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The Electron Spin Resonance Method in Photochemistry

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The electron spin resonance (ESR) method is, at the moment, one of the most sensitive physical methods of detecting, identifying, and studying free radicals, ion-radicals, and molecules in the triplet state formed during photochemical reactions. In this review, the use of the ESR method in studies of photodecomposition and photoionisation reactions of simple and of complex compounds is discussed on the basis of results obtained by Soviet and foreign workers. It is concluded that the ESR method will prove to be a powerful physical method of investigation of photochemical systems only if used in conjunction with other methods (in particular, optical spectroscopy).

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I. INTRODUCTION

For many years, chemical analysis of the final reaction products has been the most widely used method of investigating the mechanism of photochemical reactions. Knowing the products, one can surmise the nature of the intermediate stages. Methods of separation and of analysis of the reaction products have reached an advanced level of development. For the identification of products, chemists can call on methods such as chromatography, mass spectroscopic analysis, and tracer methods. It is well known that excited states, ions, and free radicals play a key role in photochemical change. If the optical absorption or luminescence spectra of these intermediate states are known, direct identification using the ultraviolet, visible, or infrared bands is possible in principle. However, this approach is often precluded by the extremely short lifetimes of photochemical reaction intermediates.

The difficulty was resolved by Norrish and Porter's publication in 1948 of the impulse photoexcitation method[1] for photo-active systems, in conjunction with fast spectrophotometric measurements, known as the flash spectroscopic or flash photolysis method. Furthermore, studies of the primary stages of photoreactions using the spectra of frozen solutions and mixtures exposed to radiation have increased in scope during the last twenty years. A programme of spectroscopic investigations of chemical reactions at low temperatures was started by Terenin[2,3] as early as in 1940: this was the first attempt to stabilise the intermediates of photochemical reactions in matrices. Subsequently, Lewis and Kasha[4] discovered, in their study of the mechanism of phosphorescence in organic compounds, that free radicals and ion-radicals formed during illumination can be stabilised in rigid, glassy solutions at low temperatures. The main difficulty in this work, pointed out by Frank and Rabinowitch[5], is that the primary products of the photoreaction are often prevented from escaping from their "cage" by the viscosity of the glassy solution, and therefore recombine. On the other hand, the glassy solution must have sufficient rigidity to prevent the active products from diffusing and taking part in secondary, dark reactions. Mixtures of hydrocarbons, alcohols, and ethers at low temperatures are ideal for the purpose: the viscosity of the medium can be controlled either by changing the composition or by changing the temperature of these mixtures.

However, it is sometimes impossible to resolve the optical absorption bands of individual intermediates in photochemical reactions, because they are masked by the absorption bands in the spectrum of the photochemical system due to some of the compounds present in the experimental mixture. If the optical spectrum of the ion or free radical is not known, identification is generally not possible.

Fortunately, photochemical reaction intermediates such as free radicals, ion-radicals, and molecules excited to the triplet state have one important physical property in common: they are paramagnetic due to the presence of unpaired electrons[6]. This makes possible their detection and identification by the electron spin resonance (ESR) method, discovered in 1944 in the Soviet Union by Zavoiskii[7]. Several excellent reviews and monographs on the theoretical and practical aspects of ESR have already been published[8-11], and it is unnecessary therefore to discuss the method in detail. We shall only remark that at the present time this is one of the most sensitive physical methods of detection, identification, and study of free radicals, ion-radicals, and molecules in the triplet (phosphorescent) state.

Hundreds of papers on studies of elementary photoprocesses by the ESR method have been published in the last ten years. As an illustration of the potentialities of the ESR method in photochemistry, we shall consider only a few of these original papers.

The writer has not attempted a detailed analysis of the results quoted in the literature, nor has he concerned himself with matters of purely physical interest. The main emphasis of this review will be a systematic treatment of photochemical investigations by the ESR method. An attempt has been made to preserve the chronological order of the work discussed.

Terenin[12] has given an excellent account of the physical processes underlying the conversion of radiant energy in photochemical systems, and a diagram of the most important photochemical reactions. Following this diagram, we shall classify the photochemical work by the ESR method published up to the time of writing (1966) into the following main photochemical reactions: (1) photodecomposition (photolysis into radicals, photolysis into ions or photoionisation); (2) phototransfer of electrons (photooxidation, photodissociative electron addition); (3) photosensitisation (photosensitised reduction, photosensitised decomposition).

A section on the detection and study by ESR of the triplet (phosphorescent) states of organic compounds has not been included in this review, in spite of its great interest. The omission was deliberate, in order to avoid overloading the article with material which is principally of interest to physicists.

In the main section of this review, we shall discuss the photochemical decomposition of molecules into free radicals and photoionisation processes, investigation by the ESR method.

The first step in any photochemical reaction is the absorption of light by one or more of the components of the photosensitive system under study. Four types of absorption band must be distinguished.

1. Strong ($\lg\epsilon = 3-4$) bands arising from π,π^* absorption in aromatic compounds. These usually occur above 250 mμm, and in conjugated aromatic compounds (dyes) they lie in the visible region of the spectrum. These bands are sharp, and are associated with the transition of one electron from the uppermost filled molecular π-orbital of the ground state to a free non-bonding π^*-orbital of higher energy.

2. Less strong ($\lg\epsilon = 2$) n,π^* absorption bands of heterocyclic compounds, usually in the long-wave part of the absorption spectrum, due to the transition of one of the unshared n-electrons from the hetero-atoms (N, O, S) from a non-bonding $2p$-orbital localised on these atoms to a non-bonding π^* molecular orbital.

3. Strong ($\lg\epsilon = 3-4$), differ σ,σ^* absorption bands of saturated hydrocarbons, found in the ultraviolet region below 200 mμm, due to the transition of an electron from an atomic, bonding σ-orbital to an excited, non-bonding σ^*-orbital (unstable state).

4. Diffuse, long-wave ($\lambda < 260$ mμm) absorption bands from aliphatic alcohols, ethers, amines, alkyl halides, etc. due to the transition of an n-electron to an excited σ^* atomic orbital.

The reactivity of the molecules is determined by the nature of the electronic state, defined by the multiplicity of the state[12] and by the type of electronic transition leading to this state[13-17].

It is known[12] that molecules can exist in the singlet unexcited (ground) state S_0, in a singlet excited state S_1^*, in the lowest (ground) triplet state T_0, and in a triplet excited state T^*. The excited electronic states S_1^*, T_0, and T^* can arise from π,π^*, n,π^*, σ,σ^*, and n,σ^* electronic transitions occurring under the influence of light. The position in energy of these states determines to a large extent the spectral characteristics (absorption and luminescence spectra) and the photochemical properties of the molecules[13-17]. As a rule, the molecules which take part in chemical reactions are not in a singlet S_1^* state, but in the long-lived T_0 state, to which the molecules are transferred by internal conversion[12].

Data on the photochemical action of short-ultraviolet light, which excites the σ,σ^* and n,σ^* transitions in molecules, are so far limited to the photodecomposition and photoionisation reactions of simple molecules in the gas phase, studied by the luminescence of the ejected radicals[18,19] and more recently by flash-photolysis[20] and mass-spectrometrically[21].

However, light absorption is a necessary but not a sufficient condition for the occurrence of a photochemical reaction. After light absorption, a compound does not invariably undergo chemical change, because the excited molecule can undergo physical deactivation processes which involve no chemical conversion[12]. Depending on the spectral composition of the exciting light, the temperature of the medium, and intermolecular interactions, different photoprocesses can take place in a photosensitive reaction system.

The presence of the energy from an absorbed photon in the molecule can manifest itself in several ways. It can: (1) be stored as potential energy of the electronically excited state and either be transferred to another molecule by collision or by exchange or inductive-resonance intermolecular interactions, or else it can be radiated in the form of luminescence; (2) it can be dissipated as heat in a chain of collisions; (3) it can be converted into intramolecular energy of the molecule.

The third way is particularly interesting to photochemists, since under suitable conditions it can lead to dissociation of the molecule into free radicals and ion-radicals. The breaking of chemical bonds in a compound under the influence of light (the photodecomposition reaction) is one of the most direct methods of preparing free radicals.

Since the free radicals formed in most photochemical reactions are very active and undergo secondary chemical interactions, various methods of stabilisation are necessary to enable them to be studied by the ESR method. In the earliest work (1954) on the study of elementary photoprocesses by the ESR method[22,23] the intermediate photoproducts were stabilised in viscous media (in polymer films at room temperature and in frozen solutions). Subsequently, the preferred technique has been the low-temperature stabilisation of the active products in solid solutions.

II. ESR STUDIES OF PHOTODECOMPOSITION REACTIONS

The work of Terenin[18,19], Lewis[24], and Porter[25,26], has produced a substantial fund of spectroscopic data on the photodecomposition of various compounds, which has been responsible for the success of the ESR method. The earliest ESR work was mostly confined to photoreactions whose mechanism had been made clear by the previous work, so that the identification of intermediates involved no difficulties and was a clear proof of the correctness of earlier conclusions.

The first ESR spectra of free radicals formed by ultraviolet irradiation and stabilised in frozen solutions at 77° and 96°K were obtained by Ingram and coworkers[23], who repeated the experiments of Norman and Porter[25] on the photodecomposition of various compounds under the influence of ultraviolet light. Free radical formation was detected by irradiating solid solutions of ethyl iodide, toluene, benzylamine, benzyl chloride, and benzene with light of $\lambda = 254$ mμm. Free radicals appeared also after irradiation of a 40% solution of hydrogen peroxide in water and of the chlorides of oxalato-complexes of tervalent iron in ether–water–alcohol mixtures. The measurements were made on an unsatisfactory ESR apparatus and did not allow accurate identification of the paramagnetic products because the ESR spectra did not show a well resolved hyperfine structure. The photochemical formation of two different free radicals from a single molecule further complicated the identification of the ESR spectra obtained. It was found that the most definite results were obtained from the photodecomposition of hydrogen peroxide by the reaction $H_2O_2 \xrightarrow{h\nu} 2\dot{O}H$. However, more recent work has shown[27-32] that in concentrated aqueous solutions of H_2O_2 ($c > 10^{-2}$ M) the observed ESR spectrum is not due to free OH radicals but to $H\dot{O}_2$ radicals formed by the dark reaction $\dot{O}H + H_2O_2 \rightarrow H\dot{O}_2 + H_2O$.

The doublet ESR spectrum of the $\dot{O}H$ radical could be observed only by irradiating dilute aqueous solutions of H_2O_2 (10^{-2} M or less).[33,34] Stabilisation of the $\dot{O}H$ radical was achieved by minimising the rate of the dark reaction in a dilute solution.

The search for specimens containing active free radicals in measurable concentrations led to the development of the matrix isolation method for these radicals[35]. Solid H_2, Ar, Kr, and CH_4 proved to be suitably inert matrices for stabilising simple free radicals produced photochemically.

1. Photolysis of Simple Compounds

Foner and Cochran[36-38] published a series of researches on the preparation and stabilisation of simple free radicals in these matrices at 4.2°K by ultraviolet irradiation of low-molecular compounds. The source of ultraviolet light was a radio-frequency discharge in a hydrogen tube with a window transparent to ultraviolet (lithium fluoride down to 100 mμm, sapphire to 145 mμm, quartz to 180 mμm, Vycor to 240 mμm). The mixture under study, consisting of the photosensitive material and the matrix gas, was deposited on a sapphire rod at 4.2°K and irradiated with ultraviolet during or after the cooling period, and it was then examined by ESR. Foner and coworkers[38] were able to observe the ESR spectrum of free $\dot{N}H_2$ radicals (triplet of triplets) and $\dot{N}D_2$ radicals (triplet of quintets), produced by photodecomposition in ultraviolet light of 0.5% NH_3 or ND_3 in an Ar matrix at 4.2°K, thus confirming the scheme for the photodecomposition of ammonia first established by Terenin and Neuimin[18]:

$$NH_3 + h\nu \rightarrow \dot{N}H_2 + \dot{H}$$

Some interesting anomalies were observed in the ESR spectrum of the $\dot{N}H_2$ and $\dot{N}D_2$ radicals: whereas the ratio of the hyperfine interaction constants (a_H, a_D) for $\dot{H}$ and $\dot{D}$ is accurately equal to the ratio of the g-factors for their nuclei (6.514), the corresponding constant for nitrogen (a_N) increases only by 15% on going from $\dot{N}H_2$ and $\dot{N}D_2$. The effect is probably associated with differences in the zero-point vibrations of these molecules.

The same workers[36] observed the ESR spectra of hydrogen atoms after ultraviolet irradiation of 1% hydriodic acid in an Ar matrix at 4.2°K. Instead of a single doublet ($I_H = \frac{1}{2}$) with a splitting of 508 Oe, the known ESR spectrum of hydrogen atoms, they found three doublets one of which accurately coincided with the known spectrum.

It is interesting to note that the ESR spectrum of hydrogen atoms obtained by the photodecomposition of water ($H_2O + h\nu \rightarrow \dot{O}H + \dot{H}$) in solid argon at 4.2°K consists of two doublets[39]. The separation of the inner doublets was 507.9 Oe, which is commonly found for condensed $\dot{H}$ atoms and corresponds to a hyperfine splitting constant a_H 0.46% lower than the value for the free hydrogen atom. For the outer doublets the splitting was 516.1 Oe, corresponding to an a_H value 1.5% higher than the free H atom value. As in the previous case, these results were interpreted theoretically[40] as evidence for the penetration of $\dot{H}$ atoms into the available octahedral holes of the face-centred cubic lattice of crystalline argon. Phenomena associated with the capture of $\dot{H}$ atoms at various positions in the

lattice were observed also with krypton and xenon at 4.2°K.

The formation of $\dot{C}H_3$ and $\dot{C}D_3$ radicals was observed by Cochran and coworkers[37] during ultraviolet irradiation of CH_3I and CD_4 respectively in Ar at 4.2°K. The ESR spectrum of the free $\dot{C}H_3$ radical was a quartet of lines with a splitting of 22.9 Oe, $g = 2.0024$, and relative intensities of the components 1 : 3 : 3 : 1, pointing to interaction of the unpaired electron with the protons of three equivalent hydrogen atoms. The $\dot{C}D_3$ radical had a seven-component ESR spectrum ($I_D = 1$) with intensity ratios 1 : 3 : 6 : 7 : 6 : 3 : 1. As was to be expected, the separation of the components of the ESR spectrum was less for the $\dot{C}D_3$ radical than for the $\dot{C}H_3$ radical as required by the ratio of the nuclear g-factors for D and H.

When more complex radicals are trapped in an argon matrix we can no longer average all anisotropic interactions by assuming free rotation in the solid matrix at 4.2°K. With the ethyl radical $CH_3\dot{C}H_2$, obtained by Cochran and coworkers[36] by ultraviolet irradiation of solid 1% ethyl iodide (C_2H_5I) solution in argon at 4.2°K, the ESR spectrum consists of a quartet ($a\beta = 26.3$ Oe) of relatively sharp lines each of which is split into a triplet ($a\beta = 18.5$ Oe) with relatively broad outer components. The sharpness of the lines suggests that the $C_\alpha H_2$ group is free to rotate about the $C_\beta C_\alpha$ bond. The outer lines of each triplet correspond to parallel orientation of the spins of the α-hydrogens, which creates additional magnetic anisotropy. It is not averaged by internal rotations, and therefore line broadening occurs.

Photodecomposition of 1% n-propyl iodide in solid Ar at 4.2°K gave a three-component ESR spectrum for the n-propyl radical C_3H_7. In order to identify the protons responsible for the hyperfine splitting, n-propyl iodide deuterated in the α and β positions was photodecomposed ($CH_3CH_2CD_2I$ and $CH_3CD_2CH_2I$). The authors concluded[36] that the observed ESR spectrum of the n-propyl radical can be explained by assuming that the main contribution to the hyperfine splitting comes from the protons of the two equivalent β-hydrogens.

Cochran and coworkers[39] decomposed SiH_4 by ultraviolet light in Ar at 4.2°K, and obtained an ESR spectrum for the $\dot{S}iH_3$ radicals stabilised under these conditions. The spectrum consisted of a quartet of lines, like that of the $\dot{C}H_3$ radical, but with a somewhat larger separation between the components.

Hayon and Saito[41] used the ESR method to investigate the photodecomposition of HNO_3 in degassed and frozen (77°K) aqueous solutions, for which the following reaction scheme had been proposed[42]:

$$HNO_3 \xrightarrow{h\nu} \dot{O}H + \dot{N}O_2;\ \dot{O}H + HNO_3 \rightarrow H_2O + \dot{N}O_3.$$

When samples of 0.1, 1.0, and 5.0 M HNO_3 are irradiated with light of $\lambda = 254$ mμm, the solid solution at 77°K develops a blue colour. The ESR spectrum of these coloured samples consisted of the well known[43-48] three-component signal of the $\dot{N}O_2$ radical ($g_\perp = 2.0055$; $g_\parallel = 1.9927$; $A/h = 160$ MHz; $B/h = -8$ MHz), the singlet line of the $\dot{N}O_3$ radical ($\bar{g} = 2.018 \pm 0.001$ and $\Delta H = 10$ Oe), and an additional singlet line with $g = 2.003$. It is interesting to note that yellow light ($\lambda > 480$ mμm) bleaches the samples and leads to the disappearance of the signal with $g = 2.018$. It is known[49-52] that the $\dot{N}O_3$ radical has three absorption bands in the region of 500–700 mμm ($\epsilon = 3000 \pm 1000$ litre mole^{-1} cm^{-1} at $\lambda = 662$ mμm). From energy considerations, the photodecomposition of $\dot{N}O_3$ can be expected to occur by two paths:

$$\dot{N}O_3 \xrightarrow{\lambda > 624\ m\mu m} \dot{N}O + O_2;\ \dot{N}O_3 \xrightarrow{\lambda < 570\ m\mu m} \dot{N}O_2 + \dot{O}.$$

Indeed, the signal of the $\dot{N}O_2$ radical and the singlet line with $g = 2.003$ which had been tentatively assigned to the $\dot{N}O$ radical became more intense in the ESR spectrum after irradiation of the coloured samples with yellow light.

2. Secondary Reactions of Photogenerated Simple Free Radicals

The photochemical formation of simple free radicals in solid matrices at low temperatures is, as stated above, one of the standard methods of investigating primary photoprocesses. The problem of the secondary reactions and subsequent photoconversions of the free radicals at low temperatures is highly relevant on the one hand to the preservation of these radicals by appropriate stabilisation and on the other hand to the realisation of low-temperature reactions involving these radicals.

Pimentel and coworkers[53] observed, in their study of the photodecomposition of HI in solid CO at 20°K, the infrared spectrum of the formyl radical HĊO, apparently produced by the chemical reaction between atomic hydrogen and molecules of the solid matrix according to the scheme

$$HI \xrightarrow{h\nu} \dot{H} + \dot{I};\ \dot{H} + C{=}O \rightarrow H{-}\dot{C}{=}O.$$

Cochran and coworkers[54] showed by the ESR method that the HCO radical is formed in this system even at 4.2°K.

However, this is not the only reaction which can take place at these very low temperatures. It is known that irradiation with vacuum ultraviolet light of 1% HCN in solid argon produces, in addition to the CN radical, a weak ESR signal from the $H_2C\dot{N}$ radical (a triplet of triplets), formed by a secondary dark reaction involving atomic hydrogen:

$$\dot{H} + H{-}C{\equiv}N \rightarrow H_2C{=}\dot{N}.$$

The activity of atomic hydrogen at 4.2°K is demonstrated also by an experiment in which HI mixed with 10% of HCN was photodecomposed in argon at 4.2°K under the influence of light ($\lambda = 254$ mμm). The ESR spectrum of the $H_2C\dot{N}$ free radical, formed by the above scheme, was again observed.

The ESR spectrum of the amino free radical ($\dot{N}H_2$) was observed by Coope and coworkers[55] in the products of the photodecomposition of hydrazoic acid (HN_3) in a krypton matrix at 4.2°K. The first product of the photodecomposition of hydrazoic acid was shown, by a study[56-58] of the optical absorption spectra of the products, to be the imino radical $\dot{N}H$. The $\dot{N}H_2$ radical can be formed by the secondary reaction

$$\dot{N}H + HN_3 \rightarrow \dot{N}H_2 + N_3.$$

In fact, the products of the photodecomposition of hydrazoic acid showed a broad, strong singlet line with $g \simeq 2$, identified as the ESR spectrum of the imino radical, on which the weak nine-component spectrum of the $\dot{N}H_2$ radical was superimposed[38].

As was stated at the beginning of the article, the intermediate products in the photodecomposition of H_2O_2 are $\dot{O}H$ radicals, which are chemically active at 77°K and can extract a labile hydrogen atom from neighbouring molecules of the medium, forming $H\dot{O}_2$ hydroperoxy radicals. Sergeeev and coworkers[32,59-62] have demonstrated the special role of phase transformations in the matrix in determining the reactions of the $\dot{O}H$ and $H\dot{O}_2$ radicals at low temperatures. Depending on the rate at which a 25% aqueous solution of H_2O_2 is cooled, a crystalline or a

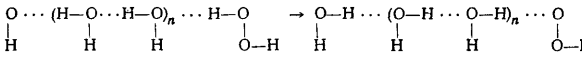
glassy phase can be obtained at 77°K. When the samples are irradiated with ultraviolet light, $H\dot{O}_2$ radicals are formed. The destruction of these radicals in a glassy phase does not begin until 143°K, and is complete at 158°K. For aqueous solutions of H_2O_2 this temperature is the glass—crystal phase transition point. The destruction of the $H\dot{O}_2$ radicals is probably caused by the increased mobility of the molecules during the phase transition. In crystalline samples there is no destruction of the radicals at 158°K. On raising the temperature from 163° to 183°K a stepwise disappearance of the radicals was observed, corresponding to the loss of a definite fraction of the radicals at a number of specific temperatures. Complete destruction of the radicals does not occur until the temperature reaches 220°K, the melting point of the eutectic mixture.

A similar type of destruction of the radicals was observed by the same authors for the phase transition point at 103°K in their work on the photolysis of H_2S frozen at 77°K.

More recently, several interesting features of the photolysis of dilute aqueous solutions of H_2O_2 have been reported. Thus, at H_2O_2 concentrations below 10^{-3} M the ESR spectrum consists of the combined signals from the $\dot{O}H$ and $H\dot{O}_2$ radicals[33,34]. On increasing the time of irradiation the ESR signal from $H\dot{O}_2$ decreases. The observed change in the concentration of the radicals can be explained by the following series of reactions:

$$H_2O_2 \xrightarrow{h\nu} 2\dot{O}H$$
$$\dot{O}H + H_2O_2 \rightarrow H_2O + H\dot{O}_2$$
$$H\dot{O}_2 \xrightarrow{h\nu} \dot{H} + O_2 \cdot$$

It is usually assumed that the formation of the hydroperoxy ($H\dot{O}_2$) radicals is due to the diffusion of $\dot{O}H$ at 77°K during the dark period. However, Sergeev and coworkers consider[61] that diffusion of $\dot{O}H$ in ice at 77°K is unlikely, and they explain the formation of $H\dot{O}_2$ in dilute aqueous solutions of H_2O_2 by postulating migration of the free valency along the system of hydrogen bonds



According to this scheme, any disturbance of the hydrogen bond structure should lead to stabilisation of the $\dot{O}H$ radical. Stabilisation of this radical can therefore be expected in solutions with a high concentration of H_2O_2. This expectation was confirmed[62], but not in a pure aqueous solution: addition of sodium perchlorate (8 M) was necessary to destroy the hydrogen bond structure of the water. Ultraviolet irradiation of such a solution produced ESR signals from the $\dot{O}H$ radical. In the absence of sodium perchlorate, photodecomposition of aqueous solutions of H_2O_2 produced only $H\dot{O}_2$ radicals. This is a clear confirmation of the proposed migration of free valencies along the system of hydrogen bonds.

The chemical activity of hydroxyl radicals produced by the photodecomposition of hydrogen peroxide at 77°K or 96°K was successfully applied by Ingram and coworkers[63-69] to the preparation of free radicals from various aliphatic alcohols and saturated hydrocarbons. The ESR spectra obtained by ultraviolet irradiation (λ = 365 or 254 mμm) of frozen hydrogen peroxide solutions (10^{-1}–10^{-6} M) in various readily oxidisable solvents were due to free radicals of the solvent molecules which had been dehydrogenated by the free hydroxyl. Thus, the reaction of $\dot{O}H$ with methanol[65] at 96°K produces an ESR spectrum consisting of three components with an intensity ratio of 1 : 2 : 1, showing that the hyperfine structure of the ESR spectrum arises from the interaction of an unpaired electron with the protons of two equivalent hydrogen atoms and is due to the $\dot{C}H_2OH$ radical. Several characteristic ESR spectra for various alcohols were obtained in this way, ranging from methanol to n-hexanol (including some secondary and tertiary alcohols). Using deuterated alcohols it was shown that the $\dot{O}H$ radical removes the α-hydrogen from the alkyl group and that the proton of the hydroxyl group of the alcohol does not interact with the unpaired electron of the radical.

Shelimov and coworkers[70,71] studied by the ESR method the kinetics of the accumulation, disappearance, and transformation of the radicals formed by ultraviolet irradiation of dilute H_2O_2 solutions in CH_3OH and C_2H_5OH at 77°K. When solutions of H_2O_2 in CH_3OH at 77°K are irradiated with light from a SVDSh-250 mercury lamp ($\lambda < 320$ mμm), an ESR spectrum appears after a few minutes, and is found to consist of the combination of the spectra of two free radicals: $\dot{C}H_3$ and $H\dot{C}O$.[70] Under prolonged irradiation the concentration of these radicals reach a limiting value. When the light is removed the form of the ESR spectrum begins to change: the intensity of the lines from the $\dot{C}H_3$ radical decreases, and at the same time the three-line ESR signal of the $\dot{C}H_2OH$ radical appears in the spectrum and begins to grow. After a second exposure to light the concentration of $\dot{C}H_2OH$ falls off quickly, with a corresponding increase in the concentration of CH_3 radicals. Meanwhile, the concentration of $H\dot{C}O$ remains practically unchanged. It should be noted that a kinetic picture very similar to the above was obtained when a solution of C_6H_6 in CH_3OH was irradiated at 77°K. The photochemical behaviour of these systems can be described by the following scheme:

$$H_2O_2 \xrightarrow{h\nu} 2\dot{O}H$$
$$(C_6H_6 \xrightarrow{h\nu} C_6H_6^*)$$
$$\dot{O}H\,(C_6H_6^*) + CH_3OH \rightarrow H_2O\,(C_6H_6 + \dot{H}) + \dot{C}H_2OH$$
$$\dot{C}H_2OH \xrightarrow{h\nu} :CH_2 + \dot{O}H \xrightarrow{+CH_3OH} \dot{C}H_3 + 2\dot{C}H_2OH + H_2O$$
$$\searrow H\dot{C}O + H_2$$
$$\dot{C}H_3 + CH_3OH \rightarrow CH_4 + \dot{C}H_2OH\,.$$

The formyl radical ($H\dot{C}O$) is known to have absorption bands in the visible region of the spectrum[72]. If the irradiation is repeated with light of $\lambda > 320$ mμm, a very fast decrease in the concentration of the $H\dot{C}O$ radical is observed, due to the photodecomposition of this radical with formation of the $\dot{C}H_2OH$ radical according to the scheme

$$H\dot{C}O \xrightarrow{h\nu} \dot{H} + CO;$$
$$\dot{H} + CH_3OH \rightarrow H_2 + \dot{C}H_2OH.$$

After the concentration of $H\dot{C}O$ radicals has fallen to zero the concentration of $\dot{C}H_2OH$ no longer increases. A mass spectroscopic analysis of the gaseous products of the photodecomposition of H_2O_2 in CH_3OH detected H_2 (57%), CO (26%), and CH_4 (17%).

It follows from this sequence of experimentally identified elementary steps that a photochemical system irradiated with the unfiltered light from a SVDSh-250 mercury lamp will undergo a peculiar type of chain reaction involving the decomposition of methanol at 77°K with photochemical acts of chain initiation and branching and with some chain propagation steps.

Shelimov and coworkers[71] also investigated by ESR the kinetics of the accumulation, disappearance, and mutual conversion of the radicals formed during irradiation by ultraviolet light (λ = 240 mμm) of H_2O_2 or C_6H_6 solutions

in ethanol at 77°K. The solutions were thoroughly degassed before photodecomposition. As in the case of the methanolic solutions discussed above, the form of the ESR spectra and all the kinetic characteristics were the same for the two solutes. The formation of the following radicals was recorded: $\dot{C}_2H_5$, $\dot{C}H_3$, $CH_3\dot{C}HOH$, and $CH_3CH_2\dot{O}$. It was shown that under the action of ultraviolet light of specific wavelengths ($\lambda > 360$ mμm) the alcoholic radicals $CH_3\dot{C}HOH$ decompose with formation of alkyl radicals ($\dot{C}_2H_5$ and $\dot{C}H_3$). When the light is removed, a gradual disappearance of the alkyl radicals is observed at 77°K, accompanied by the appearance of the radicals $CH_3\dot{C}HOH$ and $CH_3CH_2\dot{O}$ (singlet ESR line, $\Delta H = 14$ Oe). It is found that the $CH_3CH_2\dot{O}$ radicals isomerise under the action of light with $\lambda > 360$ mμm to give $CH_3\dot{C}HOH$ radicals. From mass spectroscopic data, the main gaseous products of the photodecomposition of H_2O_2 solutions in C_2H_5OH are CO (23%), CH_4 (19%), and H_2 (58%). Evidently, a very important stage in their formation is the decomposition of the alcoholic radicals under the influence of light to give alkyl radicals.

Mal'tsev and Petrov[73,74] have shown that the ESR spectra of the photodecomposition products of hydrogen peroxide in tertiary alcohols of general formula $R(CH_3)_2COH$, where $R = CH_3$, C_2H_5, $CH_2{=}CH$, $HC{\equiv}C$, consist of a combination of components associated with the alcoholic radical $R(CH_3)C(\dot{C}H_2)OH$ and the CH_3 radical. The formation of t-butanol radicals during photodecomposition of hydrogen peroxide in this alcohol had previously been reported by Ingram and coworkers[63] and by Symons and coworkers[68]. Mal'tsev's paper describes[74] the mechanism of the photoprocesses occurring in solid solutions of H_2O_2 in tertiary alcohols taking trimethylmethanol as an example. The ESR spectrum obtained after irradiation with the unfiltered light from a DRSh-500 mercury lamp contains 7 lines which can be assigned as a triplet for the alcoholic radical and a quartet for the methyl radical. Storage of the sample, after irradiation at 77°K, for 60–70 h in the dark is accompanied by gradual disappearance of the components of the quartet and growth of the triplet. When a frozen solution of H_2O_2 in trimethylmethanol is irradiated with light of wavelength 340–390 mμm the ESR signal consists of the triplet only. However, the quartet spectrum of the CH_3 radical appears after further irradiation, with light of $\lambda < 320$ mμm, of a solution in which the concentration of alcoholic radicals (triplet ESR spectrum) is below the maximum. The following reaction scheme can be proposed for this system:

$$H_2O_2 \xrightarrow{u.v.} 2\dot{O}H$$

$$(CH_3)_3COH + \dot{O}H \rightarrow (CH_3)_3C(\dot{C}H_2)OH + HOH$$

$$(CH_3)_3C(\dot{C}H_2)OH \xrightarrow{u.v.} \dot{C}H_3 + CH_3\overset{\overset{O}{\|}}{C}CH_3 .$$

But the authors[74] suggest the following mechanism

$$(CH_3)_3COH + \dot{O}H \rightarrow (CH_3)_3C\dot{O} + HOH$$

$$(CH_3)_3C\dot{O} \xrightarrow{u.v.} \dot{C}H_3 + CH_3\overset{\overset{O}{\|}}{C}CH_3 .$$

on the grounds that appreciable concentrations of methyl radicals appeared only in samples which after storage in the dark at 77°K showed a singlet ESR line in the centre of the spectrum, tentatively ascribed to the radical $(CH_3)_3C\dot{O}$.[75] The authors postulate that the penultimate reaction is caused by "hot" OH radicals which appear only under the influence of ultraviolet light with $\lambda < 340$ mμm.

Quite recently, Livingston and Zeldes[76] have used the ESR method to study the reaction of photogenerated ȮH radicals with alcohols in the temperature range from −70° to +60°C. Using a concentrated beam of ultraviolet light, they irradiated a flow of alcohol containing 1% of H_2O_2 in the cavity of their radio-frequency spectrometer. This technique allowed them to produce measurable steady-state concentrations of short-lived radicals. In the absence of dissolved oxygen the main reaction products were the radicals formed by the removal of the α-hydrogen from a molecule of the alcohol by the hydroxyl radical. The RĊHOH radicals, where R = H, CH_3, C_2H_5, C_3H_7, $(CH_3)_2CH$, and C_6H_5, had hyperfine splitting constants a_α in the range 14.7–17.4 Oe, and $g = 2.00298$–2.00334. For the alcoholic radicals with β-hydrogens, $a_\beta = 20.0$–22.2 Oe. The ring protons of the benzyl alcohol free radicals were found to be non-equivalent. Removal of the α-hydrogen from allyl alcohol by a free hydroxyl produces two geometrically isomeric free radicals of the alcohol.

Norman and Porter[77] found that solutions of iodine in ether–isopentane–ethanol (EPA) mixtures at 77°K are decolorised by visible light. When the irradiated solutions are allowed to warm up, the colour of the iodine is restored, indicating stabilisation of iodine atoms at 77°K. Filseth and Willard[78] investigated the processes involved in the bleaching of these solutions, and possible chemical reactions between iodine and saturated solvent molecules, by applying optical spectroscopy and ESR to solutions of iodine in EPA, and also in ethanol, ether, and isopropanol at 90° and 77°K before and after irradiation (AN-6-1000 W), and also after thawing the system to room temperature. Spectrophotometric measurements on solutions irradiated at 90°K showed strong absorption at 291 and 358 mμm, due to tri-iodide, which disappeared at room temperature whilst the absorption bands of molecular iodine reappeared. The ESR spectra of iodine solutions irradiated at 77°K indicate that the iodine atoms produced by the photodissociation of molecular iodine can extract an α-hydrogen atom from the solvent molecule with formation of alcoholic radicals. Hydrogen removal by an iodine atom in the ground state has a low probability at 77°K, because the process is endothermic and requires an energy of the order of 20–30 kcal. The most probable reaction mechanism is the following

$$I_2(^1\Sigma_g) \xrightarrow{h\nu} I_2(^3\Pi) \rightarrow \dot{I}(^2P_{3/2}) + \dot{I}(^2P_{1/2})$$

$$\dot{I}(^2P_{1/2}) + RH \rightarrow HI + \dot{R}$$

$$\dot{I} + I_2 \rightarrow I_2 \cdots \dot{I}$$

$$I_2 \cdots \dot{I} + \dot{I} \rightarrow 2I_2 .$$

In order to arrive at a more complete understanding of low-temperature reactions of the type $\dot{X} + RH \rightarrow \dot{R} + HX$, where X is a halogen atom, and to explain the features of the photodecomposition of mixtures of halogens and aliphatic organic compounds, Sergeev and coworkers[62] studied the formation of free radicals during ultraviolet irradiation of mixtures of bromine (or chlorine) with various hydrocarbons and alcohols at 77°K. These included chlorine and bromine mixtures with iso-octane, isopentane, pentane, and cyclohexane. Radicals were formed only in the mixtures with chlorine when irradiation was with ultraviolet light of $\lambda > 280$ mμm. From the number of components of the hyperfine structure and their separation, the ESR spectra can be assigned to radicals of the type $(CH_3)_2\dot{C}{-}CH_2{-}CH_3$ and $\dot{C}_6H_{11}$, formed by the reaction

$$Cl_2 + RH \xrightarrow{h\nu} 2\dot{C}l + RH \rightarrow HCl + \dot{R} .$$

The absence of radicals in the Br_2 mixtures can be ascribed to the strong endothermicity of these reactions, which do not readily occur at 77°K.

Ultraviolet irradiation ($\lambda > 280$ mμ) of mixtures of chlorine or bromine with methanol, ethanol, and isopropanol produced complex ESR signals, consisting of several free radical spectra superimposed. These radicals were formed by secondary photodissociation of the radicals formed in the primary process. Essentially, the processes observed in the photodecomposition of H_2O_2 in alcohols occur also in these systems. However, the activation energy of the reaction $\dot{B}r + RH_\alpha OH \rightarrow HBr + \dot{R}OH$ is ~ 9 kcal mole^{-1} in the case of methanol[79], and therefore the removal of an α-hydrogen atom from a molecule of the alcohol has a low probability at 77°K. According to Sergeev[62,80], the formation of organic free radicals in the alcohol–halogen system involves molecular charge-transfer complexes between the halogen and the oxygen of the alcohol formed in the condensation, which alter, the absorption spectrum of the system. The following mechanism is proposed for the formation of the radicals: light absorption causes excitation of the complex and transfer of an electron from the oxygen of the alcohol to the bromine, followed by the formation of the $R\dot{H}O$ radical which isomerises to $\dot{R}OH$ under the influence of light.

3. Photolysis of Complex Organic Compounds

Piette and Landgraf[75] have successfully applied the ESR method to studies of the photodecomposition of primary, secondary, and tertiary butyl hydroperoxides of structure R–O–O–H, where R = $CH_3CH_2CH_2CH_2$ (primary), $CH_3CH_2CHCH_3$ (secondary), and $-C(CH_3)_3$ (tertiary). The source of ultraviolet light was a medium-pressure mercury lamp (N85S3). From energy considerations, breaking of the O–O bond with formation of alkoxy and hydroxyl radicals could be expected under the influence of light. For the alkoxy radical $R\dot{O}$, the density of the unpaired electron can be expected to have a low value on the α-protons and a negligible value on the β-protons, because of the influence of the oxygen atom. Hence, the ESR spectrum of these radicals should show a triplet, a doublet, and a singlet for primary, secondary, and tertiary butyl hydroperoxide respectively. In all cases the hyperfine splitting constant a_H should lie between 2 and 3 Oe. Piette found a triplet ESR signal after light irradiation of primary butyl hydroperoxide, a doublet with secondary butyl hydroperoxide, and a singlet with the tertiary compound, the splitting being 3.5 and 2.8 Oe respectively. Thus, it was shown that the photodecomposition of butyl hydroperoxides goes through the formation of alkoxy radicals. The ESR spectrum of the hydroxyl radical $\dot{O}H$ was not detected, probably because of its short lifetime.

Piette[81] studied the photodecomposition of simple aliphatic alcohols during irradiation with unfiltered ultraviolet light. Irradiation of methanol at 77°K gave an ESR signal consisting of two superimposed spectra: a quartet of lines from the $\dot{C}H_3$ methyl radical and a doublet of lines with a splitting of about 120 Oe from the $H\dot{C}O$ radical. On irradiation of methanol which had been deuterated in the hydroxyl position (CH_3OD), the ESR signal was the same as with ordinary methanol. Irradiation of CD_3OH led to the appearance of a seven-line spectrum from the $\dot{C}D_3$ radical and an unresolved multiplet. The doublet with a splitting of 120 Oe was not obtained in this case. Irradiation of ethanol gave rise to a complicated ESR spectrum. As shown by Sullivan and Koski[82–84], and by Shelimov and coworkers[70,71], these free radicals stabilised at 77°K are the result of interdependent, complex photochemical reactions of alcohols, so that primary photoprocesses in these materials can be assessed only by spectral and kinetic studies at different temperatures.

Maas and Volman[85] studied the action of ultraviolet light on various pure allyl alcohols (allyl alcohol, but-2-en-1-ol, but-1-en-3-ol) at 77°K, and found that the primary photochemical act for these compounds is the breaking of the C–O bond with formation of the corresponding allylic hydrocarbon free radicals. These radicals are stable at 77°K. However, at higher temperatures (100–130°K) hydroxy-allyl radicals appear with the allyl hydrocarbon radicals: they are formed by the removal of an α-hydrogen from the alcohol by the active hydroxyl radical produced in the primary photochemical act (photodissociation of the C–O bond).

Ultraviolet irradiation of 2-hydroxy-2-methylbut-1-ene, which does not contain α-hydrogen, gives rise to the ESR spectra of the $\dot{C}H_3$ and $R\dot{C}H_2$ radicals, probably formed in the primary process.

Poole and Anderson[86] reported the observation of the ESR spectra of radicals, stable at 77°K, formed by ultraviolet irradiation of normal and branched unsaturated hydrocarbons (alkenes). Their light source was a high-pressure mercury lamp (GE-BH6), producing a flux of 16.9 W steradian^{-1} in the photochemically active wavelength range (250–380 mμ). The following compounds were irradiated with ultraviolet: methylacetylene (propyne), pent-2-ene (2-amylene), hex-1-ene and hex-2-ene, hept-2-ene, oct-1-ene and oct-2-ene, and also 3-ethylpent-2-ene, 3-methylbut-2-ene, 2,4,4-trimethylpent-2-ene, 4-methylpent-2-ene, and 2,6-dimethylhept-3-ene. The model used to interpret the observed ESR spectra assumed the absorption of a photochemically active photon by the chromophoric group of the molecule, followed by dissociation into two fragments. The light fragment (hydrogen atom, or methyl radical), being able to diffuse at 77°K, reacts with neighbouring species. The heavy fragment is stabilised at 77°K and is responsible for the ESR signal in every case. The hyperfine structure of the ESR signal results from the interaction of the unpaired electron with the protons of the hydrogen atoms in the α and β positions. However, Anderson and Beasley[87] subsequently showed that the appearance of free radicals in ultraviolet-irradiated alkenes is initiated by the photodecomposition of organic peroxides[88] present as impurities in the alkenes used for the investigation:

$$\text{a)}\quad \begin{aligned} &ROOH \xrightarrow{h\nu} R\dot{O} + \dot{O}H \\ &R\dot{O} + R'H \rightarrow ROH + \dot{R}' \\ &\dot{O}H + R'H \rightarrow HOH + \dot{R}' \end{aligned}$$

$$\text{b)}\quad \begin{aligned} &R\dot{O} + C{=}C{-}C{-}R'' \rightarrow RO{-}C{-}\dot{C}{-}C{-}R'' \\ &\dot{O}H + C{=}C{-}C{-}R'' \rightarrow HO{-}C{-}\dot{C}{-}C{-}R'' \end{aligned} .$$

Kuwata and Hirota[89] investigated the photodecomposition of organic ketones (acetone and benzophenone) by the ESR method. Several types of free radical could have been expected[90] in the photodissociation of acetone, namely

$$\begin{aligned} &CH_3COCH_3 \xrightarrow{h\nu} CH_3\dot{C}O + \dot{C}H_3 \\ &CH_3\dot{C}O \xrightarrow{h\nu} \dot{C}H_3 + CO \ . \end{aligned}$$

However, several hours' irradiation of pure acetone with ultraviolet light at 77°K did not produce a detectable amount of free radicals. A single ESR line with ΔH = 30 Oe and g = 2.003 was observed by irradiating a solution

of acetone in alcohol or in EPA mixture (ether–isopentane–alcohol), but the authors were unable to identify the radical responsible for this line. A singlet ESR spectrum (ΔH = 23–24 Oe, g = 2.003) was obtained after ultraviolet irradiation of pure benzophenone or a solution of benzophenone in ethanol or EPA at 77°K. As in the previous case, it was not possible to identify the free radicals.

In a recent investigation by Pukhal'skaya and coworkers[91] on the photoconversions of radicals in γ-irradiated frozen acetone, the photodissociation of acetone frozen at 77°K and of a 50% aqueous solution of acetone were also examined in control experiments. The light source was a DRSh-500 super-high pressure mercury lamp. The ESR signal obtained consisted of two superimposed spectra: the spectrum of the $\dot{C}H_3$ radical (a quartet of lines with intensity ratio 1 : 3 : 3 : 1) and that of the acetyl radical $CH_3C\dot{O}$ (singlet line). The authors point out that the rate of appearance of $\dot{C}H_3$ radicals, assessed from the initial portion of the kinetic curve for the accumulation of these radicals during illumination, is higher by a factor of two than the rate of appearance of acetyl radicals: this seems to be further confirmation of the generally accepted scheme for the photodecomposition of acetone. The assignment of the singlet in the ESR spectrum to the acetyl radical raises some doubt. The unpaired electron of the $CH_3\dot{C}O$ radical can interact with the protons of three methyl hydrogens, leading to an ESR spectrum consisting of four equidistant components with a binomial intensity distribution, 1 : 3 : 3 : 1. Such a spectrum was in fact obtained by Morton and Falconer[92] in the photodecomposition of biacetyl $(CH_3CO)_2$ at 77°K in a vacuum using a low-pressure mercury lamp. After 90 min irradiation the spectrum consisted of two superimposed quartets, one of which had a hyperfine splitting of 66 ± 5 MHz and g = 2.0027 ± 0.0008 and could be assigned to the methyl radical, the second having 47 ± 5 MHz and g = 2.0055 ± 0.0008 and arising, according to the authors, from the acetyl radical. The signal from the methyl radical fell in intensity by a factor of 2 in 15 min after the irradiation ceased; on the other hand, the signal from the acetyl radical did not change in the dark at 77°K, but on raising the temperature to 140°K it rapidly disappeared without changing shape. The authors point out that the initial concentration of methyl radicals was about 5 times higher than the concentration of acetyl radicals, which can be explained by two photoreactions occurring consecutively:

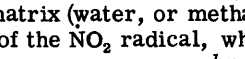
$$CH_3COCOCH_3 \xrightarrow{h\nu} 2CH_3\dot{C}O$$

$$CH_3\dot{C}O \xrightarrow{h\nu} \dot{C}H_3 + CO.$$

The formation of methane by the photodissociation of methyl iodide and of azomethane in a hydrocarbon solvent[50] at 77°K also suggested that the abstraction of a hydrogen atom by a methyl radical by the reaction $\dot{C}H_3 + RH \rightarrow CH_4 + \dot{R}$ proceeds at appreciable rates at low temperatures. To confirm the accepted views on this type of reaction, Varbanskaya and coworkers[93] made an ESR study of the photodissociation of azomethane and methyl iodide, and also of acetone and acetaldehyde in methylcyclohexane at 77°K under the influence of ultraviolet light of various wavelengths. In the first two cases the ESR spectrum showed the methylcyclohexyl radical ($\dot{R}$), formed by the removal of a hydrogen atom by a $\dot{C}H_3$ free radical from the methylcyclohexane molecule. Four narrow components of different intensity with a splitting of ~ 23 Oe and intensity ratio 1 : 3 : 3 : 1 can be resolved in the ESR spectrum, pointing to the formation and stabilisation of methyl radicals under these conditions. The results justify the conclusion that methyl radicals are undoubtedly formed during the photolysis of CH_3I and $CH_3N_2CH_3$ in the solid phase at 77°K: depending on the wavelength of the active light, they can recombine immediately after formation in the "cage" or they can enter into replacement reactions, or again they can be stabilised and emerge from the cage. It was found that methyl radicals formed by the photodissociation of methyl iodide at 77°K retain their activity also towards unsaturated compounds of the olefin type. These radicals can either add on to olefins at the double bond or they can extract a hydrogen atom from the methylene group, leading to the formation of alkyl or allyl radicals respectively, as can be verified by the ESR method[94].

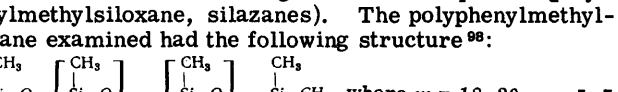
Bielski and Timmons[95] studied the photodecomposition of aliphatic nitro-compounds (nitromethane, methyl nitrite, tetranitromethane) at 77°K. Brief irradiation (from 5 s to several minutes) of these compounds with ultraviolet light from a GE-BH6 high-pressure lamp or a low-pressure lamp led to the appearance of complex ESR signals corresponding to a number of superimposed ESR spectra from different radicals. In particular, after irradiation of a solution of nitromethane in water or in CCl_4 the observed ESR signal can be interpreted, in accordance with the photoreaction scheme $CH_3NO_2 \xrightarrow{h\nu} \dot{C}H_3 + \dot{N}O_2$, as the combination of a quartet of narrow lines from the $\dot{C}H_3$ radical and a triplet of asymmetric lines from the $\dot{N}O_2$ radical. When the solution temperature is raised from 77 to 193°K the methyl radical spectrum disappears and only the $\dot{N}O_2$ radical spectrum remains. A poorly resolved ESR signal was obtained from photodecomposition of methyl nitrite (CH_3ONO). According to the photodissociation scheme proposed by Gray and Style[96], $CH_3ONO \xrightarrow{h\nu} CH_3\dot{O} + \dot{N}O$, the ESR spectrum of the methoxyl group and of $\dot{N}O$ would have been expected. Indeed, the central singlet line can be assigned to the methoxy radical[82]. However, when the temperature of the sample is raised to 193°K, there only remains the ESR spectrum characteristic of the $\dot{N}O_2$ radical, whose appearance is difficult to explain. The photodecomposition of tetranitromethane at 77°K invariably led, irrespectively of the matrix (water, or methanol), to a single ESR spectrum: that of the $\dot{N}O_2$ radical, whose formation can be described by the scheme $C(NO_2)_4 \xrightarrow{h\nu} \dot{C}(NO_2)_3 + \dot{N}O_2$. No spectrum was obtained from the $\dot{C}(NO_2)_3$ radical, probably because of strong interaction with the matrix.

The action of ultraviolet light (SVDSh-1000) on alkylphenylacetylenes (methylphenylacetylene, deuteromethylphenylacetylene, ethylphenylacetylene) produces an intense ESR spectrum pointing to the localisation of the unpaired electron on the dehydrogenated alkyl group[97]:



Irradiation of dialkylacetylenes (R–C≡C–R) produces complicated ESR spectra, probably due to the interaction of the unpaired electron with all the protons of the alkyl groups as a result of the delocalisation of this electron over the whole of the molecule. Thus, in compounds of the type of R–C≡C–Ar and R–C≡C–R (R = CH_3, C_2H_5), the formation of free radicals is due to the photo-removal of a hydrogen atom from the alkyl groups of the substituted acetylenes.

Voevodskii, and Bubnov and coworkers[98,99], have successfully applied the ESR method to the characterisation of the elementary processes of formation and of reaction of free radicals in irradiated organosilicon compounds (polyphenylmethylsiloxane, silazanes). The polyphenylmethylsiloxane examined had the following structure[98]:



where m = 18–20, n = 5–7.

Ultraviolet irradiation of this compound with condensed light from a DRSh-500 super-high pressure mercury lamp at 77°K produces a well resolved ESR spectrum in which two groups of lines with hyperfine structure can be distinguished: (1) a quadruplet with a splitting of 24 ± 0.5 Oe and intensity ratio 1 : 3 : 3 : 1, and 2) a triplet with a splitting of 21 ± 0.5 Oe and intensity ratio 1 : 2 : 1. On the basis of these findings, the authors conclude that ultraviolet irradiation of polyphenylmethylsiloxane gives rise to the radicals $\dot{C}H_3$ and $-O-\overset{\overset{CH_2}{|}}{\underset{\underset{R}{|}}{Si}}-O$, where R = CH_3, C_6H_5. On interrupting the irradiation the spectrum of the methyl radical gradually disappears, with a simultaneous increase in the intensity of the spectrum of the second radical according to the scheme

$$\dot{C}H_3 + R-CH_3 \xrightarrow{k_1} CH_4 + R-\dot{C}H_2 \quad (k_1 = 3.5 \cdot 10^{-6}\ s^{-1})$$

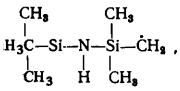
$$\dot{C}H_3 + \dot{C}H_3 \xrightarrow{k_2} C_2H_6 \quad (k_2 = 1.2 \cdot 10^{-21}\ cm^3\ s^{-1}) .$$

In addition to methyl radicals, irradiation should produce radicals with an unpaired electron on the silicon atom, $-\dot{Si}-$. Since these are not manifest in the ESR spectrum, it can be suggested that they disappear under the conditions of the experiment by a fast process whose mechanism is not clear. The kinetics of the accumulation of free radicals were studied as a function of the intensity (I) of the incident light. At low intensities of incident light the initial rate of accumulation of CH_3 radicals was found to be proportional to I^2, and the initial rate of formation of $R-\overset{\overset{O}{||}}{\underset{\underset{O}{||}}{Si}}-\dot{C}H_2$ radicals was proportional to I over the whole of the experimental range of ultraviolet light intensities. This led to the conclusion that the formation of one methyl radical requires the successive (two-stage) absorption of two photons. The absorption of the first photon ($\lambda \leqslant$ 300 mμm) breaks the $\rangle Si-CH_3$ bond, but the radical remains within the "cage". Only the absorption of a second photon ($\lambda \geqslant$ 350 mμm) results in the appearance of a free $\dot{C}H_3$ radical.

However, the formation of $R-\overset{\overset{O}{||}}{\underset{\underset{O}{||}}{Si}}-\dot{C}H_2$ radicals can apparently occur also by direct removal of a hydrogen atom from the methyl group following the absorption of a quantum of ultraviolet light by the polyphenylmethylsiloxane molecule.

In keeping with the results obtained by the ESR method, a mass spectrometric analysis of the gaseous end-products of the photodecomposition of polyphenylmethylsiloxane found 70% of methane, 5% of ethane, and 25% of hydrogen.

The ESR method has been used in conjunction with a mass spectrometric analysis of the gaseous end-products also to investigate the photoreactions of the following silazanes: (1) hexamethyldisilazane $(CH_3)_3SiNHSi(CH_3)_3$; (2) hexamethylcyclotrisilazane $[(CH_3)_2SiNH]_3$; (3) octamethylcyclotetrasilazane $[(CH_3)_2SiNH]_4$; (4) trimethylcyclotrimethylsilazane $[(CH_3)HSiNCH_3]_3$; (5) tetramethylcyclotetramethylsilazane $[(CH_3)HSiNCH_3]_4$. These compounds show remarkable absorption in the wavelength region below 300 mμm. Ultraviolet illumination of compound (1) at 77°K gives a well resolved ESR signal consisting of seven hyperfine structure lines from two superimposed ESR spectra: a quadruplet with a splitting of 24 ± 0.5 Oe ($\dot{C}H_3$) and a triplet with a splitting 21 ± 0.5 Oe from the radical



The ESR results justify the assertion that photolysis of compound (1) at 77°K follows essentially the same path as the photolysis of polyphenylmethylsiloxane, i.e.

$$M \xrightarrow{h\nu} \begin{cases} \equiv \dot{S}i + \dot{C}H_3 \\ \dot{H} + R\dot{C}H_2 \end{cases}$$

$$\dot{H} + M^{**} \rightarrow H_2 + R\dot{C}H_2$$

$$\dot{C}H_3 + M \rightarrow CH_4 + R\dot{C}H_2$$

$$\dot{C}H_3 + \dot{C}H_3 \rightarrow C_2H_6 .$$

Components from the radicals $\dot{C}H_3$ and $R\dot{C}H_2$ can be found also in the ESR spectra of compounds (2) and (3) irradiated with ultraviolet light at 77°K. However, the ESR spectrum is distorted by the presence of a broad, asymmetric line from the peroxy radical produced by a reaction between the molecular oxygen entrained in the structure of these compounds and the radicals formed by irradiation. Ultraviolet irradiation of compound (4) gives an ESR signal consisting of a broad symmetrical line superimposed on a triplet with a splitting of 21 ± 0.5 Oe from the $R-\dot{C}H_2$ radical. The singlet line is apparently due to the formation under the influence of ultraviolet of a radical with an unpaired electron on the silicon atom[100]. These results showing the type of photogenerated free radicals, combined with data on the composition of the gaseous photolysis products, allow the following scheme to be put forward for the radical processes in compound (4):

$$M \xrightarrow{h\nu_1,\ I_a} \dot{H} + \rangle\dot{S}i$$

$$\dot{H} + M \xrightarrow{k_1} H_2 + R\dot{C}H_2$$

$$\dot{H} + R\dot{C}H_2 \rightarrow M$$

$$\rangle\dot{S}i + \dot{S}i\langle \rightarrow \rangle Si-Si\langle$$

$$M \xrightarrow{h\nu_1,\ \beta I_a} \dot{C}H_3 + \rangle\dot{S}i$$

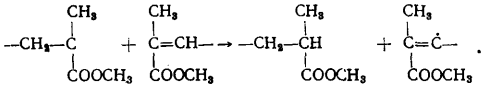
$$\dot{C}H_3 + M \rightarrow CH_4 + R\dot{C}H_2 .$$

Ultraviolet irradiation of compound (5) gave rise to an ESR spectrum similar to the previous one, its only distinguishing feature being that the singlet signal was significantly stronger than in compound (4). From the kinetics of the accumulation of free radicals, in conjunction with the composition of the gaseous products of the photodecomposition of (5), it was concluded that under the influence of ultraviolet light compound (5) undergoes the same processes as compound (4), but the breaking of the $\rangle Si-C$ and $\rangle Si-H$ bonds is more efficient, and the rate of reaction of $\dot{H}$ with silazane (5) is greater. This conclusion is in keeping with chemical considerations of the decreased stability of cyclosilazanes with increase in molecular chain length.

The photodecomposition of the hydroperoxide of atactic polypropene was investigated by Ershov[101] using the ESR method. This worker attempted a quantitative assessment of the rate of photodecomposition of the hydroperoxide obtained by thermal oxidation of polypropene, to give a concentration of hydroperoxide groups of 0.5–1 mole kg^{-1}. The sample (~ 0.05 g) of polypropene hydroperoxide, in a vacuum of 10^{-2} mmHg, was irradiated at 77°K in the cavity

of the radio-frequency spectrometer with filtered light from a DRSh-1000 mercury lamp. Formation of free radicals began immediately after the beginning of irradiation. The ESR signal is asymmetric ($g = 2.0047$, $\Delta H \simeq 60$ Oe) and consists of the ESR spectra of hydrocarbon radicals resulting from the isomerisation of alkoxy radicals superimposed on the spectra of peroxy radicals[102]. The rate of production of radicals, measured by the linear portion of the kinetic curve, is 4 times higher for irradiation with $\lambda < 300$ mμm than with $\lambda > 300$ mμm, and amounts to 6×10^{14} radicals min^{-1}. Thus, the hydroperoxide of atactic polypropene is decomposed at a significant rate not only by short-wave radiation but by longer-wave radiation as well. It is suggested that the high rate of decomposition of the hydroperoxide and of accumulation of radicals under the influence of light of $\lambda > 300$ mμm, i.e. in the region where the hydroperoxide absorbs very weakly, is due to the high quantum yield of this photoreaction.

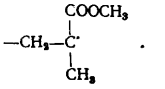
As has already been stated, free-radical concentrations during photoreactions in the liquid phase are minimal, and their detection lies at the very limit of performance of modern ESR radio-frequency spectrometers. However, ESR has been used with success[103-196] to study photoreactions in media which are very viscous at ordinary temperatures, as for example in the late stages of photopolymerisation. We shall discuss, as an illustration, the results obtained by Bresler and coworkers[106] in their ESR study of the photoinitiated polymerisation of methyl methacrylate (MMA), vinyl acetate (VA), and methacrylic acid (MAA). Photopolymerisation was induced both directly inside the cavity and externally, using PRK-4 lamps as the light source. When photopolymerisation was carried out outside the cavity of the radio-frequency spectrometer, the bulb containing the sample was placed in a quartz tube through which water from an ultrathermostat was circulated. Attempts to detect PMMA macroradicals in the early stages of photopolymerisation inside the cavity were unsuccessful because of the low sensitivity of the apparatus. Beyond about 50% conversion in the photopolymerisation of MMA and VA at 300°K, formation of a considerable number of macroradicals with a five-line ESR spectrum was observed (intensity ratio of the components 1 : 4 : 6 : 4 : 1, splitting 26 Oe). If the photoinitiation of the polymerisation is stopped at 60–80% conversion, the polymerisation effectively ceases. Most of the macroradicals under these conditions remain stable, and can undergo neither recombination nor monomer addition at room temperature. The ESR spectrum of the PMAA macroradicals is in no way different from the corresponding spectrum of the PMMA macroradicals. Since the polymer formed by the polymerisation of MAA is precipitated, the accumulation of macroradicals, captured by the gel being deposited, is not surprising[103,104]. The observed ESR spectra relate in the main to "captured" radicals, whose concentration is only indirectly related to the kinetics of the photopolymerisation process. The accumulation of "captured" radicals in homogeneous systems at relatively early stages of polymerisation stresses the inadequacy of the generally held views on the kinetics of the growth and disappearance of macroradicals. Evidently, a considerable proportion of the macroradicals is relatively stable because of the difficulty of access to the reactive centre deep within the tangle formed by the macromolecule. An important factor in this "capture" of macroradicals is whether the monomer is a good solvent or a poor solvent for the polymer. Hence, not all polymers "capture" macroradicals to the same extent. Furthermore, the higher the molecular weight, the more likely is the reactive centre to be screened by the polymer tangle. An attempt was made to study the fate of the radicals captured in PMMA after completion of the polymerisation: even at 330°K the ESR spectrum of a low-molecular-weight polymer changed quite rapidly, and the original five-component spectrum was replaced by a four-component spectrum with a 1 : 3 : 3 : 1 intensity ratio. This spectrum points to the appearance of a new radical in which the unpaired electron interacts not with four equivalent protons (as in the original radical) but with three. The rearrangement of the ESR spectrum is ascribed[106] to the ability of the macroradicals to capture a labile hydrogen atom at 330°K by the reaction



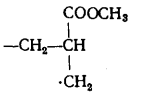
The ESR spectra in PMAA and PVA disappeared instantaneously on crossing the glass transition point.

However, the possibility must be considered that the initial ESR spectra were due to radicals formed by the photodecomposition of the resulting polymer rather than to radicals appearing during photopolymerisation.

Sorin and Tsaregradskii[107] have reported a study by ESR and optical spectroscopy of the photodegradation of PMMA at 77° and 300°K. By using molecular spectroscopy it was shown[108,109] that CO_2, CO, H_2, CH_3OH, methyl formate, etc. are produced when PMMA is irradiated with ultraviolet. It was also found that the photodegradation of PMMA is accompanied by a decrease in molecular weight, formation of monomer, and a decrease in strength. There is no doubt that photodegradation is accompanied by the appearance of intermediate free-radical products. In fact, irradiation of PMMA with the light of a DRSh-500 mercury lamp or with the filtered light (BS type filters) of a DKSSh-1000 xenon lamp produces free radicals whose ESR signal is the combination of a quintet and a quartet of lines of relative intensities 1 : 4 : 6 : 4 : 1 and 1 : 3 : 3 : 1 respectively. These radicals are stable and persist for several months. It has been shown that the first spectrum is produced by the radicals



For the second type of radical, the authors proposed the structure



arising from the first when the free valency on the carbon of the polymer chain captures a proton from the methyl group. It is found experimentally that the relative intensities of the quintet and the quartet are functions of the temperature and of the spectral composition of the active light: the intensity of the quartet decreases with rise in temperature and at 290°K only the quintet remains; the quartet is not formed when irradiation is with light of $\lambda \geq 340$ mμm, but it appears on subsequent irradiation with unfiltered light. Thus, the second (quartet) ESR signal could alternatively be assigned to the $\dot{C}H_3$ radical, formed in the primary act of short-wave ultraviolet irradiation.

4. Photodecomposition of Adsorbed Organic Compounds

The formation and stabilisation of active intermediate products on the surface is of enormous importance in heterogeneous catalysis. These intermediate products could be free radicals and ion-radicals. The first systematic study of adsorption by spectral methods is due to Terenin[110-113]. Under his direction, methods were developed for investigating adsorbed molecules and also the surface properties and the catalytic properties of adsorbents from visible, ultraviolet, and infrared absorption spectra. In recent years, the ESR method has been successfully applied to the study of the properties of adsorbed free radicals and of the nature of their interaction with the surface. In particular, the possibility of low-temperature stabilisation, on a silica gel surface, of active radicals such as atomic hydrogen and alkyl radicals has been demonstrated.

Kazanskii and coworkers[114,115] described a photochemical procedure for preparing and stabilising methyl radicals at 77°K from methyl iodide, adsorbed in a vacuum from the vapour onto the surface of silica gel. After irradiating this system for 4–6 h at 77°K with ultraviolet light (from a PRK-7 lamp), they observed the ESR spectrum of adsorbed methyl ($\dot{C}H_3$) radicals, consisting of four hyperfine structure components of half-width 1–2 Oe, splitting 23.3 Oe, and an unusual distribution of the intensity of the individual components (1 : 8.5 : 13 : 2.5 instead of 1 : 3 : 3 : 1). This is ascribed to the fact that adsorption of a methyl radical on the surface of silica gel causes the loss of two rotational degrees of freedom because of the coupling of the unpaired electron to the adsorbent. Only one axis of rotation remains, around the orbital of the unpaired p-electron. This rotation produces incomplete averaging of the anisotropic hyperfine and spin–orbital interaction, and therefore the ESR spectrum adopts an asymmetric form with a non-binomial distribution of component intensities[114]. The intensity of the signal does not alter on keeping the specimen for several hours at liquid nitrogen temperature. A decrease in intensity of the spectrum becomes noticeable 5 min after allowing the sample to warm up to −130°C. The spectrum has not completely disappeared after 30 min storage at −40°C. Hence it is evident that methyl radicals adsorbed on the surface of silica gel have a relatively high stability, well in excess of the stability of alkyl radicals in frozen solutions. These results show that quite active radicals prepared by photodecomposition of adsorbed compounds can be stabilised on the surface of solids. Furthermore, the results also show that the ESR method can give fairly detailed information on the geometry of the bond between adsorbed radicals and the surface, and on the type of motion of the radicals.

Tolkachev and coworkers[116] used the method (proposed by Kazanskii and Pariiskii) of photodecomposition of molecules adsorbed on a silica gel surface in order to stabilise and detect, at 77°K, benzyl radicals ($C_6H_5\dot{C}H_2$) produced by ultraviolet irradiation of benzyl chloride[98,104]. Theoretical calculations of the density distribution of the unpaired electron in the benzyl radical have been published[117,118]. The first experimental attempts at observing the hyperfine structure of the ESR spectrum of this radical in solid hydrocarbon glasses were unsuccessful[23]. In the more recent work[116] the benzyl chloride was adsorbed from the vapour phase, in a vacuum, on the surface of silica gel (of specific surface area 300 $m^2\ g^{-1}$) at room temperature, and was then irradiated with ultraviolet light from a PRK-7 high-pressure mercury lamp for 2–4 h at 77°K. The resulting ESR spectrum consisted of a triplet with a separation of 16.5 ± 1 Oe between the components. Each of the components was further split into a quadruplet with a constant spacing of 5.5 ± 0.5 Oe between its components. The triplet in this spectrum was due to the interaction between the unpaired electron and the protons of the $-\dot{C}H_2$ group. The low value of the splitting on the protons of the methylene group (16.5 instead of 23 Oe) suggests delocalisation of the unpaired electron into the π-system of the ring, and this is confirmed by the splitting of each component of the triplet into a quadruplet, due to interaction of the unpaired electron with three protons of equivalent hydrogen atoms of the ring. The agreement between experimental results and theoretical calculations is evidence that the spectrum was correctly interpreted. As in the previous case, no ESR spectrum could be obtained from the halogen atoms ($\dot{C}l$).

5. Photo-ejection of an Electron (Photoionisation)

Photoionisation is the extraction of an electron, under the influence of light, from a photoexcited molecule into a vacuum or into a medium, accompanied by free existence or capture of the photoemitted electron in the medium (trapping, solvation, etc.). Terenin[12] treats the photoionisation of organic molecules as a special case of the photodecomposition reaction: the photodissociation of the compound into oppositely charged ions (a molecular cation and an electron). However, the photoionisation reaction is often considered to be[119,120] the primary, elementary act of the oxidation–reduction process[121]. The term elementary photo-oxidation usually refers to the removal of an electron from a photoexcited molecule (the oxidisable component) to another molecule (the oxidising agent or electron acceptor), which has a positive electron affinity. The photo-oxidation of one compound is invariably accompanied by the reduction of another compound (the oxidiser). The mechanism and the energetics of the photoionisation and the elementary photo-oxidation process are quite different: this defines their individual roles and allows us to discuss the photo-extraction of an electron independently of oxidation–reduction photoreactions.

The removal of an electron under the influence of light (i.e. the photoelectric effect) has long been known for aromatic molecules in the solid state and in solution. The emission of an electron by light from organic molecules in the condensed phase was clearly demonstrated for the first time by Lewis and coworkers[119,120] by a spectroscopic investigation. It has also been known for a long time that the vapours of anthracene, diphenylmethane, aniline, diphenylamine, and α-naphthylamine show electrical conductivity under the influence of short ultraviolet light[122-124]. Terenin and Vilesov[125,126] have recently developed a powerful mass-spectrometric method of studying the photoionisation of vapours of aromatic compounds (including dyes) which enables the critical energy for the photoremoval of an electron in a vacuum to be determined with high precision.

Lewis and coworkers[119,120], and more recently Linschitz and coworkers[127], observed, in their spectroscopic investigations, coloured products from the interaction of near ultraviolet with frozen solutions at 90°K in EPA (a mixture of alcohol, isopentane, and ether in the ratio of 2 : 5 : 5 by volume) of various colourless aromatic compounds: amines, phenols, and the leuco-forms of dyes. The colouration of the solutions upon irradiation was caused by the photo-extraction of an electron from the colourless

aromatic compound with formation of a positively charged molecular radical-ion, for example

$$(C_6H_5)_3\dot{N} \xrightarrow{h\nu} (C_6H_5)_3\dot{N}^+ + e\,.$$

An analogous process occurs during the photo-extraction of an electron from aromatic compounds containing N, O, and S atoms, which have unshared electron pairs. The electron split off by the light remains trapped in the solid solution at 90°K. However, even a small temperature rise allows the medium to lose its rigidity and the trapped electron to recombine with the ion. Photoionisation of molecules can be induced also at ordinary temperatures by using a medium (such as boric acid glass, or polymers†) rigid enough to trap the photo-extracted electrons for an appreciable time. Since one of the products of the electron photo-extraction reaction is an unstable molecular ion with an unpaired electron and therefore paramagnetic, such a product can in principle be detected by the ESR method in the condensed phase.

Bijl and Rose-Innes[22] were among the first to apply the ESR method to the study of photo-processes in organic compounds, and in particular to the study of photoionisation. Their experimental materials were aromatic diamines, which are readily oxidised by light: tetramethyl-*p*-phenylenediamine (Wurster's base) and *p*-phenylenediamine. To stabilise the resulting radical-ions a, polymeric medium [poly(methyl methacrylate)] having a glassy state at ordinary temperatures was used instead of a low-temperature hydrocarbon glass. After 5 min irradiation with ultraviolet light from a high-pressure mercury lamp the film developed a brown and greyish-green colour accompanied by the appearance of an ESR signal consisting of a single line with $g = 2.001 \pm 0.002$. The paramagnetic product stabilised in this way survived for several months at room temperature. It is known[119] that the cation-radical of tetramethyl-*p*-phenylenediamine (Wurster's Blue) has absorption bands at 630, 580, 520, and 500 mμm, and therefore has a blue colour. Since the product obtained in these experiments is brown in colour, it may be assumed not to be the cation-radical of the diamine, but rather a free radical resulting from the interaction of that cation-radical with the medium.

Bennema and coworkers[130] made a detailed study of the formation of coloured photo-products by the ultraviolet irradiation of various aromatic hydrocarbons in boric acid glasses. Solid, glassy solutions of the following hydrocarbons in boric acid were irradiated: biphenyl, phenanthrene, terphenylene, tetracene, pyrene, perylene, and coronene. In every case the authors observed the formation of coloured products whose optical absorption and ESR spectra indicated the presence of singly charged, positive molecular ions of the corresponding hydrocarbons, produced by photoionisation. On heating the coloured glasses the colour disappeared, with simultaneous emission of the characteristic recombination phosphorescence of the particular hydrocarbon molecule.

Hoijtink and Zandstra[131] exposed to ultraviolet light methyltetrahydrofuran solutions of the negative ions of aromatic hydrocarbons in a vacuum at 77°K, and obtained spectroscopic evidence of their photoionisation:

$$M^{2-} \xrightarrow{h\nu} M^- + e;\ M^- \xrightarrow{h\nu} M + e\,.$$

† Electron photo-extraction has recently been observed in the flash-irradiation of a liquid solution of triphenylamine in hexane[128] and of diphenylamine and triphenylamine in electron-acceptor solvents like CCl_4, $CHCl_3$, and CH_2Cl_2 at 300°K,[129] by the appearance of a short-lived (10^{-4} s) optical absorption spectrum due to the corresponding radical cation.

In the first experiments, no evidence could be found of capture of the ejected electrons by the alkali metal cation (Na^+) or by the solvent matrix. However, on repeating the experiments including ESR, visible, and infrared spectroscopy of the irradiated solutions, van Voorst and Hoijtink[132] obtained clear proof of the capture of the ejected electrons in the holes of the network of the frozen matrix. As in the earlier experiments, negative ions were obtained by treating a 3-methyltetrahydrofuran solution of the appropriate aromatic hydrocarbon (tetracene, perylene, pyrene) with an alkali metal in a vacuum:

$$M + X \rightarrow M^- + X^+;\ M^- + X \rightarrow M^{2-} + X^+;\ (X = \text{Li, Na, K})\,.$$

After irradiation at 77°K, with light corresponding to their absorption bands, the optical absorption spectra of the frozen solutions of singly and doubly charged ions of the solution changed to those of uncharged and singly charged ions respectively. At the same time, an absorption band ($\epsilon = 3-4 \times 10^4$) appeared in the infrared region at 1300 mμm, accompanied by a singlet ESR line with $g = 2.002$ and $\Delta H = 4.5$ Oe, increasing with duration of exposure to the photoionisation process. On thawing the glassy solution, or under the influence of visible light ($330 < \lambda < 600$ mμm), the infrared band disappears, and the initial spectra of the negative ions are re-established. These results imply that the phototransfer of an electron is a reversible process in a solid solution. The minimum quantum energy (2 eV) needed to inhibit the infrared band can be identified with the depth of the trap in which the ejected electron is captured. Since both the shape and the position of the infrared band and of the ESR signal are independent of the nature of the aromatic hydrocarbon and of the alkali metal ion, the author concludes that these signals are due to unpaired electrons trapped in holes of the matrix at 77°K.

The photoionisation of aminoacids and proteins at low temperatures was first investigated by the ESR method by Allen and Ingram[133], who attempted to obtain unpaired electrons by ultraviolet irradiation ($\lambda = 365$, 254 mμm) of four amino-acids (tyrosine, methionine, cystine, and leucine) and four proteins (insulin, insulin with protamine, ox albumen, and egg albumen). All preparations were examined as aqueous solutions or suspensions at 96°K. The experimental results obtained led the authors to the conclusion that radicals are formed by ultraviolet irradiation of proteins and amino-acids, photoionisation of the starting compounds being involved in the primary process. Relatively little has been published on free-radical states in amino-acids and proteins. The first papers on this topic by Grossweiner[134,135] appeared after the development of the techniques of flash photolysis and fast spectroscopy, which allow short-lived radical-ion intermediates to be studied in solutions of aromatic hydrocarbons. Studies of low-temperature thermoluminescence in ultraviolet-irradiated aqueous solutions of aromatic amino-acids and proteins allowed to warm up from 77° to 110°K led Vladimirov and Roshchupkin[136] to ascribe the effect to the recombination of two intermediate products of the first step of the photochemical reaction.

By using the ESR method to study the primary photochemical processes in amino-acids and proteins, Azizova[137-140] was able to investigate the paramagnetic species resulting from ultraviolet irradiation and to give a convincing account of the photoionisation of the biologically important compounds being examined. Ultraviolet irradiation of aromatic amino-acids in the crystalline state at 77°K produces a singlet ESR signal with a *g*-factor close to the free-electron value and $\Delta H = 16$ Oe (tyrosine, tryptophan) or 20 Oe (phenylalanine). A singlet ESR

signal with $\Delta H = 13$ Oe appears in ultraviolet-irradiated glycyltyrosine and glycyltryptophan. Subsequent irradiation of the amino-acids with light of $\lambda = 320–700$ mμm, or a rise in temperature to 300°K of the ultraviolet-irradiated sample, produces a 1.5–2-fold decrease in the intensity of the singlet ESR signal. Irradiation with ultraviolet light of aqueous solutions of aromatic amino-acids (tryptophan, tyrosine) at 77°K causes photoionisation, accompanied by the appearance of positive radical-ions of the amino-acids and of electrons trapped in the medium. The evidence for this is a singlet ESR signal with $\Delta H = 20$ Oe and a g-factor close to the free-electron value, which is suppressed by light of $\lambda = 320–700$ mμm or by heating the sample. The paramagnetic centres which absorb light in this region and disappear on heating are hydrated electrons. Ultraviolet irradiation of water solutions of proteins at 77°K also causes photoionisation of the aromatic amino-acid residues and decomposition of the sulphur-containing amino-acid residues. Hélène and coworkers[141] observed, in aqueous solutions of purine, adenosine, and guanosine at 77°K, the formation under ultraviolet irradiation of a singlet ESR signal by the photoreaction

$$Pu \xrightarrow{h\nu} Pu^{+} + e$$

The singlet ESR signal consists, strictly, of a signal from the Pu^{+} radical-cation and a signal from the hydrated electron. The latter can be set free from the "traps" in the ice lattice under the influence of visible light of $\lambda < 450$ mμm, and this is manifest (as in the previous work of Azizova and coworkers) by a decrease in the amplitude of the ESR signal. The electrons set free by the light can be captured by Pu^{+} ions or by neutral Pu molecules, which have a high electron affinity[142]. A theoretical calculation of the ionisation energy of π-electrons gives a value of the order of 8 eV for nucleic acid bases[143]. The energy quantum of the active photon ($\lambda = 254$ mμm) corresponds to 5 eV and cannot produce photoionisation of these molecules. The energy of the triplet state in purine, adenosine, and guanosine is close to 3.4 eV. Assuming a two-photon mechanism for the photoionisation of nucleic acid bases, as suggested by the authors[141], an ionisation potential of the order of 8 eV can be attained by the absorption of the second photon ($\lambda = 254$ mμm) by the triplet molecule of the base ($3.4 + 5 = 8.4$ eV).

The possibility of a two-quantum process of this kind for the ionisation of aromatic compounds in solid solutions at 77°K was first proposed in 1963 by Terenin and the present writer[144,145]. Since then, the two-photon mechanism of the photoionisation of aromatic compounds has been convincingly demonstrated in a number of instances[146–154].

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The purpose of this review has been to give a systematic and ordered account of the very numerous photochemical investigations in which the ESR method has been used to throw light on the paths followed by photodecomposition reactions. Most of the photochemical processes had been previously investigated spectrophotometrically. The EST method, on the other hand, had been used mainly to confirm various photodissociation mechanisms. In a number of instances the ESR method has given new and original results. It must be stressed, however, that the successful application of the ESR method in photochemical investigations requires a sound knowledge of the spectral properties of photochemically active systems, a keen appreciation of possible photoprocesses in these media, including secondary processes, and skilful experimentation (choice of medium, temperature, light source, etc.). The ESR method will become a powerful physical method of investigation only if used in conjunction with other methods, and in particular with optical spectroscopy and mass-spectroscopic analysis.

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Application of the Ferromagnetic Resonance Method in the Study of Heterogeneous Catalysts

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The main features of the ferromagnetic resonance method are discussed in the context of the study of heterogeneous catalysts. Results obtained by this method are examined, and possible future developments are pointed out.

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