FLASH SPECTROSCOPY, A METHOD FOR INVESTIGATING RAPID PHOTOCHEMICAL REACTIONS

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CONTENTS

1.	Introduction	721
2.	Identification and reactions of free radicals	722
3.	Study of the triplet state	723
4.	Investigation of explosive reactions	725
5.	Heterogeneous flash initiation of thermal reactions	727
6.	Investigation of the photoreactions of chlorophyll	727

1. INTRODUCTION

The mechanism of most chemical reactions involves the formation as intermediate products of free atoms, radicals, diradicals, and radical-ions, which determine the subsequent character of the reactions.

The method of flash spectroscopy, proposed by Norrish and Porter, has been used since 1949 to study rapid photochemical reactions effected by free radicals and also to investigate the primary intramolecular processes of excited molecules. Work on flash spectroscopy was reviewed in 1954 by one of us[1]. As new possibilities have been opened up for the method and a considerable amount of research has been published since then, it has appeared necessary to prepare a fresh survey.

Let us describe briefly the principle of the method of flash spectroscopy. Reaction is initiated by a momentary high-intensity discharge in a flash lamp. The changes occurring in the illuminated system are studied by means of the absorption spectra in the ultra-violet, visible, and near infra-red regions, the spectra being recorded photoelectrically or photographically (each method has its advantages).

The absorption spectra are photographed by using a second, less powerful lamp, which is triggered at a certain time, determined by a timer, after discharge of the first, powerful flash lamp (see Fig.1). The photographic method is convenient in preliminary investigations when the whole spectral range is recorded, and also in the simultaneous measurement of relative intensities at different wavelengths. Furthermore, the lifetimes of the reaction intermediates are determined from a series of spectra obtained at different times after discharge of the main lamp. However, it is less convenient in kinetic investigations, where the photoelectric method is especially useful.

The photoelectric method, unfortunately, allows measurements to be made only over a very narrow range of wavelengths. Usually, both methods are employed for recording spectral changes.

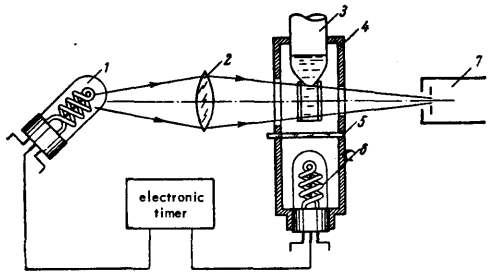


Fig.1. Optical arrangement for spectrosopic measurements with two flash lamps: 1) ISS-250; 2) condenser; 3) cell; 4) jacket; 5) ZhS-18 light filter; 6) ISS-250; 7) spectrograph.

Several arrangements have been suggested for the photographic recording of a spectrum using only one lamp[2] (see Fig.2); in several cases the reaction vessel and the flash lamp are combined as a single unit[3,4].

Lamps of varying power are used depending on the nature of the investigations. The lamps are designed on the general principle that a quartz tube into which are sealed electrodes (usually of tungsten) is filled with an inert gas (argon, krypton, xenon). The flash produced by the discharge of high-voltage condensers gives a high-intensity light flux with a flash of duration 10^{-4} sec or less. Recently Brody and Rabinowitch[5] have produced a lamp in which the flash duration is of the order of 10^{-9} sec. Information on the types of flash lamps manufactured in the Soviet Union is given by Marshak[6].

By means of flash lamps a light flux can be obtained having an energy of the order of 10^6 W sec, corresponding to a flux of 10^{23} quanta per flash. In this way large changes are produced photochemically, and thereby one of the main difficulties in photochemical investigations is overcome.

The method of flash photolysis can give very high concentrations of free atoms and radicals, as a result of which it becomes possible to investigate their reactions in many chemical systems. Reactions lasting for 1–3 μsec can be studied in this way.

In spite of the broad possibilities of flash spectroscopy in the ultra-violet, visible, and near infra-red regions of the spectrum for the identification of free atoms, radicals,

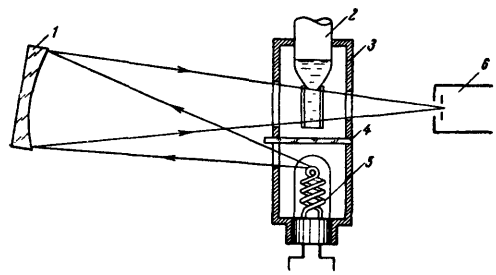


Fig.2. Optical arrangement for spectroscopic measurements with one flash lamp: 1) mirror; 2) cell; 3) jacket; 4) ZhS-18 light filter; 5) ISS-250; 6) spectrograph.

and diradicals in a reaction mixture, this method has substantial limitations. It is quite difficult to determine several reaction intermediates because their absorption spectra are in the far ultra-violet or because they have no specific absorption for comparison with other compounds. In several cases, moreover, it is difficult to obtain direct information on many changes occurring in the molecule under the influence of light. For this purpose it would be useful to examine the infra-red region of the spectrum. However, scanning is very slow in present-day infra-red spectrometers, and it is probably for this reason that they have not been used in flash photochemistry. They will no doubt be employed in the future, when the rate of scanning has been increased.

A recently described method for investigating short-lived ions, radical-ions, and electrons produced in flash photolysis using an electric field is worth considering. The formation of a short-lived triphenylamine radical-ion in hexane has been demonstrated in this way[7,8]. Concentration of ions as low as 10^{-7} M with lives as short as 10^{-13} sec can be detected by this method[8].

A mass-spectroscopic method, by which the spectra of substances can be determined every 50 μsec[9], has also been successfully employed to analyse the intermediate products formed in flash photolysis. With keten, CH_2CO, for example, this method has shown that the CH_2 formed by photolysis reacts with the initial CH_2CO with a very high probability. The reaction product C_3H_4O exists for several hundred microseconds.

Photochemical flash initiation of reactions is very convenient because the photochemical system can be exposed to light of definite wavelength, and thereby only a definite molecule or even part of it can be excited, which greatly facilitates the theoretical interpretation of the results. Use of sensitisers enables photochemically inactive systems to be excited, so that the range of application of photochemistry is extended. Photochemical initiation has advantages over the use of sources of ionising radiation, with which it is difficult to effect selective absorption of the incident energy by definite components of the system. Further, ionising radiation, without giving any appreciable advantage in the concentration of the free radicals formed, produces a large variety of excited molecules and atoms, as well as ions, which greatly complicate the process under investigation. Furthermore, the solvent cannot remain inert in the radiation method of initiation. This is not generally the case with flash photolysis.

Successful study of processes involving interaction between radiation and matter requires the use of both radiation-chemical and flash-photolytic initiation as complementary methods. This enables a bridge to be built between two allied branches of chemistry, photochemistry and radiation chemistry.

Since flash spectroscopy is at the same time a method of initiating and of recording free radicals and excited molecules, it has enabled a successful start to be made on investigating the rapid processes described below, which determine the kinetics of most chemical reactions.

2. IDENTIFICATION AND REACTIONS OF FREE RADICALS

Flash photolysis was first applied to the photochemical breakdown of simple or more complicated substances in the gaseous state, in the first instance of the halogens: chlorine[10-12], iodine[13-16], and bromine[13-17]. It was possible by absorption spectroscopy to follow the formation of the free atoms and their subsequent recombination. The reaction of chlorine atoms with oxygen was studied, a new radical ClO being formed, the absorption spectrum of which was later obtained in the photolysis of ClO_2.[18]

The absorption spectra of radicals were obtained in a similar manner by the flash photolysis of the compounds listed in Table 1.

The life of the resulting free atoms and radicals varies between quite wide limits, from fractions of a millisecond to several minutes, *i.e.* it depends on their nature. For example, the radical ClO has a life of 4×10^{-3} sec, while that of the CS radical is 2 min. The reactions of excited oxygen atoms and molecules, obtained in the flash photolysis of ozone, have also been studied[32].

However, in the photochemical flash decomposition of several organic compounds, such as keten[33], acetaldehyde[34,35], biacetyl[34], acetone[34,36,37], diethyl ketone[38], methyl iodide[39], azomethane[40], tetraethyllead[41], and benzene[4,42], a steady-state concentration of radicals could not be obtained, owing to the formation of stable end-products of the photochemical reactions by the occurrence of secondary reactions between the initially formed radicals at high concentrations of the latter.

Although the early work on flash photolysis was carried out with gases, as already noted, at the present time most effort is devoted to the photolysis of liquid systems. This is partly because a large amount of energy is evolved during photolysis, being the excess energy of the photodecomposition products and also the energy evolved on recombination of the atoms and radicals. The energy which

TABLE 1. Radicals formed in flash photolysis.

Substance	Radicals found from absorption spectra	References
CS_2	CS, S_2	10, 11, and 12
NH_3	NH_2* and NH	3, 19, 20, 21, 22
N_2H_4	NH_2 and NH	22, 23
HN_3	NH_2, NH, and N_2	24
PH_3	PH_2, PH, and P_2	3, 22, 25
NOCl	NO	26
B_2H_6	BH	3, 22
SiH_4	SiH	3, 22
HCN	CH, C_2, and CN*	3, 22
CH_3CN	CH, C_2, and CN	3, 22
S_2Cl_2	S_2, SCl	27
H_2O	OH	3, 22
H_2S	SH	19, 20
D_2S	SD	19, 20
C_2H_2	CH, C_2, and C_3	3, 22
CH_3CHO	HCO	22, 28, 29
CH_3CDO	DCO	28, 29
$C_6H_5CH_3$		
$C_6H_5CH_2NH_2$	$C_6H_5CH_2$	30
$C_6H_5CH_2OH$		

* In subsequent investigations the absorption spectra of the radicals NH_2 and CN were obtained in low intensity, under conditions of continuous illumination but with a long absorption path[31].

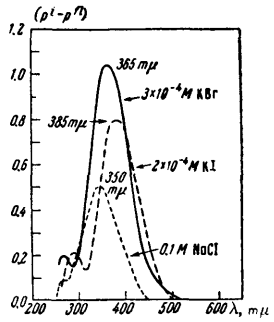


Fig. 3. Absorption spectra of dihalogen ions produced by flash illumination of aqueous solutions of NaCl, KI, and KBr at pH 6.0: 1) Cl_2^-; 2) I_2^-; 3) Br_2^-.

is liberated may produce substantial changes in the course of the reaction, and it is extremely difficult to establish the nature of the effect.

To eliminate the thermal effect in gaseous systems, a considerable amount of an inert gas is usually introduced (partial pressure of gas up to 1 atm). Thus in an investigation by the flash method of the rate of recombination of iodine atoms[15,16] the calculated rise in temperature after introduction of the inert gas was ~1°, although the percentage decomposition into atoms was ~50%: *i.e.* the effect of temperature gradient could be neglected. However, introduction of a foreign gas may cause additional phenomena affecting the course of the reaction, and associated mainly with energy-transfer processes.

In liquid systems, owing to their great heat capacity, the temperature rise during photolysis seldom exceeds a fraction of a degree, which is insignificant.

Intensity measurements on the absorption bands can be used to determine the relative concentrations of the radicals, and from these the rate constants of the reactions in which they take part can be calculated. As an example, photolysis of aqueous solutions of NaCl, KBr, and KI involved the intermediate formation of the dihalide ions, *i.e.* Cl_2^-, Br_2^-, and I_2^- respectively[43] (their spectra are shown in Fig. 3).

The flash photolysis of potassium iodide solutions has been investigated in greater detail. The I_2^- ions are formed by the reaction

$$I + I^- \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} I_2^- \qquad (1)$$

and are removed by the following bimolecular reactions

$$2I \xrightarrow{k_2} I_2, \qquad (2)$$

$$I + I_2^- \xrightarrow{k_3} I_3^-, \qquad (3)$$

$$2I_2^- \xrightarrow{k_4} I_3^- + I^-. \qquad (4)$$

Breakdown of the I_2^- ion was found to be kinetically second order, being greatly dependent on the concentration of I^- ions. Analysis of the results showed which of the reactions (1) or (4) was responsible for the breakdown of the I_2^- ion. The constant of reaction (4) was found to have the maximum value: $K_4 = 2k_4 = (7.7 \pm 1.5) \times 10^9$ mole^{-1} sec^{-1}, whereas the minimum value $K_1 = k_1/k_1' = 1.2 \times 10^4$.

High-intensity flash illumination of some solutions results in the appearance of intermediate products having variable life times. In solutions of bromine and iodine in carbon tetrachloride and hexane, for example, absorption appears in the range 280–330 mμ, lasting for 70 μsec or less[43]. In aqueous $KBrO_3$ solutions, after the flash, absorption is observed in the range 350–390 mμ, which is due to the radical $BrO_3\cdot$ (~10 μsec), while absorption in the neighbourhood of 460 mμ is due to a $BrO\cdot$ radical (duration of existence 1 μsec)[44,45]. A long-lived intermediate was also observed in the photodecompositionn of oxalato-complexes of iron, cobalt, and uranyl[46]. Aqueous solutions of aromatic hydroxy-compounds show a short-lived (15 μsec) shift in the electrolytic dissociation equilibrium

$$R\cdot OH + H_2O \overset{h\nu}{\rightleftharpoons} RO^{-*} + H_3O^+.\ ^{42}$$

When in the ground state the resulting ion RO^- recombines with the H_3O^+ ion to form the original compounds.

3. STUDY OF THE TRIPLET STATE

Under certain conditions dyes and aromatic compounds show, in addition to fluorescence, a prolonged afterglow or phosphorescence, which can sometimes continue for several seconds. This phenomenon is well developed when the molecules are trapped in various organic and inorganic matrices or even when they are attached to the surface of adsorbents, and especially at low temperatures.

It follows from the occurrence of phosphorescence that the molecules of the dyes and aromatic compounds contain, in addition to an excited state (with the normally short life of 10^{-8}–10^{-9} sec), an intermediate long-lived metastable state (lying below the excited level), into which the molecule can pass from the excited state[48].

Terenin advanced and justified the view[49] that the metastable electronic state is a triplet–diradical (bivalent) state having two unpaired electrons differing from the singlet excited and ground state, in which all the electrons are paired.

The important role of the triplet state of molecules in the occurrence of many photochemical reactions is now generally recognised, especially in photooxidation and photoreduction processes, but up till now the triplet state has not been taken into account in considering thermal reactions, although this state can become populated at low temperatures. The transition of several substances to a triplet state is favoured by illumination with a high-intensity flash.

Thus the spectra of solutions of aromatic compounds freed from oxygen show a diminution of the singlet state and the appearance of new absorption bands. These disappear about 10^{-2}–10^{-5} sec after the termination of photolysis, the absorption due to the singlet state regaining its original value[50]. The new absorption bands are due to molecules in a triplet state, the transition to which is effected by the flash illumination; the probability of the transition is independent of the nature of the solvent or its viscosity.

Fig. 4 shows the absorption spectra of anthracene before and after the flash. Table 2 gives the frequencies of the triplet spectra of several organic compounds.

The quenching of molecules in the triplet state does not occur exactly according to a first-order law, which indicates that quenching can take place by collision between two molecules in this state[50,51]. The mechanism of quenching is a radiationless transition of the molecule from the triplet state to the upper vibrational levels of the singlet ground state Within certain limits transition is independent of the concentration of the substance (with anthracene between 2×10^{-6} and 10^{-3} M), but it diminishes with increase in viscosity of the solvent. Experimental data indicate that the probability of the transition to the triplet state may exceed that of the transition from the triplet to the singlet ground state by a factor of 10^4. This phenomenon has not yet received a theoretical explanation.

Anthracene molecules in the triplet state are quenched considerably more strongly in the presence of oxygen or nitric oxide. The effect of paramagnetic ions on triplet naphthalene molecules in ethylene glycol has also been investigated[51]. The ions Cu^{2+}, Ni^{2+}, Co^{2+}, and Mn^{2+} have a strong quenching effect. The diamagnetic ions Zn^{2+} and Ca^{2+}, as also the paramagnetic ions Ce^{3+}, Nd^{3+}, and Gd^{3+}, do not have an appreciable quenching effect[51].

By means of the flash technique[52] a triplet diradical state has been observed also in the vapours of aromatic compounds. The probability of the transition from the excited singlet to the triplet state was found to be independent, within wide limits, of the pressure of the inert gas, and to vary little with different states of aggregation, its value for aromatic compounds being of the order of 10^6–10^9 sec^{-1}. The probability of a transition from the triplet state to the singlet ground state also depends little on the pressure of the inert gas, but is greatly dependent on the state of aggregation. In the vapour phase this probability is of the order of 10^4–10^5 sec^{-1}, whereas for most aromatic molecules in a solid medium it ranges from 10^3 to 10^{-1} sec^{-1}.

During the flash photolysis of the vapours of such aromatic compounds as toluene, ethylbenzene, benzyl chloride, benzylamine, benzyl alcohol, etc., identical electronic absorption spectra, due to the free benzyl radical, are observed[53]. Benzyl radicals and also radicals obtained from other compounds have a life which is shorter than 10^{-4} sec, indicating a high efficiency of recombination.

TABLE 2. Band maxima of triplet–triplet absorption.

Compound	In hexane[60], cm^{-1}	In liquid paraffin[60], cm^{-1}	In vapour (CO_2 gas)[22]	
			temp., °C	cm^{-1}
Naphthalene	24 210 25 640 27 210	(1) 24 100 25 550 26 880 (2) 38 500	50	25 180 26 550 27 930 29 340 30 900
1-Methyl-naphthalene	23 700 25 130	23 700 25 060 26 320	40	24 720 26 410
Anthracene	23 790 25 130	(1) 21 370 (2) 23 580 24 940 (3) 35 700	120	24 810 26 230
Phenanthrene	(1) 19 230 19 670 (2) 20 790 22 060 23 500	—	200	21 880 23 250 24 590
Naphthalene	from 20 400 to 25 000	(1) 21 000 (2) 21 740 23 320 25 000 (3) 31 900 (4) 35 030	160	23 630 24 900
1,2-Benzanthracene	20 620 22 200 23 260	(1) 18 520 (2) 20 620 21 690 23 010 24 100 (3) 31 750	200	broad band from 21 740 with maximum at 22 120
Pyrene	24 330 25 840 27 100	(1) 19 250 20 700 (2) 24 040 25 220 26 910 (3) 27 780	100	25 350
Fluorene	broad band from 25 000 to 29 400	—	95	20 410 broad band from 26 300 to 31 250 with maxima at 28 360 and 30 230
Triphenylene	(1) 23 360 24 750 (2) 28 900	—	200	24 390

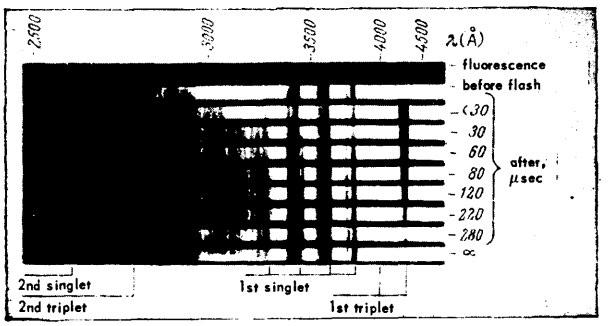


Fig. 4. Series of absorption spectra of triplet state of anthracene in hexane.

The formation of these radicals is due to the weak bond in the side-chain and their relatively high stability. Subsequently, these and other radicals were obtained by the continuous illumination of frozen solutions at a low light intensity, when their survival time reached many hours[54].

Transitions to the triplet state and the formation of radicals have been detected by a similar spectroscopic method in solutions of albumin, ovalbumin, amino-acids, and phenol[55–57], rhodopsin[58], and also quinones (benzoquinone, acetophenone, derivatives of anthraquinone), acridine, and other compounds[59–62].

Solutions of derivatives of anthraquinone and acridine showed momentary selective fading of their main absorption band under the influence of flash illumination[60]. These compounds were subject to reversible decolorisation which show delayed fluorescence in the adsorbed state, indicating the presence of a nearby triplet level. These compounds also sensitise the photooxidation of organic compounds[60].

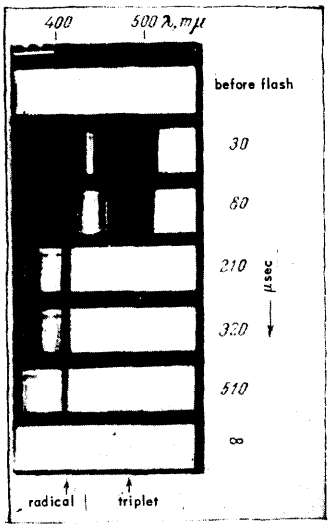


Fig. 5. Absorption spectra of triplet state and radical of duroquinone.

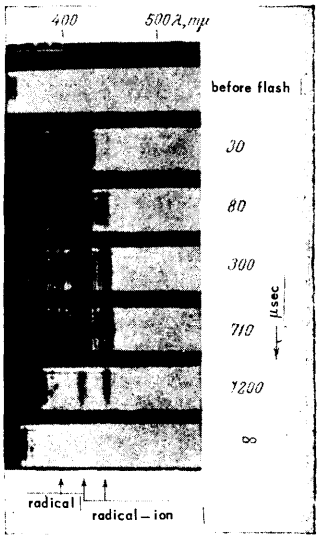


Fig. 6. Absorption spectra of radical and radical–ion of durosemiquinone (in ethyl alcohol).

The momentary reversible fading of several anthraquinone and acridine derivatives under the influence of a high-intensity flash is explained by the accumulation of excited molecules in the triplet diradical state.

This postulate was confirmed for the sensitisers of anthraquinone derivatives, duroquinone and benzophenone, which exhibit strong absorption by intermediate forms (triplet state and radical–ions)[61,63,64]. Thus with duroquinone the semiquinone radical and, under special conditions, the semiquinone radical–ion were detected[61] together with the triplet form (see Figs. 5 and 6). Flash spectroscopy has also established that it is an $n \rightarrow \pi^*$ transition, not $\pi \rightarrow \pi^*$, which is photochemically active in sensitised reactions[62].

Temporary and reversible fading in the main absorption band is observed also when solutions of Methylene Blue or thionine in sulphuric acid are exposed to a flash source, with the appearance of strong absorption in the range 360–440 mμ, which disappears after less than 30 μsec. This absorption is ascribed to the triplet state of the dye. Under different conditions of illumination (shorter ultra-violet rays) another intermediate product, the semiquinone radical of the dye[65], is formed. The appearance of two absorption bands after flash illumination has been observed also with eosin solutions; these last for different times, and are due to the dye in a triplet state and to the semiquinone radical of the dye[66]. A triplet form appears in fluorescein solutions after exposure to a flash, and as it decays radicals appear (bearing positive and negative charges)[67]. With thin films of solid organic dyes, for example, Crystal Violet, eosin, Rhodamine B, Methylene Blue, and erythrosin, momentary fading was observed, on exposure to high-intensity flashes, under vacuum conditions both at +20° and on cooling with liquid air[60,68]. With thin films of Crystal Violet, trypaflavine, and Rhodamine B, the life of the decolorised form of the dye was found to be $(0.8–1.0) \times 10^{-3}$ sec, while with Methylene Blue and eosin it was $(1–1.5) \times 10^{-3}$ sec (at -180°).

4. INVESTIGATION OF EXPLOSIVE REACTIONS

The flash technique has been successfully employed to investigate the explosive oxidation of hydrogen and several hydrocarbons with oxygen. It has proved possible not only to obtain the absorption spectra of the reaction intermediates (free radicals and atoms) but also to measure their relative concentration throughout the reaction. Several complicated radicals, which do not emit light and hence are not detected in the flame emission spectra, were observed from the absorption spectra. Moreover, it is difficult from the emission spectra of the radicals and atoms to follow rapid changes in their concentrations, and hence to analyse the whole course of the combustion. The flash technique enables the mechanism of burning to be established with sufficient precision.

In order to study the process of combustion by the flash technique, however, simultaneous initiation of the reaction (ignition) throughout the reaction vessel is necessary. This is achieved by adding a photosensitiser, which under the influence of the high-intensity flash breaks down into free radicals and atoms, and these initiate the chain reaction. If, however, a reactant in the explosive reaction forms free radicals and atoms on absorption of light from the flash lamp, there is no need for a sensitiser. In the explosive oxidations of hydrogen and hydrocarbons with oxygen, the sensitiser used is nitrogen dioxide (at a pressure of 0.75 mm), which is half-decomposed by the flash, and has almost completely disappeared after 0.8×10^{-3} sec.

The mechanism of the photolysis of nitrogen dioxide is as follows:

$$NO_2 + h\nu \rightarrow NO + O.$$

The following secondary reaction is also possible:

$$O + NO_2 \rightarrow NO + O_2.$$

It is assumed that, since N_2O and O_2 are formed

in equivalent quantities, reaction takes place also between "hot" NO* molecules and the initial NO_2:[9]

$$NO_2 + NO^* \rightarrow N_2O + O_2.$$

The absorption spectra of the radicals OH and NO are observed[69] in the reaction between hydrogen and oxygen sensitised with nitrogen dioxide. The most interesting is the OH radical, the intensity of whose spectrum is high immediately after the flash, then falls rapidly. The relative concentration of OH radicals was found to diminish with increase in the pressure of hydrogen. In the presence of nitrogen as inert gas, the concentration increases insignificantly, but the survival time of the OH radicals becomes much longer. Excess of oxygen has a similar effect to nitrogen.

Formation of OH radicals in this reaction takes place immediately after the photochemical decomposition of the nitrogen dioxide:

$$O + H_2 \rightarrow OH + H.$$

In the presence of excess of hydrogen there is a rapid decrease in the number of OH radicals:

$$OH + H_2 \rightarrow H_2O + H;$$

but in the absence of hydrogen:

$$OH + OH \rightarrow H_2O_2 \text{ or } OH + OH \rightarrow H_2 + O_2.$$

Formation of the HO_2 radical was not detected spectroscopically in these experiments, probably because this radical cannot exist for a long time in the presence of hydrogen, with which it reacts:

$$HO_2 + H_2 \rightarrow H_2O_2 + H;$$

and perhaps also because it has no characteristic spectrum in the range studied.

In the explosive oxidation of acetylene[70], ethylene[71,72], ethane, and methane[71] with oxygen sensitised by nitrogen dioxide, the absorption spectra of a series of radicals: OH, CH, C_2, C_3, CN, and NH, were obtained with all the hydrocarbons. Quantitative measurements of the absorption spectra of these radicals were obtained only in different stoichiometric mixtures, which is quite understandable.

From the variations in the relative concentrations of different radicals, *i.e.* their formation and disappearance throughout the reaction as a function of the pressure of the reactants and the time, it was possible to establish exactly the kinetics of the explosive oxidations. As example we can cite the kinetics of the explosive photochemical reaction of acetylene with oxygen (see Figs. 7 and 8), which takes place in the following stages: (1) an induction period lasting from 0 to 3×10^{-3} sec, at the end of which OH radicals begin to appear; (2) a period in which diatomic radicals, OH, CH, and C_2, are formed (in the presence of nitrogen dioxide the radicals CN and NH are also produced), of duration $\sim 10^{-4}$ sec; (3) a period of reaction between hydrogen and oxygen with the formation of the OH radical and the disappearance of all the remaining intermediate radicals, lasting for $\sim 10^{-4}$ sec; (4) a period of slow reaction of the atoms and radicals remaining from periods (2) and (3), with formation of the final reaction products. The most important reactions are those of the OH radical with hydrogen and with carbon monoxide.

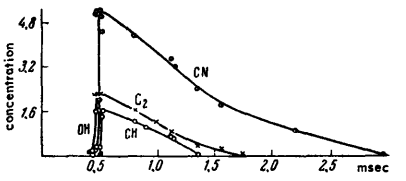


Fig. 7. Concentrations of various radicals as a function of time at pressures of 10 mm O_2 + + 13 mm C_2H_2 + 1.5 mm NO_2.

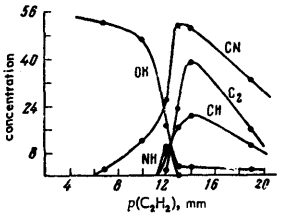


Fig. 8. Maximum concentrations of radicals as a function of the pressure of acetylene. Oxygen pressure 10 mm, NO_2 pressure 1.5 mm.

All explosive reactions involving the oxidation of hydrocarbons are fundamentally homogeneous as a result of the simultaneous initiation of reaction (ignition) throughout the space, which is produced by the sensitiser radicals. However, the formation of a large number of diatomic radicals during the reaction is accompanied by intense emission of light lasting several microseconds, due to the formation of shock waves passing through the reactant gases and causing detonations in the vessel. Addition of tetraethyllead to the reaction mixture was found to lengthen the induction period and almost completely to destroy the strong emission. Tetraethyllead promotes the homogeneity of explosive oxidations in a gaseous medium[73,74] by reacting with the oxidised intermediate products and forming lead oxide. This diminishes the source of spontaneous ignition causing detonation in the second period. Furthermore, the lead oxide terminates chain reactions leading to explosion.

Subsequently a study was made of the explosive combustion of hydrogen sulphide, which is effected in the absence of a sensitiser. The absorption spectra of the radicals SH and OH were obtained in the initial stage of the reaction, these then forming the final reaction products H_2O and SO_2. A strong emission of wavelength $\lambda > 2000$ Å was noted in this reaction, this being ascribed to an excited sulphur dioxide molecule[75].

Similar experiments, using very brief high-intensity flashes (15 μsec or less[42]), were made on the combustion of benzene, propane, and acetaldehyde.

Investigations have also been made on the oxidation of phosphine and methyl iodide by oxygen[76,77], and also of ammonia, hydrogen, hydrogen chloride, methane, and water by ozone[78].

It was mentioned earlier that the flash illumination of endothermic reaction systems ($H_2 + O_2$, etc.) causes explosions. This proved to be true also of many other endothermic substances [79], as, for example, nitrogen iodide, which decomposes under the influence of a flash of light as follows:

$$NH_3 + NI_3 \xrightarrow{h\nu} N_2 + 3HI,$$

$$3HI + 3NH_3NI_3 \rightarrow 2NH_4I + 1.5N_2 + 4.5I_2.$$

Several nitrides, carbides, azides, perchlorates, and other compounds are decomposed explosively by flashes of light. In the case of very thin layers of silver nitride only impressions can be obtained since the light produces photochemical action only where it is incident, which cannot extent to other parts of the layer.

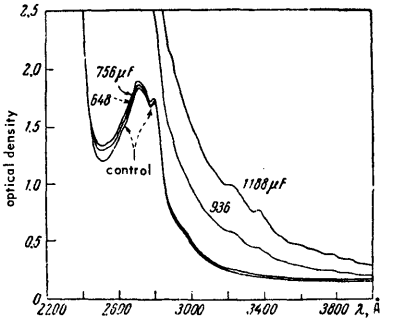


Fig. 9. Effect of energy of flash on pyrolysis of mineral oil. Absorption spectra of oil samples after exposure to flashes of various energies (648, 756, 936, and 1188 μF at 4 kV).

5. HETEROGENEOUS FLASH INITIATION OF THERMAL REACTIONS

In the investigation of thermal reactions, a considerable rise in temperature of the system is often required for a brief period. However, it is quite difficult to achieve this. The action of an intense flash of light on a transparent gaseous, liquid, or solid thermal conductor containing finely dispersed opaque solid particles (carbon, metals) produces a marked rise in temperature of the sytem. After a flash of a few milliseconds, for example, finely divided tungsten powder was observed to vaporise explosively in a vacuum. This indicates that the temperature in the illuminated system was of the order of several thousand degrees. Carbonisation, explosion, vaporisation, fusion, pyrolysis, and other thermal processes can be initiated in a similar manner. Extremely interesting results have been obtained by the flash initiation of thermal reactions. For example, gaseous methane and tungsten (25 mm of wire, dia. 7.5 μ) were exposed to the flash from a lamp of energy 25 J. Deposition of carbon was observed, as well as the formation of H_2, C_2H_6, C_2H_4, and C_2H_2. A control sample (without the wire) underwent no change. Calculation of the quantity of hydrogen formed showed that 400 volumes of methane decomposed per unit volume of the wire. Since methane does not absorb in the near ultra-violet or the visible region, the reaction investigated was a typical example of heterogeneous sensitisation. Experiments with non-absorbing systems (CH_4–O_2, H_2–O_2) were analogous, irradiation resulting in explosions. Initiation of the pyrolysis of mineral oil containing molybdenum (particle diameter < 74 μ) or carbon (particle diameter < 36 μ, 0.03% by weight) by a flash of 7500 J gave the oil a jet-black colour (formation of carbon of particle diameter ~100 Å), and on exposure to a mercury lamp (3661 Å) the oil showed a light blue fluorescence. Examination of the dependence of the pyrolysis of oils on the flash energy showed the presence of a threshold energy (see Fig. 9).

The heterogeneous flash initiation of a reaction has been used also to diminish the period of exposure in studying the photodegradation polymers [80]. On the illumination of a polyethylene film into which had been introduced a tungsten wire (130 μ), pyrolysis of the polymer was observed, the number of molecules of gas evolved per gramme of polymer being proportional to the square root of the number of flashes. It is interesting that pyrolysis does not occur in the vicinity of fluorescent impurities accidentally present in the polymer.

In heterogeneous photolysis the energy of the whole spectrum of the lamp can be utilised for the excitation. This allows systems which absorb little if at all to be initiated and hence intermediate compounds can be studied which are not found in photochemical reactions. A disadvantage of the method is the formation of a very reactive surface, which complicates interpretation of the results and comparison with processes of homogeneous sensitisation.

6. INVESTIGATION OF THE PHOTOREACTIONS OF CHLOROPHYLL

Application of the flash technique, with photographic and spectrophotometric recording of the spectra, to the study of the primary photoreactions of chlorophyll has enabled their detailed mechanism to be revealed. Spectroscopic measurements have been carried out in the near ultra-violet and the visible regions of the spectrum. The main absorption bands of chlorophyll (660–645 mμ and 460–470 mμ) were found to be momentarily and reversibly decolorised in solutions free from oxygen (in ethanol, methanol, acetone, benzene, pyridine, and other solvents) by powerful flashes of light [60,68,81-88]. The lifetime of the decolorised form is 1.5×10^{-4} sec with chlorophyll *a*, 1.3×10^{-3} sec [81] to 10^{-3} sec [85] with chlorophyll *b*, and 10^{-3} sec [60,68] with chlorophyll *a* + *b*.

Reversible fading was observed also in frozen solutions of chlorophyll (at -190°) under steady illumination [83]. Here the decrease in absorption in the above regions of the spectrum was accompanied by an increase in the ranges 740–700 and 500–480 mμ.

Similarly, new absorption bands appear in the spectrum of solutions of decolorised chlorophyll during flash illumination (see Fig. 10). Use of lamps giving flashes of duration 10^{-3} sec resulted in quite strong absorption at 525 mμ [81,82,85,86]. With lamps giving shorter flashes, however, new absorption bands were observed, the most intense being at 460 ± 5 mμ with chlorophyll *a*, 480 ± 5 mμ with chlorophyll *b* [84,87,88], and at 460 mμ with pheophytin *b*. [87] Momentary reversible bleaching was found also in both absorption bands (665–680 and 345–360 mμ) with the chlorophyll analogues magnesium and zinc phthalocyanines and metal-free phthalocyanine [60,68],

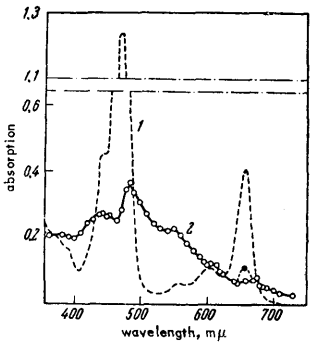


Fig.10. Absorption spectrum of chlorophyll *b*: 1) before flash; 2) after flash from lamp.

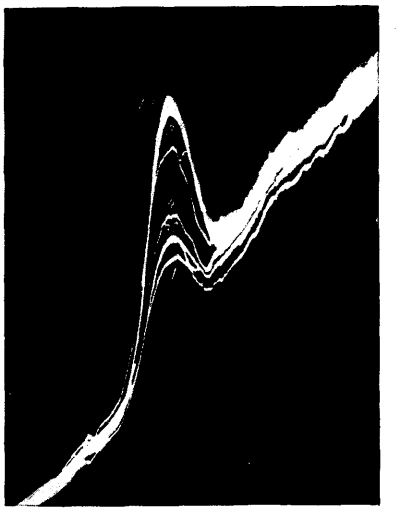


Fig.11. Microdensitometer tracings of absorption spectra of a solution of magnesium phthalocyanine in pyridine. Spectrum from flash lamp at intervals after illumination with lamp No.1: 1) 20 μsec; 2) 50 μsec; 3) 200 μsec; 4) 300 μsec; 5) 800 μsec; 6) 2500 μsec; 7) 4000 μsec; 8) 0.01 sec; 9) 0.1 sec; 10) 1 sec.

and the life of this form (see Fig. 11) was found to be $(0.8-1.0) \times 10^{-3}$ sec. With magnesium phthalocyanine new absorption bands were discovered with maxima at 410 and 400 mμ,[87] and also the appearance of a band at 560 mμ, which is ascribed to a photoreducing form of the pigment in the absence of foreign reducing agents[89]. Phthalocyanines containing copper, iron, or cobalt, as well as iron and copper pheophytinates, did not show reversible bleaching under the influence of light flashes.

Solutions of chlorophyll and magnesium and zinc phthalocyanines in ethanol and acetone showed considerably weaker reversible bleaching in the presence of water than in the dry solvents. It was also found that the long-wavelength absorption bands of the pigments were considerably more intense in the moist than in the dry solvents, in agreement with published data on the action of traces of water on the spectrum of the pigments[83,90]. The converse rule is observed with pyridine, ether, toluene[60,68], and benzene solutions[87].

Momentary reversible decolorisation is observed with pigments in other states of aggregation (frozen solutions at -180°, thin solid films, and adsorbed on silica gel[60,68]).

Reversible fading of the red absorption band of chlorophyll occurs also in homogenised solutions of chloroplasts, and in leaves and algae, in which an intermediate form having an absorption maximum at 525 mμ was detected[91-93].

The suggestion is made in all the papers that the momentary reversible decolorisation of molecules of chlorophyll and its derivatives and analogues under the influence of a high-intensity flash of light is caused by the accumulation of excited molecules in a metastable triplet level. This is also indicated by the fact that oxygen prevents decolorisation, since it strongly deactivates such a state. The presence of a nearby metastable triplet level in the above pigments is indicated by the phosphorescence which has been found in frozen solutions of chlorophyll *a* and *b*,[94-98] and also by the strong quenching effect of oxygen on the fluorescence of the pigments[60,98].

However, the transition of pigment molecules to a metastable triplet state is accompanied by formation of their photoproducts, which have characteristic absorption bands depending on the experimental conditions: 470 mμ with the primary photoreducing form of the pigment, the radical-ion of the semiquinone[99]; and 525 mμ with the secondarily reduced, hydrogenated (semiquinone) form of the pigment[100,101].

The flash spectroscopy of the pigments has enabled the primary photochemical act of photosynthesis accomplished in plants to be established. After having absorbed a quantum of red light, the chlorophyll first passes from an excited to a metastable triplet state possessing greater reactivity and a long life, which determines its chemical properties in the further reactions of photosynthesis.

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OVERLAP INTEGRALS AND APPROXIMATE ESTIMATES OF THE ENERGIES OF CHEMICAL BONDS

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CONTENTS

1. Introduction 730
2. Estimation of chemical bond strength by means of overlap integrals 731
3. Use of overlap integrals to explain the properties of compounds containing *d* electrons 733
4. Determination of the amount of ionic character in bonds by means of overlap integrals 734
5. Use of overlap integrals to determine the most advantageous hybridisation of atomic orbitals in a molecule 734

1. INTRODUCTION

Estimation of the strength of a chemical bond constitutes one of the most important problems of theoretical chemistry, since in several cases there are no reliable experimental data on bond energies.

However, quantum-mechanical calculations of these quantities are very complicated, and there is no great certainty that the results obtained are correct. Therefore approximate, semiquantitative calculations, which enable comparative assessments to be made[1], now play a great part in quantum chemistry.

A simple method for the quantum-mechanical estimation of the strength of a chemical bond is the use of overlap integrals. These integrals may also be used to solve several other chemical problems, and we therefore think it necessary to bring them to the attention of a wide circle of chemists.

Overlap integrals are the simplest of all molecular integrals. If the state of an electron in an atom A is described by the wave function χ_A, and that in an atom B by the function χ_B, the overlap integral of these two functions is

$$S_{AB} = \int \chi_A \chi_B \, d\tau. \qquad (1)$$

Integration is carried out with respect to the coordinates of one electron over the whole configurational space. Only non-orthogonal wave functions can overlap, their degree of non-orthogonality being a measure of their overlap; therefore overlap integrals are still termed also "non-orthogonality integrals".

The energy of a bond can be regarded as roughly proportional to the overlap integral[2], since it consists mainly of the exchange energy. If, however, the expression is written down for the exchange integral in the case of the formation of the simplest molecule H_2^+, it is evident that almost all its terms contain overlap integrals as cofactors:

$$H_{12} = H_{21} = \int \chi_A \left(E_0 + \frac{1}{R} - \frac{1}{r_B}\right) \chi_B dr =$$

$$= E_0 \int \chi_A \chi_B dr + \frac{1}{R} \int \chi_A \chi_B dr - \int \chi_A \frac{1}{r_B} \chi_B dr =$$

$$= E_0 S + \frac{1}{R} S - K, \qquad (2)$$

where E_0 is the energy of the hydrogen atom, R the internuclear distance, r_B the instantaneous distance between the electron and the nucleus B, and K the resonance integral.

The following semiempirical formula has been suggested for the exchange integral $H_{ij} = \int \chi_a^2 \chi_b^2 (1/r_{12}) d\tau_1 d\tau_2$, which presupposes that the latter is proportional to the overlap integral S_{ij}:

$$H_{ij} = \frac{1}{2} F_x S_{ij} (H_{ii} + H_{jj}), \qquad (3)$$

where H_{ij} and H_{jj} are integrals representing the energy of the electron in the i-th or the j-th orbital in the field of the nuclear skeleton of the molecule and the remaining valence electrons, and F_x is an empirical correction, its value being 1.67 for a σ bond and 2.00 for a π bond[3]. The exchange energy calculated according to this formula agrees well with experimental data for several compounds[3,4].

Hence it can be seen that overlap integrals vary in the *same* sense as exchange integrals, *i.e.* in the *same* sense as the energies of chemical bonds.

However, overlap integrals cannot be "absolute" measures of the energy of a chemical bond or other characteristics of chemical interaction in a molecule. Whether it is more advantageous for the molecular orbital formed by the overlapping of atomic orbitals to be occupied by one or two electrons cannot be determined from an examination of the overlap integrals.