium. The pK of the anilino radical is found to be 7.0.

These seven π-electron radicals are the prototype of many of the most important, resonance-stabilised radicals of organic chemistry. For example, benzyl is the prototype of the Gombergtype radicals such as triphenyl methyl whilst OH substitution in the β position gives ketyl radicals, anilino is the prototype of Würster radical cations whilst phenoxyls, on substitution by OH, become semiquinones. The spectra and physico-chemical properties of

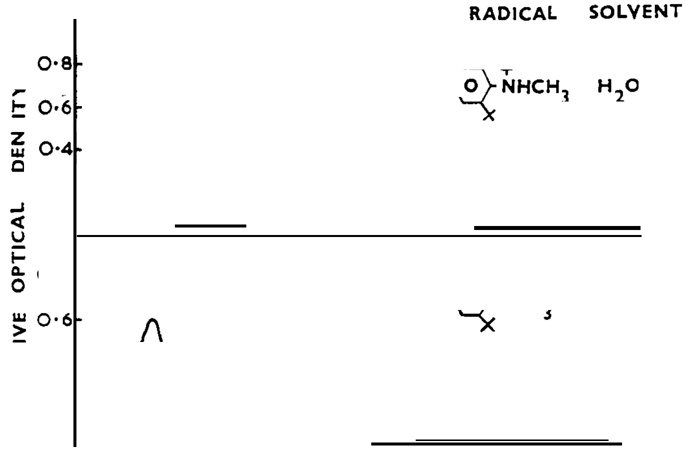


Fig. 8. Absorption spectrum of a substituted anilino radical showing acidic form in water and deprotonated form in hexane solution.

all these radicals are closely similar and provide a large and interesting field of study, of considerable importance both in chemistry and biology. For example the flavins have been shown to behave similarly and to yield semiquinone radicals on flash photolysis[27] and the principal transients observed on flash photolysis of proteins such as ovalbumin are phenoxyl-type radicals derived from tyrosine groups[28].

Flash-photolysis studies carried out more recently by Porter and Ward[29], on aromatic vapours at high resolution have succeeded in detecting many other aromatic free radicals of interest, which are not of the seven π-electron type. The most important of these is phenyl, obtained from benzene and halogeno benzenes and substituted phenyls derived from disubstituted benzene derivatives (Fig. 9).

Phenyl nitrene (or imine), an even electron-number radical analogous to the methylenes, is obtained from flash photolysis of phenyl isocyanate and, by

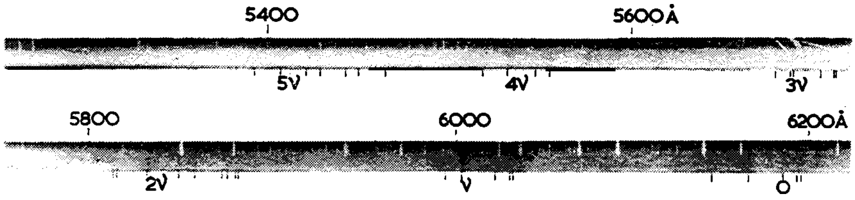


Fig. 9. Spectrum of the *ortho*-fluorophenyl radical after flash photolysis of *ortho*-chlorofluorobenzene.

molecular elimination of HCl followed by tautomeric change, from *ortho*-chloroaniline[30]. One of the most surprising transformations of all is the formation[30,31] of cyclopentadienyl (C_5H_5) radicals from flash photolysis of aniline, phenol, nitrobenzene and many other substituted benzenes, as well as a variety of substituted cyclopentadienyls from disubstituted aromatic compounds (Figs. 10 and 11).

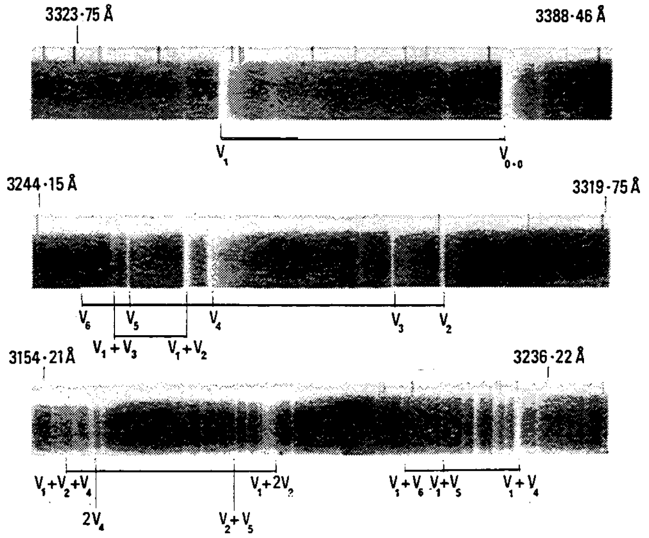


Fig. 10. Absorption spectrum of the cyclopentadienyl radical.

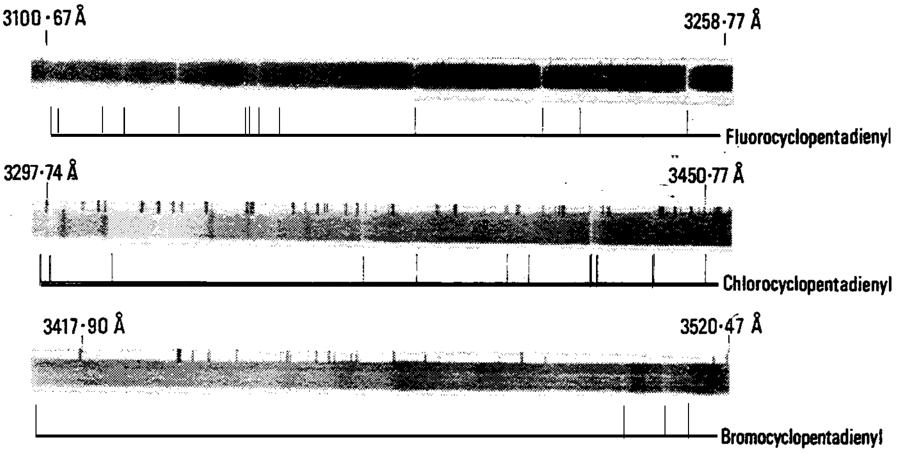


Fig. 11. Absorption spectra of three halogenated cyclopentadienyl radicals.

The assignment of spectra in all these cases is made on the basis of studies of a series of related substituted compounds, and the method is both convenient and reliable in the aromatic series, since so many compounds are available with the possibility of cross checks in most cases. The data on cyclopentadienyl radical formation, Fig. 12, illustrate the method. Although little or no assistance in the identification is possible from the spectra, apart from general similarity and positions of electronic transitions in related radicals, none of the assignments which have been made so far has subsequently had to be revised; a situation which is not always found in the assignment of spectra, even those of much simpler compounds.

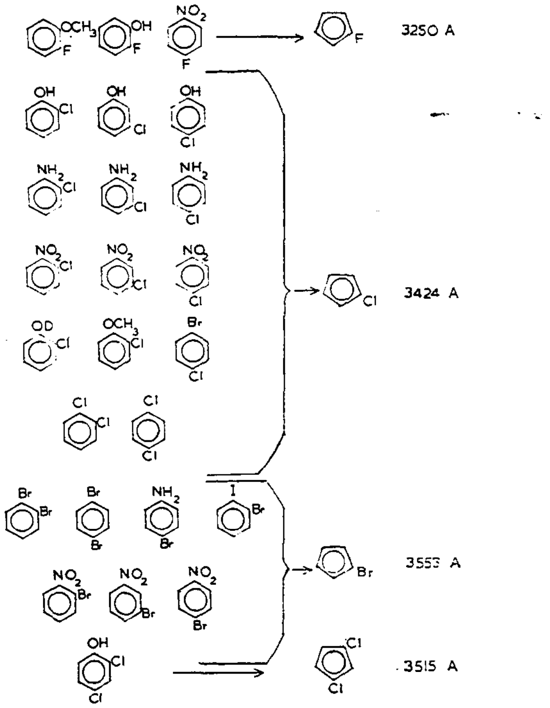


Fig. 12. Observed fission processes of benzene derivatives to form cyclopentadienyl radicals.

The field of aromatic free-radical spectroscopy is relatively new and what has been done already is little more than an indication of what will be done by flash-photolysis techniques in this field in the future. The hundred radicals so far assigned are prototypes of thousands of others which may be observed whenever there is a reason for wanting to study them. Many of the spectra show fine detail which, with the help of computer programmes, should eventually yield information about the radical structures. The chemical problems are almost untouched, and represent a much more extensive series of problems than mere identification. Extinction coefficients are known in only a few cases, usually in solution. Finally there are the intriguing photochemical problems of the primary processes in the excited state by which these often remarkable transformations take place. At the present time it cannot even be taken for granted that the vapour phase dissociations are monophotonic and in the case of cyclopentadienyl it seems probable that a biphotonic process, involving radicals such as phenosyl anilino as intermediates, may be operative. In the formation of phenyl, benzyl and similar radicals, biphotonic mechanisms in the gas phase appear less probable and I have tentatively suggested[5] that a mechanism is operative in which radiationless conversion to the ground state is followed by what is essentially a thermal dissociation of a highly vibrationally excited molecule.

The Triplet State

In 1944, Lewis and Kasha[32] showed that the phosphorescence of organic molecules which is observed in rigid media is the emission of light from the lowest excited state of these molecules and that this state is of triplet multiplicity. This work opened up a new realm of spectroscopy and physical investigation which continues with increasing activity today.

The influence of this discovery on chemistry and photochemistry was, at first, very slight. The reason for this was that the chemist does little work in rigid solutions at low temperatures and only under these conditions could the triplet states be observed. The reasons for the absence of phosphorescence in gases and fluid solutions were not altogether clear, though-Lewis and Kasha clearly stated their view that the triplet state was formed under these conditions, presumably with much shorter lifetime. If this were the case, it should be possible to detect the triplet state by means of its absorption spectrum in flash-photolysis experiments provided its lifetime was greater than a few microseconds, a question about which there was little information.

In 1952, Windsor and I decided to attempt the observation of triplet absorption spectra of organic molecules by flash photolysis in ordinary fluid solvents at normal temperatures. The scheme of transitions involved in these studies is shown in Fig. 13. Almost immediately the experiments were suc-

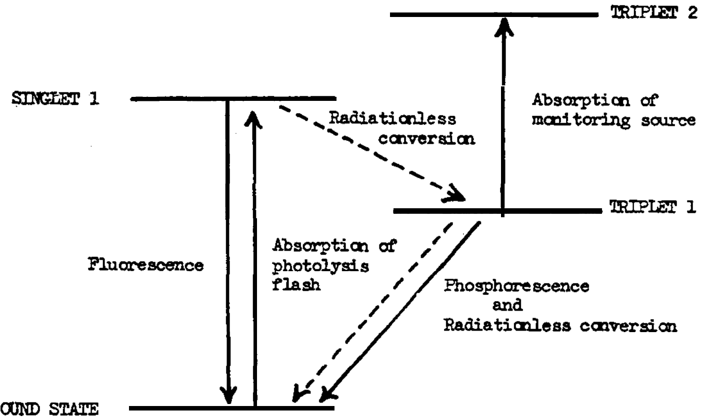


Fig. 13. Transitions involved in flash photolysis studies of the triplet state.

cessful; it transpired that triplet-state lifetimes under these conditions were of the order of a millisecond, ideal for studies by flash photolysis, provided oxygen was excluded. Some of the first flash-photolysis records oftriplet states of aromatic molecules in solutions3 are shown in Figs. 14 and 15.

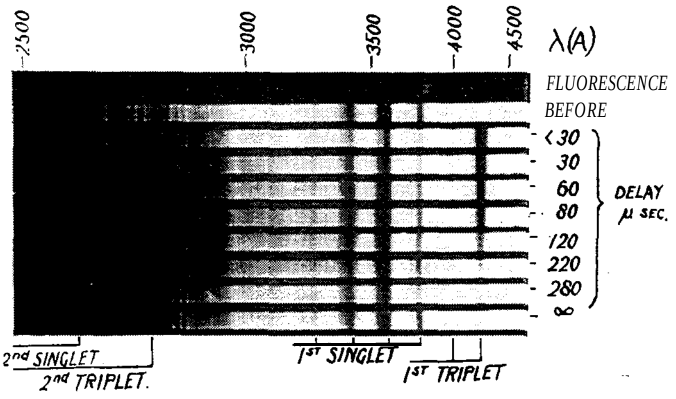
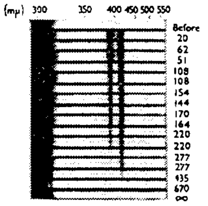


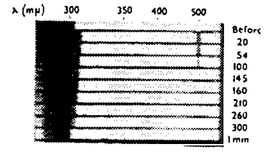
Fig. 14. Absorption spectra following flash photolysis of a solution of anthracene in hexane solution.

Immediately F. J. Wright and I investigated the possibility of detecting triplet states in the gas phase and although the lifetime was shorter the triplet spectra of a number of aromatic hydrocarbons were successfully recorded in 1-m paths of the vapour[34].

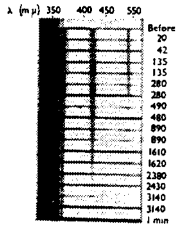
It is these studies, perhaps more than any others, which have brought flash photolysis into the chemical laboratory as a routine method of investigation.



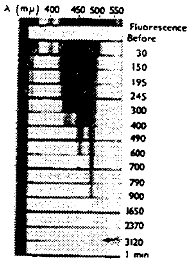
NAPHTHALENE



PENTACENE



PYRENE



1,2-BENZANTHRACENE

Fig. 15. Sequences of spectra after flash photolysis of four aromatic hydrocarbons in solution showing formation and decay of their triplet states. Delays in microseconds.

Any discussion of mechanism in organic photochemistry immediately involves the triplet state and questions about this state are most directly answered by means of flash photolysis. It is now known that many of the most important photochemical reactions in solution, such as those of ketones and quinones, proceed almost exclusively *via* the triplet state and the properties of this state therefore become of prime importance. Its relatively long lifetime, compared with the time of a flash experiment, has made it possible to study the triplet state almost as readily as the ground state, and in many systems its physical and physico-chemical properties and its chemical reactions are now as well characterised as those of the ground state. The spectrum itself, being a transition between two excited states and usually diffuse, has been of less interest for structural studies than as a means of identification and quantitative estimation of triplet concentrations and, therefore, once identified, most kinetic studies have been carried out at a single wavelength using photoelectric methods.

Studies in our laboratory and others, particularly those of Livingston and of Linschitz, over the last fifteen years, have established the following properties of triplet stat& in fluid media:

(1) The radiationless decay processes which occur in solution are principally first order under normal conditions and due to traces of quenching impurities which are still largely unknown. This apparently trivial and uninteresting process has been the most difficult of all to establish and is still the most unsatisfactory aspect of the work. That the decay in solution is a quite separate process from the true radiationless and radiative conversion which occurs in rigid media is most clearly shown by flash experiments carried out over the whole range of viscosity and temperatures[35].

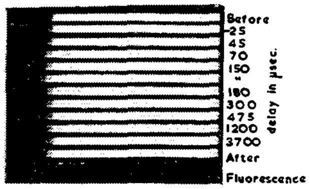
(2) At high concentrations of triplet and low quencher concentrations Porter and M. Wright showed that a second-order process of triplet-triplet annihilation is predominant[36]. Parker and Hatchard[37] have shown that part of this process results in the formation of singlet excited states and delayed fluorescence. In the gas phase Porter and West[38] showed that triplet-triplet annihilation is the predominant means of decay.

Physical quenching of the triplet state can be brought about in four principal ways involving the following species: (a) Heavy atoms which increase spin-orbit interaction[39]. (b) Atoms and molecules with. unpaired electrons which can interact with the triplet to form a collision complex *via* which conversion to the ground state can occur without contravention of the spin selection rules[36]. (c)Molecules which form charge-transfer complexes with the triplet (ref.40). (d) Molecules with lower electronic states (singlet or triplet), to which energy can be transferred[41].

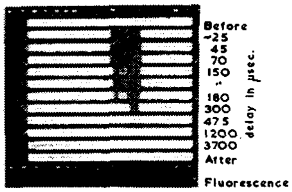
The last of these processes is of particular interest in photosensitisation and biological systems and it was first observed, under conditions of high concentration in rigid media, by Terenin and Ermolae[42]. In solution it is readily studied by flash photolysis and, in favourable cases, both the decrease in donor triplet and the increase in acceptor triplet can be followed independently. An early example of this type of transfer studied by Porter and Wilkinson, between phenanthrene and naphthalene, is shown in Fig. 16.

The efficiencies of triplet state formation have recently beenstudied quantitatively and directly by Bowers and Porter[43] using an optical arrangement of flash photolysis which makes it possible to monitor the light absorbed. At present, in all molecules studied which do not present complexities such as dimer formation, the sum of fluorescence and triplet yields is unity within the precision of the combined measurements (Table 3).

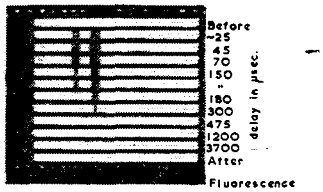
As examples of chemical processes in the triplet state we may mention proton transfer, and electron or hydrogen atom transfer. It is usually easy to arrange, by using buffered solutions, that protonic equilibrium is established



6.9×10^{-3} M Naphthalene.



2.3×10^{-3} M Phenanthrene.



6.9×10^{-3} M Naphthalene.
& 2.3×10^{-3} M Phenanthrene.

Fig. 16. Energy transfer from triplet phenanthrene to naphthalene. The flash is filtered through a strong solution of naphthalene so absorption is by phenanthrene only. In the bottom sequence, obtained from a solution containing both compounds, the triplet of phenanthrene has been completely quenched and replaced by triplet naphthalene.

Table 3

Fluorescence yield Φ_F, triplet yield Φ_T determined directly by flash photolysis insolution, and the sum of these yields for several organic compounds

Compound	*Solvent*	Φ_F	Φ_T	$\Phi_F + \Phi_T$
Anthracene	Liquid paraffin	0.33	0.58 ± 0.10	0.91
Phenanthrene	3-Methylpentane	0.14	0.70 ± 0.12	0.84
1,2,5,6-Dibenzanthrancene	3-Methylpentane	—	1.03 ± 0.16	1.03
Fluorescein (fl)	Aqueous pH 9	0.92	0.05 ± 0.02	0.97
$flBr_2$	Aqueous pH 9	—	0.49 ± 0.07	—
Eosin ($flBr_4$)	Aqueous pH 9	0.19	0.71 ± 0.10	0.90
Erythrosin (flI_4)	Aqueous pH 9	0.02	1.07 ± 0.13	1.09
Chlorophyll *a*	Ether	0.32	0.64 ± 0.09	0.96
Chlorophyll *b*	Ether	0.12	0.88 ± 0.12	1.00

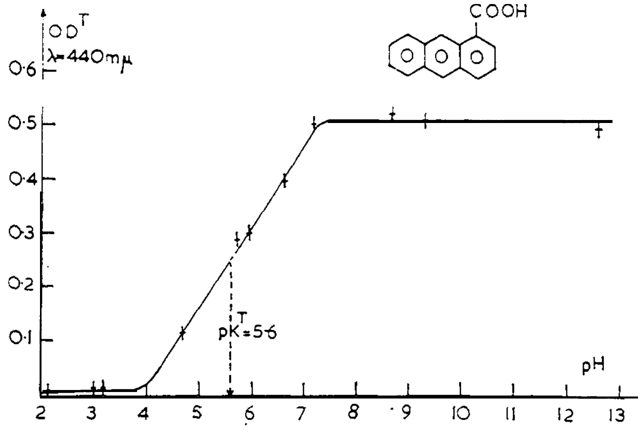


Fig. 17. Optical density plot of triplet anthroic acid *versus* pH used to derive the triplet-state acidity constant of this compound.

during the lifetime of the triplet and, in this case, a titration can be carried out almost as readily as when one determines the *pK* of the ground state, though now the "indicator" is the molecule in its triplet state. It is interesting to compare the results not only with the ground-state properties, but with those of the first excited singlet state which can be determined by fluorescence studies using the methods developed by Forster and Weller[44]. Such studies of triplet states were first carried our in collaboration with Jackson and later with Van der Donckt[45,46]. A typical *pK* plot for the triplet state of anthroic acid is shown in Fig. 17 and a summary of results on *pK's* in the three states of interest for a variety of molecules is given in Table 4.

Electron and hydrogen atom transfer, particularly from solvent to triplet states of ketones, aldehydes and quinones have been the subject of very extensive investigations in a number of laboratories. My interest in this type of reaction first arose in a rather practical way when I was consulted about a technical problem known as phototendering, in which a dyed fabric, such as cellulose, becomes degraded under illumination in sunlight. The mechanism of this presented few problems; it was merely abstraction, by the excited dye molecule, of a hydrogen atom from the cellulose followed by addition of oxygen to the resulting radicals followed by degradation of the cellulose chain. What was surprising was that dyes, such as the anthraquinones, fell into two classes, one very reactive and one almost completely unreactive, the difference between the two classes being caused by the apparently small effects of substitution[47]. After a long and interesting series of investigations, mostly carried

Table 4

Acidity constants expressed as pK values for the ground state (G), the first excited singlet (S_1) and the lowest triplet (T_1) of a number of aromatic molecules

Compound	$pK(G)$	$pK(S_1)$	$pK(T_1)$
2-Naphthol	9.5	3.0	8.1
1-Naphthoic acid	3.7	7.7	3.8
2-Naphthoic acid	4.2	6.6	4.0
Acridine	5.5	10.6	5.6
Quinoline	4.9	(7)	6.0
2-Naphthylamine	4.1	−2	3.3
N,*N*-Dimethylaniline	4.9	—	2.7
1-Anthroic acid	3.7	6.9	5.6
2-Anthroic acid	4.2	6.6	6.0
9-Anthroic acid	3.0	6.5	4.2
2-Aminoanthracene	3.4	(−4.4)	3.3

out on benzophenone derivatives which show exactly the same phenomena, the matter became quite clear[48, 49]. It is always the lowest triplet state which reacts and the electronic structure of this state is, therefore, the prime consideration. Depending on substituents and solvent, this lowest triplet state may be n–π, with electrophilic oxygen and therefore reactive or π–π, with considerable charge-transfer character in the opposite sense to that of the n–π state (CT), and therefore unreactive (Fig. 18).

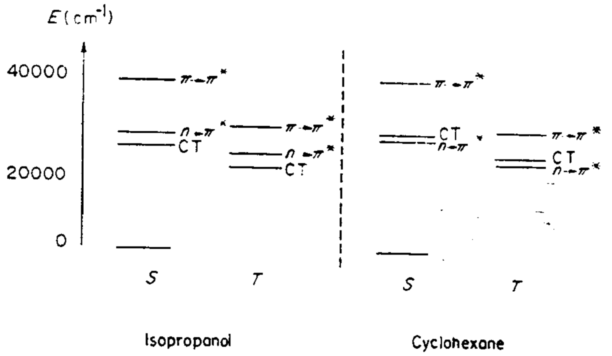


Fig. 18. Energy levels of singlet (S) and triplet (T) states of *p*-aminobenzophenone in isopropanol and in cyclohexane. In isopropanol the lowest triplet is of charge transfer (CT) type and therefore no reaction occurs; in cyclohexane the lowest triplet is the reactive n–π * type and hydrogen abstraction occurs from cyclohexane to yield a ketyl radical.

These studies, both of proton and hydrogen atom transfer illustrate how the excited electronic state must be treated as a new species, with its own structure, electron distribution and chemical reactivity and how flash-photolysis techniques make it possible to study these characteristics of the excited triplet almost as readily as those of the ground state. Since each molecule has only one ground state, but several excited states, it is clear that this field of investigation is, in principle, a bigger subject than the whole ofconventional chemistry.

At the present time efforts are being made to extend flash photolysis techniques in many ways, but particularly to shorter times. Although gas discharge lamps are unlikely to be much improved beyond the microsecond region, the giant pulsed laser promises to bring nanosecond times into the range of investigation and these, as well as nanosecond sparks coupled with integrating techniques, are now being developed in our laboratory and several others[5]. The nanosecond region will be particularly valuable for the direct study of excited singlet states.

The first flash apparatus resolved times of milliseconds, later ones worked comfortably in microseconds and nanosecond flash photolysis is now possible. This is a very short time. If we carry out an experiment every nanosecond then the results of a few seconds' work are enough to fill all the books and journals of the world. Advances of technique, such as the extension of our chemical experiments into the range of very short times, greatly increases the number of questions we can ask and the number of experiments to be done. To solve a problem is to create new problems, new knowledge immediately reveals new areas of ignorance, and the need for new experiments. At least, in the field of fast reactions, the experiments do not take very long to perform.

In conclusion, I express my deep gratitude to the collaborators who are referred to at the end of this paper and to all the other students and colleagues with whom it has been my good fortune to be associated. I share with them this great honour.

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