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Reactions of Electronically Excited Radicals and the Quenching of Excited States by Radicals

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The reactions of electronically excited radicals of different types in liquid and solid phases and the electronic structures of the excited radicals and their kinetic characteristics are discussed. A relation is established between the type of excitation and the type of chemical reaction of the excited radicals. The kinetics and mechanisms of the quenching of excited singlet and triplet states by radicals in solid and liquid phases are discussed.
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I. INTRODUCTION

The interest in the reactions of electronically excited radicals and quenching processes involving radicals has been aroused by the following factors. Firstly, in electronic excitation the atomic skeleton of molecules and radicals changes little; major rearrangements occur only in the electron shell. A consequence of these electronic transformations of the radical is a change in its reactivity. Comparison of the reactivities of radicals in the ground and excited states and determination of a relation between the nature of the excited state and the nature of its chemical reactions is of significant importance for the theory of structure and reactivity. Secondly, excited radicals play a definite role in the degradation of polymers and it is important to know their place and role in the solution of problems concerned with the photoresistant and photolabile polymers. Thirdly, high (nearly unity) quantum yields of reactions are characteristic of radicals and one cannot, therefore, rule out the possibility that radical systems may be promising from the standpoint of utilising solar energy and developing effective methods for its trapping and transformation.

These problems have been studied mainly by empirical procedures, because the reactions of the electronically excited radicals are highly varied and it is extremely difficult to predict theoretically the mode and direction of the reaction and even more so to derive its quantitative characteristics.

This paper surveys the available experimental results obtained for chemical reactions of electronically excited radicals in solid and liquid phases, and an attempt is made to give a general account of such reactions and to establish certain relations. Furthermore, the review deals with the quenching of excited molecules by radicals and with the quenching of excited radicals.

II. PHOTOCHEMICAL REACTIONS OF RADICALS IN THE SOLID PHASE

1. Allyl Radicals

Absorption bands in the region of 230–270 nm, [1-3] 310 nm, [3] 408 nm, [4] and 500 nm [5] have been detected in the absorption spectra of allyl radicals. Quantum-chemical calculations on allyl radicals predict the presence of two absorption bands—in the long-wavelength region with $\lambda_{max} \simeq 450$ nm (a low-intensity electronic transition which is symmetry forbidden), and in the short-wavelength region with $\lambda_{max} \simeq 220$ nm, ($\epsilon \simeq 10^3$–10^4 litre mole^{-1} cm^{-1}). [6-10] Both bands are due to the $\pi \rightarrow \pi^*$ transition. The electronic ground state of the allyl radical is $(b_1)^2 (a_2)$, where b_1 and a_2 are bonding and antibonding orbitals (Fig. 1). The electron transitions from b_1 to a_2 and from a_2 to the antibonding orbital $\bar{b}_1$ give rise to excited states of the radical.

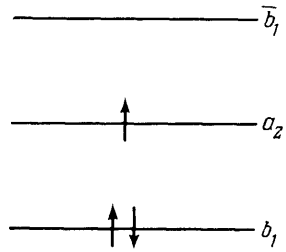


Figure 1. Schematic illustration of the molecular orbitals of the allyl radical.

The photochemical reactions of allyl radicals due to the $\pi-\pi^*$ electronic transition can occur by the following mechanisms: (1) intra- or inter-molecular transfer of a hydrogen atom with transformation into an alkyl radical; (2) dissociation of the alkyl radical with elimination of a hydrogen atom.

The photochemical reactions of allyl radicals with γ-irradiated olefins have been investigated[9,10]. The allyl radical $CH_2=CMe\dot{C}H_2CHMe$ (A), which is transformed under the influence of ultraviolet light (λ = 2537 Å) into the alkyl radical $CH_2=CMeCH_2\dot{C}HMe$ (B) was detected by ESR in 2-methylpent-1-ene (2MP-1) γ-irradiated at 77 K. According to the authors, the photochemical conversion of allyl radicals into alkyl radicals occurs either intramolecularly or intermolecularly. This alternative holds also for all the radicals investigated by Roginskii[11] and

Hamill[12]. To elucidate the possibility, in principle, of an intermolecular transfer of hydrogen atoms, a study was made of the effect of light on the radicals $\dot{C}H_2-CH=CH_2$ formed on γ-irradiation of dilute solutions (frozen glasses) of allyl chloride and allyl bromide in 3-methylpentane (3-MP) [13] and other matrices. On γ-irradiation, allyl radicals are formed as a result of the dissociative capture of slow electrons via the mechanism

$$CH_2=CH-CH_2X + e \rightarrow CH_2=CH-\dot{C}H_2 + X^- .$$

Under the influence of light with $\lambda \leqslant 410$ nm, the concentration of allyl radicals falls to zero and 3-MP alkyl radicals appear; the overall concentration of radicals does not change.

The same behaviour has been observed also in other matrices: the decrease in the concentration of allyl radicals under the influence of light is accompanied by a parallel increase of the concentration of alkyl radicals derived from the solvent. These results show that the reactions of allyl radicals proceed without intramolecular isomerisation.

However, two variants of such transformation are possible; the intermolecular abstraction of hydrogen by the excited allyl radical and the dissociation of the latter followed by the interaction with a matrix molecule of the hydrogen atom formed on dissociation. In the former case molecular hydrogen is not formed in the photochemical reaction, while in the latter one H_2 molecule should be evolved for each allyl radical reacting. Gas-chromatographic determination of the yield of molecular hydrogen after the photochemical reaction of allyl radicals showed that the latter do not dissociate, i.e. the allyl → alkyl transformation proceeds via an intermolecular transfer of a hydrogen atom:

$$CH_2=CH-\dot{C}H_2 \xrightarrow{rH,h\nu} CH_2=CH-CH_3 + \dot{r} ,$$

where rH is a hydrocarbon.

The photochemical conversion of allyl radicals has also been investigated in olefins (dec-1-ene, oct-2-ene, hept-1-ene, hex-1-ene, and pent-1-ene)[14]. The radiolysis of these olefins results in the formation of alkyl radicals of two types—terminal and central. After being kept for a long time in liquid nitrogen, they are converted into allyl radicals, which are reconverted into alkyl radicals under the influence of light. It is suggested that the transformation occurs as a result of an intramolecular transfer of a hydrogen atom.

To confirm the mechanism involving an intermolecular transfer of a hydrogen atom, a study was made[15] of the effect of light on the allyl type radicals $CH_2=CH-\dot{C}HR$ ($R = C_2H_5$, C_3H_7, or C_4H_9) stabilised in the 3-methylpentane matrix. These radicals were obtained by the radiolysis of solutions of olefins in 3-methylpentane. Under the influence of light, allyl radicals are destroyed and alkyl radicals derived from 3-methylpentane are formed. Molecular hydrogen is not formed in the photolysis of the radicals. Thus in this case too the allyl → alkyl transformation takes place as a result of an intermolecular transfer of a hydrogen atom. Similar results were obtained in another study[16], where the photochemical conversion of radicals in the γ-irradiated isobutene–3-methylpentane system was investigated.

We shall now consider the photochemical reactions of radicals in polymers. Alkyl, allyl, and polyenyl radicals, which may be determined and distinguished on the basis of their ESR spectra, are stabilised in γ-irradiated polyethylene (PE) and polypropylene (PP).[14,16-28] When γ-irradiated polyethylene specimens are kept at room temperature, alkyl radicals are converted into the more stable and long-lived allyl radicals. Under the influence of ultraviolet light ($\lambda = 254$ nm) at 77 K, allyl radicals are reconverted into alkyl radicals[1,17,18], but only up to a limit[1]. The overall concentration of radicals during irradiation remains constant under these conditions.

Fig. 2 presents kinetic curves for the photochemical destruction of allyl radicals and the accumulation of alkyl radicals at 77 K and 25 °C.[1] The limiting ratio of the concentration of alkyl and allyl radicals is independent of the intensity of light and amounts to 43 : 57. The rate of formation of alkyl radicals is proportional to the light intensity and is independent of temperature. The quantum yield of the conversion of the radicals amounts to about 0.1. According to the authors[1], the mechanism of the photochemical reaction involves the transfer of a hydrogen atom via the polymer macromolecule (migration of the valence via the chain):

$$\sim CH_2\dot{C}HCH=CHCH_2CH_2 \sim \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \sim CH_2\dot{C}HCH_2CH=CHCH_2 \sim .$$

However, bearing in mind the fairly reliable results obtained in studies on the photochemical reactions of low-molecular-weight allyl radicals, the mechanism involving an intermolecular transfer of a hydrogen atom should probably be adopted in this case too.

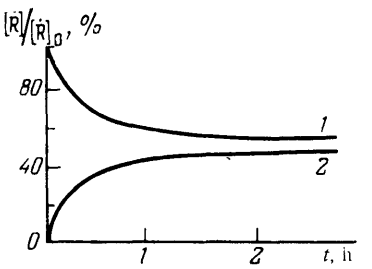


Figure 2. Kinetic curves for the photochemical destruction of allyl radicals and for the accumulation of alkyl radicals: 1) allyl; 2) alkyl.

Since the limiting ratio of the concentrations of alkyl and allyl radicals is independent of the light intensity, one may conclude that the photochemical equilibrium $R^{\cdot}_{all} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R^{\cdot}_{alk}$ is established, the rate constants for the forward and reverse reactions depending on the light intensity, i.e. the alkyl → allyl transformation is also a photochemical reaction. This result conflicts with data for the kinetics of the photochemical reactions of allyl radicals in polypropylene[29], where the rate of the photochemical transformation of such radicals into alkyl radicals is independent of temperature and varies linearly with light intensity. As in polyethylene, allyl radicals in polypropylene are not fully converted into alkyl radicals, the limiting concentration of the latter obeying the relation

$$[R^{\cdot}_{alk}]_{lim} = \frac{k_1 I [R]_0}{k_1 I + k_2} ,$$

where $[R^{\cdot}]_0$ is the initial concentration of radicals and I the light intensity. The constant k_2 is independent of

light intensity, i.e. the reverse reaction $R^{\cdot}_{alk} \rightarrow R^{\cdot}_{all}$ is not photochemical (in conflict with the previous result). However, if it is assumed that the reaction $R^{\cdot}_{alk} \rightarrow R^{\cdot}_{all}$ is a dark process, then it is necessary to assume that the dark reaction proceeds at a high rate, comparable to that of the photochemical reaction $R^{\cdot}_{all} \rightarrow R^{\cdot}_{alk}$ (this follows from the fact that the limiting concentrations of $R^{\cdot}_{all}$ and $R^{\cdot}_{alk}$ are similar). The hypothesis that at the instant of the photochemical transformation $R^{\cdot}_{all} \rightarrow R^{\cdot}_{alk}$ the alkyl radical contains an excess of vibrational energy and for this reason is reconverted into the initial allyl radical is likewise unjustified and cannot account for the attainment of limiting concentrations of $R^{\cdot}_{all}$ and $R^{\cdot}_{alk}$.

Thus the kinetics and mechanism of the photochemical reactions $R^{\cdot}_{all} \rightleftharpoons R^{\cdot}_{alk}$ have been inadequately investigated. Both the forward and reverse reactions probably involve photochemical stages. This is supported by the finding that, at a higher temperature (above 170 K), allyl radicals undergo complete photochemical recombination under the influence of light (by a second-order reaction)[29]. Evidently, the recombination proceeds via photochemically induced relay transfer of valence with participation of alkyl radicals.

2. Polyenyl Radicals

In polyene radicals the energy of the lowest excited state ($\pi-\pi^*$ transition) depends on the number of π electrons in the radical[39]:

$$h\nu = 4\beta \sin \frac{\pi}{2(N+1)} ,$$

where N is the number of π electrons in the radical and β is the resonance integral. Evidently, with increase of the number of π electrons in the radical, the absorption bands should be displaced towards longer wavelengths. Such data for certain conjugated radicals are presented in Table 1.

Table 1. The parameters of the absorption spectra of certain conjugated radicals.

Radical	Matrix	λ^*_{max}, nm	References
$CH_2{=}CH{-}\dot{C}H_2$	Allyl chloride in 3-MP, allyl bromide in cyclohexane	232, 225, 220	3,6,13
Allyl	PP	255	2,30,31
	PE	258	2,30—32
Dienyl	PP	310	2,30—32
	PE	285	2,30—32
Trienyl	PP	368	2,30—32
	PE	323	2,30—32
Tetraenyl	PE	359	2,30—32
Pentaenyl	PE	396	2,30—32
	Cyclohexane	338	33
	Benzene	315	5,34,35
	Toluene	310	34,36—38

*The λ_{max} for the intense absorption bands of radicals only are quoted.

The positions of the electronic levels are relatively insensitive to substituents. For example, the substitution of hydrogen atoms in the allyl radical shifts the maxima of the short-wavelength bands by 10–12 nm.[5] Different substituents (Cl, Br, OH, alkyl, etc.) cause little change in the positions of the electronic levels of the benzyl and cyclohexadienyl radicals[34,37-39].

The photochemical reactions of polyenyl radicals have been investigated in greater detail in polyethylene and polypropylene. Such radicals, having the general formula

$$\sim CH_2{-}\dot{C}H(CH{=}CH)_n CH_2 \sim \text{ (in PE) and } \sim CH_2{-}\dot{C}Me(CH{=}CMeCH_2)_n \sim$$

are formed when polymers are treated with high radiation doses (about 100 Mrad and more), the number of polyenyl radicals with higher values of n increasing as the dose is increased. The ESR spectra of polyenyl radicals consist of a singlet line, which becomes narrower with increase in the length of the conjugation chain.

During the photochemical reaction the conjugation energy of the π-electron system diminishes[29]. With increase in the length of the conjugation chain, the difference between the conjugation energy of the polyenyl radical and the polyene molecular chain increases in absolute magnitude. The difference ΔG, calculated by Hückel's method, is described by the equation

$$\Delta G = 2\pi\left[\sin^{-1}\frac{\pi}{2n} - \cot\frac{\pi}{2(n+1)}\right].$$

It follows from this that there exists a critical value of n in the polyenyl radical for which the energy of the absorbed light quantum is insufficient to compensate the difference between the conjugation energies of the polyenyl radical and the polyene chain. Calculations showed that, for $n > 5$, the photochemical transformation of polyenyl radicals already becomes unfavourable on energy grounds and such radicals should not be converted into alkyl radicals.

In order to determine experimentally the light wavelength at which the transformation of polyenyl radicals begins, γ-irradiated polypropylene specimens were illuminated at 77 K through various light filters. An appreciable change in the ESR spectrum was observed at $\gamma \geqslant 380$ nm. Under the influence of shorter-wavelength light, the ESR spectrum becomes better resolved. The 380 nm light wavelength is apparently limiting; it corresponds to absorption by the polyenyl radical with $n = 3$ ($\lambda_{max} = 385$ nm). With increase of radiation dose, the number of polyenyl radicals having $n > 3$ increases and there is a corresponding decrease of the fraction of radicals having $n \leqslant 3$, which are incapable of being converted into alkyl radicals. For radiation doses in excess of 500 Mrad, photochemical reactions of polyenyl radicals were not observed. This is probably because such doses lead to the formation of appreciable concentrations of polyenyl radicals with $n \geqslant 5$.

3. Alkyl Radicals

The unpaired electron in alkyl radical occupies the p orbital of the carbon atom; its energy level is located between the σ and σ^* levels. Electronically excited states of radicals can be obtained in $\pi-\sigma^*$ and $\sigma-\pi^*$ transitions, where σ and σ^* are the bonding and antibonding orbitals of σ bonds. These transitions are forbidden on symmetry grounds and the corresponding absorption bands are of low intensity. However, they have been observed for certain alkyl radicals. Thus, flash photolysis of $HgMe_2$ [40,41] led

to the observation of the spectrum of the $\dot{C}H_3$ radical. The longest-wavelength absorption band of the radical is located near 216 nm. It is suggested that in the ground and excited states the radical has a planar configuration (sp^2 hybridisation). Weak absorption bands have also been observed in the spectra of other alkyl radicals[42-44]. Thus alkyl radicals absorb light in the range 200–240 nm.

On photoexcitation, alkyl radicals can dissociate, isomerise, or enter into substitution reactions. The photoinduced isomerisation of the t-butyl radical into the isobutyl radical in γ-irradiated isobutyl bromide has been investigated. The ESR spectrum of the t-butyl radical consists of 10 lines with a splitting constant of 25 G and a binomial intensity distribution. On illumination with ultraviolet light at 77 K, the spectrum is converted into one with five lines, i.e. the t-butyl radical isomerises to the isobutyl radical:

$$CH_3-\dot{C}Me_2 \underset{\text{dark}}{\overset{h\nu}{\rightleftharpoons}} \dot{C}H_2-CHMe_2 \quad .$$

The reverse reaction takes place in the dark.

The t-butyl cation is known[45] to have an intense absorption band at 290–295 nm. On the basis of the properties of molecular orbitals, the t-butyl radical presumably also absorbs ultraviolet light at 290 nm, which gives rise to the photoinduced isomerisation.

When isobutene[43] was γ-irradiated, the ESR spectrum of isobutyl radicals CH_2-CHMe_2 was observed, together with a singlet line, which the authors attribute to the 2-methylallyl radical $\dot{C}H_2-CMe=CH_2$. Under the influence of light ($\lambda > 340$ nm), the t-butyl radical is formed, its appearance being associated with the reaction of the electronically excited allyl radical with matrix molecules. On subsequent irradiation with light of shorter wavelengths ($\lambda \leqslant 340$ nm), the t-butyl radical isomerises to the isobutyl radical.

When the copolymer of tetrafluoroethylene (TFE) and hexafluoropropene was γ-irradiated[46], an ESR spectrum consisting of eight hyperfine structures (HFS) lines with a splitting of 29 G, due to the radical $\sim CF_2-\dot{C}(CF_3)-CF_2\sim$, was recorded. This radical absorbs light with $\lambda_{max} = 265$ nm, being converted into the radical $\sim CF_2-\underset{\displaystyle \dot{C}F_2}{\underset{|}{CF}}-CF_2\sim$, the spectrum of which consists of three lines (a central singlet and two extreme components with a splitting of about 450 G between the latter). It is suggested that the transformation proceeds via the isomerisation of the excited radical according to the mechanism

$$\sim CF_2-\underset{\displaystyle CF_3}{\underset{|}{\dot{C}}}-CF_2\sim \xrightarrow{h\nu} \sim CF_2-\underset{\displaystyle \dot{C}F_2}{\underset{|}{CF}}-CF_2\sim \quad .$$

Similar transformations of radicals have been observed in polypropylene[43] and have also been explained by isomerisation.

A serious difficulty encountered in the studies discussed above is the lack of a reliable and unambiguous interpretation of the ESR spectra of radicals in solid matrices. In γ-irradiated substances allyl as well as alkyl radicals are formed and one cannot rule out the possibility that the reactions of the former obscure the results of the photochemical transformations of the alkyl radicals. Furthermore, the photochemical reactions of alkyl radicals, which are treated as isomerisations, can be interpreted as intermolecular transfer of a hydrogen atom. For this reason, although the occurrence of photochemical isomerisation is in principle possible, additional evidence is required.

As already stated above, in $\pi-\sigma^*$ excitation of alkyl radicals there is a possibility of a photochemical decomposition of the radicals. A number of studies[47,48] have confirmed this hypothesis. Thus, in the photolysis of polypropylene in the presence of nitroxy-radicals the composition and kinetics of the accumulation of gaseous photolysis products was investigated together with the kinetics of the destruction of the nitroxy-radicals[48]. Hydrocarbons (methane, ethane, propane, propene, and isobutene) were detected in the gaseous products. In the presence of nitroxy-radicals the yield of methane increases by approximately a factor of 250, while the yields of the other products depend little on the presence of these radicals. Under these conditions, the photochemical decomposition of nitroxy-radicals is not accompanied by the formation of methyl radicals from them. Evidently the vigorous formation of methane is due to the photochemical decomposition of polypropylene macroradicals. The latter are formed by the mechanism

$$\dot{R}^* + \sim CH_2-CHMe-CH_2\sim \rightarrow RH + \sim CH_2\dot{C}MeCH_2\sim \, ,$$

where $\dot{R}^*$ is an electronically excited nitroxy-radical.

The decomposition of central radicals proceeds when macroradicals absorb a light quantum. Thus an electronically excited radical can decompose at any of the three C–C bonds near the localised free valence. However, the decomposition at two of the bonds leads to the formation of terminal macroradicals, while the decomposition at the third bond yields $\dot{C}H_3$. Terminal radicals undergo cage recombination with a high probability, while the light $\dot{C}H_3$ radical diffuses into the bulk, forming methane. The biradical $\sim CH_2-\ddot{C}-CH_2\sim$ formed is converted into the radical $\sim CH_2-\dot{C}H-CH_2\sim$ as a result of reaction with the polymer, the radical $\sim CH_2-\dot{C}Me-CH_2\sim$ being formed simultaneously. The absorption spectra of alkyl radicals in polypropylene are unknown; presumably they absorb in the same region as t-butyl radicals. A similar conclusion concerning the photochemical decomposition of alkyl radicals in polypropylene was reached in another investigation[49].

In the photolysis of isotactic polypropylene[47] in the range $260 < \lambda < 360$ nm the ESR spectrum reveals the presence of the central radical $\sim CHMe-\dot{C}H-CHMe\sim$. Under the influence of light with $\lambda < 270$ nm, this radical is converted into a methyl radical. A similar reaction has also been observed in polyisobutylene.

Methyl radicals are apparently formed in both cases by the decomposition of alkyl radicals in an excited state with occupied antibonding σ^* orbitals. Under these conditions, the dissociation of C–Me bonds in the radical is accompanied by the rupture of other C–C bonds involving the α-carbon atom with decomposition of the macromolecules. However, owing to cage effects, these processes are less important, while the methyl radical leaves the primary cage comparatively readily and avoids recombination.

The effect of light in the range $240 < \lambda < 270$ nm at 77 K on radicals in γ-irradiated 3-methylpentane, 3-ethylpentane, 3-methylheptane, and 4-methylheptane also causes their decomposition and isomerisation[50]:

$$CH_3\dot{C}HCH\,(CH_3)\,CH_2CH_3 \rightarrow C_2H_5 + \text{molecular products},$$
$$CH_3\dot{C}HCH\,(C_2H_5)\,CH_2CH_3 \rightarrow \dot{C}_2H_5 + \text{molecular products},$$
$$CH_3\dot{C}HCH_2CH\,(CH_3)\,CH_2CH_2CH_3 \begin{cases} \rightarrow \dot{C}_2H_5 + \text{molecular products}, \\ \rightarrow \dot{C}H_2CH_2CH_2CH\,(CH_3)\,CH_2CH_2CH_3 \quad . \end{cases}$$

Considerable amounts of ethane were detected among the gaseous products formed in the photolysis of the radicals[50].

4. Peroxy-radicals

Peroxy-radicals absorb light in the band at 240–280 nm [51,52] owing to the transition of an electron from the n orbital of the oxygen atom to the antibonding π^* orbital ($n-\pi^*$ excitation).

When allyl and polyenyl radicals come into contact with oxygen in γ-irradiated polypropylene, peroxy-radicals are formed[53,54]. Their ESR spectra are identical, consisting of an asymmetric line due to the anisotropy of the g-factor. Under the influence of light with $\gamma > 280$ nm, peroxy-radicals are converted into alkyl radicals, but the overall concentration of radicals remains unchanged. The kinetics of the disappearance of peroxy-radicals are described by the first-order equation

$$ROO^{\bullet} + RH \rightarrow ROOH + \dot{R},$$

the rate of the reaction being independent of temperature. Under the influence of short-wavelength light ($\lambda \leqslant 280$ nm), the hydroperoxide formed dissociates with formation of free radicals[55].

$$\begin{aligned} ROOH &\rightarrow R\dot{O} + \dot{O}H \quad , \\ \dot{O}H + RH &\rightarrow \dot{R} + H_2O \quad , \\ R\dot{O} + RH &\rightarrow \dot{R} + ROH \quad . \end{aligned}$$

As a result, the experimental overall radical concentration increases almost by a factor of three. In the presence of oxygen, when alkyl radicals are continuously converted into peroxy-radicals, all these reactions lead to a chain process with degenerate photochemical branching.

In consequence of the photochemical reactions of peroxy-radicals, the rate of graft polymerisation increases sharply; thus, at a light intensity of 10^{15} quanta $cm^{-2}\ s^{-1}$ ($\lambda < 300$ nm), the rate constant increases by two orders of magnitude compared with that for the dark reaction.

The oxidation of polytetrafluoroethylene (**PTFE**) subjected to preliminary irradiation *in vacuo* at 300 K results in the formation of the central peroxy-radicals $\sim CF_2-\underset{\underset{O-\dot{O}}{|}}{CF}-CF_2\sim$. Under the influence of light ($\lambda < 280$ nm), these radicals are converted into terminal fluoroalkyl radicals[57,58]. The rate of this reaction obeys first-order kinetics, the effective activation energy being about 1 kcal $mole^{-1}$.[57] The following reaction mechanism has been proposed:

$$\sim CF_2-\underset{\underset{O-\dot{O}}{|}}{CF}-CF_2\sim \rightarrow \sim CF_2\dot{C}F_2 + CO + CF_2O + CF_3CF_2\sim \quad .$$

This process is accompanied by the degradation of the polymer chain: the gaseous photolysis products (CO, CF_2O) were identified mass-spectrometrically[59]. In oxygen the terminal **PTFE** allyl radical is oxidised and converted into the terminal peroxy-radical $\sim CF_2-CF_2-\dot{O}O$, the ESR spectrum of which at 77 K is completely identical with that of the central peroxy-radical[60-62]. On illumination *in vacuo*, this radical is reconverted into the initial terminal fluoroalkyl radical. The rate of conversion is described by a first-order kinetic equation with an effective activation energy of about 2–3 kcal $mole^{-1}$. The quantum yield of the destruction of peroxy-radicals is close to unity. It is suggested[62] that terminal **PTFE** peroxy-radicals are converted into terminal alkyl radicals in the following way:

$$\sim CF_2CF_2O\dot{O} \xrightarrow{h\nu} 2CF_2O + \sim CF_2\dot{C}F_2 \quad .$$

The detailed mechanism of the photochemical transformations of peroxy-radicals in **PTFE** is unknown. However, presumably the first stage is, as in polypropylene, the conversion of the peroxy-radical in an electronically excited $n-\pi^*$ state into a peroxide via the mechanism

$$\sim \underset{\underset{O\dot{O}}{|}}{CF_2CFCF_2}\sim \xrightarrow{\sim CF_2\sim} \sim \underset{\underset{OOF}{|}}{CF_2CFCF_2}\sim + \sim \dot{C}F\sim \quad .$$

The fluorine-containing peroxide is probably unstable and decomposes photochemically under the influence of light at longer wavelengths than the polypropylene hydroperoxide:

$$\sim \underset{\underset{OOF}{|}}{CF}\sim \xrightarrow{h\nu} \sim \underset{\underset{\dot{O}}{|}}{CF}\sim + \dot{O}F \quad .$$

The subsequent photochemical decomposition of the oxy-radical leads to the formation of a terminal radical:

$$\sim \underset{\underset{\dot{O}}{|}}{CF_2CFCF_2}\sim \rightarrow \sim CF_2C\begin{matrix}O\\ \diagup\\ \diagdown\\ F\end{matrix} + \sim \dot{C}F_2 \quad .$$

Terminal peroxy-radicals probably decompose similarly:

$$\sim CF_2O\dot{O} \xrightarrow{h\nu} \sim CF_2OOF \xrightarrow{h\nu} \sim CF_2\dot{O} \rightarrow CF_2O + \dot{C}F_2 \quad .$$

In the presence of oxygen all these reactions lead to a branched chain process accompanied by the displacement of the free valence by a relay mechanism and the recombination of the radicals. The photo-induced recombination of peroxy-radicals in **PTFE** has not, in fact, been observed. Determination of the fluoride ions formed on hydrolysis of the gaseous photolysis products from peroxy-radicals established that between 50 and 90 fluoride ions are produced for each peroxy-radical which disappears[52]. This result confirms the chain mechanism of the photochemical reactions of peroxy-radicals.

However, the reaction $R\dot{O}_2 + RH \rightarrow RO_2H + R^{\bullet}$ is probably not the only possible pathway whereby excited peroxy-radicals are destroyed. One cannot rule out also the possibility of the decomposition of radicals via the scheme $R\dot{O}_2^{*} \rightarrow R^{\bullet} + O_2$, for example, or via other mechanisms[63]; the situation in this field is not well defined and clear-cut.

5. Radicals Derived from Alcohols, Ethers, and Carbonyl Compounds

In alcohol and ether radicals $R_1R_2\dot{C}OR_3$ (where R_1, R_2, R_3 are hydrogen atoms or alkyl groups) the lone pair electrons of the oxygen atom are involved in conjugation with the unpaired π electron of the carbon atom and the absorption spectra of these radicals are therefore displaced towards longer wavelengths compared with the spectra of alkyl radicals and alcohol and ether molecules. The absorption band maxima of certain alcohol radicals are listed below.

Radical	λ_{max}, nm	References
$CH_2\dot{O}H$	223	64,65
$CH_3\dot{C}HOH$	231	65,66
$C_2H_5\dot{C}HOH$	250	65
$C_3H_7\dot{C}HOH$	244	65
$C_4H_9\dot{C}HOH$	263	65
$C_5H_{11}\dot{C}HOH$	322	65
$(CH_3)_2\dot{C}OH$	250—400	67

The red limit of the absorption of alcohol and ether radicals is near 340 nm. The extinction coefficients are comparatively small, amounting to about 700–900 litre mole^{-1} cm^{-1}.[65,66] The similarity of the optical absorption spectra of these radicals suggests that, when they absorb light, excited states of the same type are produced. On the basis of the results of CNDO calculations on the $\dot{C}H_2OH$ radical[68], the electronic configuration of its ground state can be formulated in terms of the following sequence of molecular orbitals $(1\sigma)^2\ (2\sigma)^2\ (3\sigma)^2\ (4\sigma)^2\ (1\pi)^2\ (5\sigma)^2\ (2\pi)^1$; the unpaired electron is located in the π orbital (80% at the carbon atom and 20% at the oxygen atom). The transfer of the unpaired electron from the 2% orbital to the lowest vacant orbital (6σ) is responsible for the optical absorption of the $\dot{C}H_2OH$ radical in the region with $\lambda < 340$ nm. The $2\pi \rightarrow 6\sigma$ transition is forbidden on symmetry grounds, in agreement with the low extinction coefficient of the $\dot{C}H_2OH$ radical in the range 200–350 nm. Evidently similar electronic transitions occur also in other radicals derived from alcohols and ethers. The principal photochemical reactions of these radicals involve their photochemical dissociation, the mechanism of which is discussed below.

The photochemical reactions of alcohol and ether radicals have been the subject of numerous investigations[69-98]. The primary radicals are formed in alcohols and ethers either on γ-irradiation or on photolysis in the presence of various additives (peroxides, aromatic compounds, stable radicals, etc.). Together with radicals, electrons giving rise to a singlet ESR spectrum ($g \simeq 2.0015$) are stabilised in all alcohols and ethers after γ-irradiation; they give rise to an intense optical absorption in the range 500–600 nm.[65] Under the influence of visible light, ($\lambda > 500$ nm), they are readily destroyed and only alcohol radicals remain.

Light with $\lambda < 320$–350 nm induces the transformations of primary alcohol radicals into secondary radicals. We shall consider them using as an example the photolysis of methanol radicals. The photolysis of the $\dot{C}H_2OH$ radicals has been studied in greatest detail by Shelimov et al.[76] When the full light of the mercury lamp was allowed to act on H_2O_2 and C_6H_6 solutions in methanol at 77 K, the ESR spectra revealed the presence of $H\dot{C}O$ and $\dot{C}H_3$ radicals. In the dark the concentration of $H\dot{C}O$ radicals remained unchanged, while the $\dot{C}H_3$ radicals were destroyed via the reaction $\dot{C}H_3 + CH_3OH \rightarrow CH_4 + \dot{C}H_2OH$. When illumination was switched on again, the ESR spectrum again revealed the presence of $H\dot{C}O$ and $\dot{C}H_3$ radicals. The $H\dot{C}O$ radicals are destroyed under the influence of light with $\lambda > 320$ nm, by the dissociation reaction

$$H\dot{C}O \xrightarrow{h\nu} \dot{H} + CO \quad , \qquad (1)$$

$$\dot{H} + CH_3OH \rightarrow \dot{C}H_2OH + H_2 \quad . \qquad (2)$$

The second reaction results in an increase of the $\dot{C}H_2OH$ concentration.

Mass-spectrometric analysis of the gaseous photolysis products revealed the presence of H_2 (57%), CO (26%), and CH_4 (17%), the composition of the products being independent of the duration of the irradiation. Shelimov et al.[76] proposed two mechanisms for the photolysis of $\dot{C}H_2OH$. The first involves the dissociation of the C–O bond in the radical and presupposes the following sequence of reactions:

$$\dot{C}H_2OH \xrightarrow{h\nu} \ddot{C}H_2 + \dot{O}H \quad , \qquad (3)$$

$$\ddot{C}H_2 + CH_3OH \rightarrow \dot{C}H_3 + \dot{C}H_2OH \quad , \qquad (4)$$

$$\dot{O}H + CH_3OH \rightarrow \dot{C}H_2OH + H_2O \quad . \qquad (5)$$

In the second mechanism it is postulated that the complex of the radical and the molecule absorbs light:

$$(\dot{C}H_2OH + CH_3OH) \xrightarrow{h\nu} \ddot{C}H_2 + H_2O + H\dot{C}O + H_2 \quad , \qquad (6)$$
$$\ddot{C}H_2 + CH_3OH \rightarrow \dot{C}H_3 + \dot{C}H_2OH \quad .$$

Both mechanisms describe a chain process with photochemical branching: a single paramagnetic species destroyed gives rise to three. Both mechanisms presuppose dissociation with formation of carbene ($\ddot{C}H_2$).

The results of other studies[64,79] in which $\dot{C}H_2OH$ radicals were obtained by the radiolysis of frozen methanol are inconsistent with the conclusions that their photolysis has a branched chain mechanism. It was found that illumination with ultraviolet light leads to a decrease of the concentration of $\dot{C}H_2OH$ and the formation of $H\dot{C}O$ radicals, but the total number of radicals remains unchanged.

In the photolysis of $\dot{C}H_2OH$ radicals[68], a decrease of the overall concentration of paramagnetic species was observed, whence the authors concluded that reactions (3) and (6) are not responsible for the formation of $\dot{C}H_3$, because they should have resulted in an increase of the total number of radicals.

According to Chervonenko et al.[94], the main photochemical process in the photolysis of $\dot{C}H_2OH$ is the dissociation of the radicals at the O–H bond:

$$\dot{C}H_2OH \rightarrow H_2CO + \dot{H} \quad . \qquad (7)$$

This mechanism is supported by the maximum yield of H_2 in the photolysis products of the $\dot{C}H_2OH$ radical relative to other products, and also the finding that large amounts of $\dot{C}_2H_5$ radicals are formed by addition in the photolysis of $\dot{C}H_2OH$ in the presence of ethylene as the acceptor of hydrogen atoms, while the rate of destruction of $\dot{C}H_2OH$ increases markedly owing to the suppression of the competing reaction (2).

The dissociation of the O–H bond in the $\dot{C}H_2OH$ radical is favourable on energetic grounds: its energy is less than 1.5 eV. CNDO calculations on the radical[68] have also shown that, when the π electron is excited to the lowest vacant σ orbital, the O–H bond order diminishes, i.e. the bond is weakened, since this σ orbital is antibonding in relation to the O–H bond.

Thus the dissociation of the O–H bond on π–σ^* excitation of the $\dot{C}H_2OH$ radical constitutes one of the principal mechanisms involved in the transformations of the radical. Other reactions of the radical, leading to the formation of $\dot{C}H_3$, are much less definite and unambiguous.

Two mechanisms have now been proposed for the formation of the methyl radical on excitation of $\dot{C}H_2OH$. The first, involving the dissociation of the radical at the C–O bond, was discussed above and the second proposed by Chervonenko[68], presupposes decomposition according to the following scheme:

$$H_2\dot{C}OH \ldots \underset{\displaystyle CH_3}{\overset{\displaystyle |}{O}}H \xrightarrow{h\nu} H_2CO + H_2O + \dot{C}H_3 \quad . \qquad (8)$$

In this mechanism an important role is attributed to the hydrogen bond between the radical and a neighbouring alcohol molecule.

The first pathway should lead to the "multiplication" of $\dot{C}H_3$ radicals, since the photolysis of $\dot{C}H_2OH$ is a chain process with degenerate photochemical branching. The fact that such "multiplication" is frequently not observed in the photolysis of $\dot{C}H_2OH$ at first sight conflicts with the first mechanism. However, one should bear in mind that according to the photolytic mechanism

$$\dot{C}H_2OH \xrightarrow{h\nu} (\ddot{C}H_2,\ \dot{O}H) \rightarrow (\dot{C}H_3,\ \dot{O}H,\ \dot{C}H_2OH)$$

three radicals are formed in a single "cage" and for this reason the probability of the recombination of any radical pair is high, so that the probability of degenerate branching (i.e. the radical "multiplication" factor) is low. If it is less than the probability of the destruction of radicals as a result of recombination in the bulk phase, a decrease of radical concentration is observed on photolysis. Therefore, the absence of the "multiplication" of $\dot{C}H_3$ radicals on photolysis is not by itself an argument against the first mechanism.

The energy of the C–O bond in the ground state of the $\dot{C}H_2OH$ radical is 3.6 eV, However, CNDO calculation has shown[68] that, on $\pi-\sigma^*$ excitation of the radical, the bond is strengthened and its order increases from 0.40 (in the ground state) to 0.80. The C–O bond is also strengthened on deprotonation of the $\dot{C}H_2OH$ radical, i.e. when it is converted into $\dot{C}H_2O^-$ (in alkaline media). In conformity with this, the yield of $\dot{C}H_3$ radicals in the photolysis of $\dot{C}H_2OH$ in alkaline media decreases. These observations are inconsistent with the first mechanism.

The second mechanism agrees with the facts quoted above and formally provides a quite satisfactory explanation of the composition of the photolysis products. We believe that there is a difficulty in the operation of this mechanism in that the excitation region and the region where the excitation energy is utilised are very remote in the $CH_2OH...\underset{|}{\overset{}{O}}H$ molecular system. In other words, it is
$\quad\quad\quad

When the $C_2H_5\dot{C}HOC_3H_7$ radicals derived from propyl ether were acted upon by light, the n-$\dot{C}_3H_7$ and $C_2H_5\dot{C}O$ radicals were detected[68]; under the influence of visible light, the latter decompose with formation of $\dot{C}_2H_5$ radicals. H_2, C_2H_6, and C_3H_8 were detected in the gaseous photolysis products. Evidently in this case the photolysis of the radicals also proceeds via mechanisms involving the dissociation of the bond in the β-position relative to the atom with the unpaired electron.

On photolysis of the primary $Me_2\dot{C}OCHMe_2$ radicals in isopropyl ether, $Me_2\dot{C}H$ radicals are formed[68]. When they are kept in the dark at 77 K, the initial radicals are regenerated. As in other ethers, H_2 is not formed. In contrast to straight-chain ethers, in this case acetone is produced, as in isopropyl alcohol, and not an aldehyde. For this reason $R\dot{C}O$ radicals are absent in the photolysis of $Me_2\dot{C}OCHMe_2$.

When straight-chain alcohols and ethers are photolysed together with $R\dot{C}H_2$ radicals, a single asymmetric line also appears in the ESR spectrum, its intensity decreasing under the influence of light with $\lambda > 500$ nm; alkyl radicals $R\dot{C}H_2$ appear under these conditions.

The interpretation of the singlet is extremely contradictory. Many investigators[75,79,80,86,88,93] attribute it to alkoxy-radicals $R\dot{O}$, which are formed either during the isomerisation of $R\dot{C}HOH$ radicals or when a hydroxyl hydrogen atom is abstracted from ROH. Both processes are unlikely. It is more reasonable to assume[68,82,92,94] that the singlet is due to acyl radicals $R\dot{C}O$, which are derived from the formyl radical $H\dot{C}O$.

There are many common features in the photochemical behaviour of the species responsible for the singlet and of the $H\dot{C}O$ radical. Like the $H\dot{C}O$ radical, acyl radicals absorb light in the range 400–650 nm. The values of λ_{max} in the absorption spectra of certain acyl radicals in γ-irradiated acyl chlorides and methyltetrahydrofuran at 77 K are listed below[90]:

Radical	λ_{max}, nm
$CH_3\dot{C}O$	340, 500, 540
$C_2H_5\dot{C}O$	330, 480, 540
$PhCH_2\dot{C}O$	320, 510, 550
$Ph\dot{C}O$	320, 450
$Ph{-}CH{=}CH\dot{C}O$	400, 500, 550

The angle between the bonds in the $H\dot{C}O$ radical is about 120°; in its ground state the radical is appreciably bent and the unpaired electron is localised in the sp^2 hybrid orbital of the carbon atom[101,102]; the g-factor of the radical is 2.0008. Acyl radicals have been obtained as a result of the dissociative addition of electrons to the molecules of acid chlorides on γ-irradiation[90]:

$$RCXO + e \rightarrow R\dot{C}O + X^- \ ,$$

their g-factor being 2.0010 and $a_{\alpha-H} = 5.1$ G. Acyl radicals are σ-electron radicals; as in $H\dot{C}O$, the unpaired electron is localised in the sp^2 hybrid orbital of the carbon atom; the unpaired electron density at the atom amounts to 52%.[103] The weak absorption by acyl radicals $R\dot{C}O$ in the range 400–650 nm is probably due to a transition from the state in which the CCO angle is close to 120° to one where it is 180°. In the case of $CH_3\dot{C}O$ this corresponds to the excitation of the electron from the singly occupied σ orbital to the lowest vacant π orbital.[68]

Like $H\dot{C}O$ radicals, on σ–π^* excitation acyl radicals dissociation with formation of carbon monoxide and R radicals. The energy of the dissociation

$$R\dot{C}O \rightarrow \dot{R} + CO \qquad (13)$$

is about 0.5 eV.[104] Carbon monoxide adds reversibly in the dark to the primary alcohol and ether radicals with formation of the corresponding acyl radicals $R\underset{\dot{C}O}{\underset{|}{C}}HOH$ and $R\underset{\dot{C}O}{\underset{|}{C}}HOR$.[68,92] Under the influence of visible light, the latter again decompose with regeneration of the initial radical.

$\dot{C}H_2COMe$ radicals are stabilised at 77 K in γ-irradiated acetone[105]. The action of light with $\lambda < 340$ nm lowers their concentration and leads to the appearance of lines due to the methyl radical[105–107]. For low conversions, the overall radical concentration hardly changes. A single ESR line, the intensity of which increased linearly with time, was observed simultaneously with the methyl radical.

The following mechanism has been proposed for the photochemical reactions[107]:

$$\dot{C}H_2COCH_3 \xrightarrow{h\nu} CH_2{=}C{=}O + \dot{C}H_3 \ , \qquad (14)$$

$$\dot{C}H_3 + CH_3COCH_3 \rightarrow CH_4 + \dot{C}H_2COCH_3 \ . \qquad (15)$$

The single line, which is insensitive to either visible or ultraviolet light, was not identified.

The study of the dependence of the rate of accumulation of methyl radicals on the wavelength of the exciting light yielded a spectrum representing the effect of the light on the acetonyl radical[106] which is virtually identical with the absorption spectrum of acetone (280–340 nm). However, it is difficult to conclude that either the acetonyl radical itself absorbs light in this region or there is energy transfer from the excited acetone molecule to the radical; there is a possibility under these conditions of excitation to a higher electronic state of the radical which then dissociates. These hypotheses require proof.

The photochemical reactions of the radicals obtained from ethyl methyl ketone and the isopropyl methyl ketone are similar, i.e., as in the case of acetone, photolysis ($\lambda \leq 340$ nm) leads to the formation of both methyl and alkyl radicals[108]:

$$CH_3\dot{C}HCOCH_3 \xrightarrow{h\nu} CH_2{=}C{=}O + \dot{C}_2H_5 \ , \qquad (14a)$$

$$Me_2\dot{C}COCH_3 \xrightarrow{h\nu} Me_2\dot{C}H + CH_2{=}C{=}O \ . \qquad (14b)$$

However, whereas one can assume that $\dot{C}H_3$ is formed in reaction (14) via the dissociation of the C–C bond in the β-position, this cannot be postulated for reactions (14a) and (14b). Their mechanism remains obscure and is hardly likely to involve a single fundamental step.

Together with alkyl radicals, a singlet appears in the ESR spectra on photolysis of ethyl methyl ketone and isopropyl methyl ketone; the authors[108] correctly attributed it to acyl radicals $R\dot{C}O$, which decompose under the influence of visible light ($\lambda > 400$ nm) with formation of alkyl radicals and carbon monoxide (as in the photolysis of alcohols). H_2, hydrocarbons, and CO were detected among the gaseous photolysis products.

The radicals derived from monocarboxylic acids and anhydrides absorb light in the region $\lambda \leq 350$ nm. The absorption band maxima and the extinction coefficients are listed in Table 2.[109]

The radicals $\dot{C}$–COOH absorb at longer wavelengths than the corresponding acids. This effect is a consequence of the interaction of the unpaired electron at the α-carbon atom with the electrons of the adjacent COOH

group. The $\dot{C}H_2Me_2CCOOH$ radicals, in which the unpaired electron is located at the β-carbon atom, do not absorb light with $\lambda > 300$ nm.

Table 2. Parameters of the absorption spectra of radicals derived from monocarboxylic acids.

Acid	pH	Radical	λ_{max}, nm	ϵ, litre mole^{-1} cm^{-1}
Acetic	3	$\dot{C}H_2COOH$	320	650
	10	$\dot{C}H_2COO^-$	350	800
Propionic	3	$CH_3\dot{C}HCOOH$	300	700
	10	$CH_3\dot{C}HCOO^-$	335	900
Butyric	3	$CH_3CH_2\dot{C}HCOOH$	280	—
	9	$CH_3CH_2\dot{C}HCOO^-$	335	900
Trimethylacetic	3	$\dot{C}H_2Me_2CCOOH$	240	—
	9	$\dot{C}H_2Me_2CCOO^-$	240	1800

It follows from CNDO calculations on the electronic state of the $\dot{C}H_2COOH$ radical[68,110] that its excited state is obtained when an electron passes from a doubly occupied σ orbital to a singly occupied π orbital. The σ bonds in the radicals of acids and anhydrides are then weakened and readily dissociate. Indeed, as will be shown subsequently, such dissociation constitutes the principal mechanism of the photochemical reactions of the radicals.

When light at wavelengths in the range $300 < \lambda < 400$ nm was allowed to act on the $\dot{C}H_2COOH$ radical in acetic acid, the radical was destroyed with the simultaneous increase of the $\dot{C}H_3$ concentration[109-111] and the appearance in the ESR spectrum of an asymmetric singlet. The paramagnetic species responsible for this line are destroyed under the influence of light with $\lambda \geqslant 500$ nm, being converted quantitatively into $\dot{C}H_2COOH$ radicals; there is no doubt that these species are the acyl radicals $\dot{C}H_2(CO)COOH$. The principal gaseous products of the photolysis of $\dot{C}H_2COOH$ radicals are CH_4 and CO_2,[110] which are obtained in equal amounts.

The main photochemical process in the photolysis of the $\dot{C}H_2COOH$ radical is, according to Chervonenko and Roginskii[110], the dissociation of the radicals at the C–OH bond:

$$\dot{C}H_2C(=O)OH \rightarrow CH_2=C=O + \dot{O}H \ . \qquad (16)$$

The dissociation of the C–OH bond in the $\dot{C}H_2COOH$ radical is more favourable on energetic grounds; its energy amounts to about 2.5 eV. CNDO calculation on the radical[68] also showed that the C–OH bond order does not decrease on $\sigma-\pi^*$ excitation.

Presumably the methyl radical is formed by the reactions

$$\dot{C}H_2COOH \rightarrow \dot{C}H_3 + \dot{C}OOH \ , \qquad (17)$$

$$\dot{C}H_3 + CH_3COOH \rightarrow \dot{C}H_2 + \dot{C}H_2COOH \ . \qquad (18)$$

However, the most probably mechanism is apparently photolysis of keten. Calculation by the CNDO method has also shown that the C–C bond in the radical is strengthened on $\sigma-\pi^*$ excitation and its order increases from 0.45 (in the ground state) to 0.63, i.e. reaction (17) is unlikely.

Another mechanism for the formation of the methyl radical has been proposed in other investigations[65,68], presupposing the decomposition of the radical in accordance with the scheme

$$\dot{C}H_2C(O\cdots HO)(OH)(O=)CCH_3 \rightarrow CH_2=C(OH)_2 + CH_3C\dot{O}_2 \ , \qquad (19)$$

$$CH_2=C(OH)_2 \rightarrow CH_2=C=O + H_2O \ , \qquad (20)$$

$$CH_3C\dot{O}_2 \rightarrow \dot{C}H_3 + CO_2 \ . \qquad (21)$$

An important role is attributed in this mechanism to the hydrogen bond between the radical and the adjoining acid molecule. This mechanism resembles that postulated for the photolysis of alcohol radicals; the difficulties in its operation were discussed above.

In propionic acid $Me\dot{C}HCOOH$ radicals are destroyed under the influence of light at wavelengths in the range $300 \leqslant \lambda < 400$ nm and $\dot{C}_2H_5$ radicals accumulate[110]. A singlet is not observed in the ESR spectrum. Photolysis terminates after the complete conversion of $Me\dot{C}HCOOH$ radicals into C_2H_5; the principal gaseous photolysis products are ethane and CO_2.

The formation of the $\dot{C}_2H_5$ radical and the accumulation of C_2H_6 and CO_2 in the gaseous products are consistent with the mechanisms discussed in connection with the photolysis of $CH_2\dot{C}OOH$ radicals derived from acetic acid. The absence of $Me\dot{C}H(C=O)COOH$ radicals can probably be accounted for by the rigidity of the propionic acid matrix in which CO is hardly formed owing to the high probability of the reverse reaction between the keten dissociation products. The photochemical behaviour of the $C_2H_5\dot{C}HCOOH$ radicals derived from butyric acid[110] is analogous to the behaviour of $\dot{C}H_2COOH$ radicals in acetic acid. Under the influence of light at wavelengths in the range $300 < \lambda < 400$ nm, the concentration of primary radicals fell and $\dot{C}_2H_5$ and n-$\dot{C}_3H_7$ radicals appeared. As in other acids, C_3H_8 and CO_2 were detected in the photolysis products. The mechanisms of the formation of n-$\dot{C}_3H_7$ and $C_2H_5CH(\dot{C}O)COOH$ radicals and of the photolysis products are analogous to those discussed previously. The primary radicals $C_2H_5CH_2\dot{C}HCOOH$ derived from valeric acid undergo similar reactions[110].

The photochemical behaviour of the protonated radical-anions $(RCH_2\dot{C}OO)^{2-}$, obtained on γ-irradiation of monocarboxylic acids at 77 K, is somewhat unusual[112]. Under the influence of light with $\lambda \geqslant 380$ nm, these radicals disappear irreversibly without the formation of other paramagnetic species. The mechanism of the photolysis probably consists in the protonation of the radical-anions and liberation of electrons with subsequent capture of the electrons by positive ions:

$$(RCH_2\dot{C}OO)^{2-}\ H^+ \rightarrow RCH_2COOH + e \ , \qquad (22)$$

$$e + (RCH_2\dot{C}OOH)^+ \rightarrow RCH_2COOH \ . \qquad (23)$$

Other radicals are not formed in the photolysis, so that $(RCH_2\dot{C}OO)^{2-}H^+$ radicals do not dissociate and the recombination of $(R\dot{C}OO)^+$ and e explains the decrease of the concentration of paramagnetic species on photolysis.

After γ-irradiation at 77 K the radicals $R\dot{C}H{-}C(=O)O{-}C(=O){-}CH_2R$ are stabilised in monocarboxylic acid anhydrides[113]. These radicals dissociate under the influence of light at wavelengths in the range $300 < \lambda < 400$ nm similarly to radicals

derived from acids, i.e. with dissociation of the bond in the β-position:

$$R\dot{C}HCOCCH_2R \xrightarrow{h\nu} RCH{=}C{=}O + RCH_2\dot{C}O_2 \quad , \tag{24}$$

$$RCH_2\dot{C}O_2 \rightarrow R\dot{C}H_2 + CO_2 \quad , \tag{25}$$

$$R\dot{C}H_2 + (RCH_2CO)_2O \rightarrow RCH_3 + R\dot{C}HCOCCH_2R \quad . \tag{26}$$

The quantum yield of reaction (24) in acetic anhydride is 0.8 ± 0.2.[113] Hydrocarbons, CO_2, and CO were detected in the gaseous photolysis products. The formation of hydrocarbons and CO_2 can be explained by the proposed mechanism and the detection of appreciable amounts of CO in the products is evidence for the formation of ketens, which effectively decompose under the influence of light with $\lambda \geq 300$ nm, forming CO.

6. Amine and Amide Radicals

When amines are γ-irradiated, radicals are formed by the abstraction of a hydrogen atom from the carbon atom in the α-position with respect to the heteroatom[114,115]. The hyperfine structure in the spectra of such radicals in an adamantane matrix is satisfactorily resolved[116].

As in alcohol radicals, in amine radicals the unpaired electron interacts with the lone pair of electrons at the nitrogen atom, which leads to a bathochromic shift of the absorption spectra of the radicals relative to the initial molecules[117]. The absorption spectra of amine radicals contain an intense broad band, the long-wavelength limit of which is at $\lambda \leq 400$ nm. The structure of the radicals obtained on γ-irradiation of amines and on subsequent illumination with ultraviolet light is indicated below together with the λ_{max} for the absorption bands of the radicals.

Amine	Radical after γ-irradiation	λ_{max}, nm	Radicals formed on illumination with ultra-violet light
CH_3NH_2	$\dot{C}H_2NH_2$	230	$CH_2\dot{N}$
Me_2NH	$\dot{C}H_2NHCH_3$	—	$Me_2\dot{N}$
Me_3N	$\dot{C}H_2NMe_2$	260	$Me_2\dot{N}$, $\dot{C}H_3$
$C_2H_5NH_2$	$CH_3\dot{C}HNH_2$	240	$\dot{C}_2H_5$, $CH_3CH{=}\dot{N}$
$(C_2H_5)_3N$	$CH_3\dot{C}HN(C_2H_5)_2$	250	$\dot{C}_2H_5$
$(C_2H_5)_2NH$	$CH_3\dot{C}HNHC_2H_5$	—	$\dot{C}_2H_5$

The most probable photochemical process on excitation of amine radicals is (as in alcohol radicals) their photodissociation with formation of various products.

The evidence for the mechanisms of the photochemical reactions of amine radicals is weak. Certain hypotheses have been put forward in a number of studies[114,115,118] concerning the photochemical dissociation of the N–R bonds in $\dot{C}$–NH–R radicals (where R = H, Me, C_2H_5, etc.). The dissociation of the N–R bond is probably the main photochemical reaction of amine radicals. In addition there is also the possibility of the dissociation of the C–N bond in the radical. However, the probability of this reaction is much lower than that of the dissociation of the N–R bond in the β-position (by analogy with radicals derived from alcohols, ethers, and other carbonyl compounds discussed in the previous section).

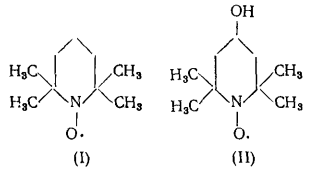
As in alcohols and ethers, the active radical species ($\dot{C}H_3$, $\dot{C}_2H_5$, $Me_2\dot{N}$, $H^{\cdot}$) formed in amines under the influence of light abstract hydrogen in the dark from the matrix molecules with regeneration of the initial photochemically active radicals.

When amine salts, in which there is no lone electron pair (a proton is attached to it), are γ-irradiated, $\dot{C}\overset{+}{N}H\begin{matrix}R_1\\R_2\end{matrix}$ radicals are formed following the abstraction of a hydrogen atom from the α-carbon atom[119]. Under the influence of light ($\lambda > 260$ nm), there is no photodissociation of radicals, the form of the ESR spectra of the radicals remains unchanged, and gas evolution is not observed. This is associated with the fact that the absorption by radicals of amine salts in which there is no $n-\pi$ conjugation, is displaced towards shorter wavelengths ($\lambda < 260$ nm), compared with the absorption by the corresponding radicals with a lone electron pair. Radicals of the type $\dot{C}\overset{+}{N}HR_1R_2$ therefore behave similarly to alkyl radicals.

III. PHOTOCHEMICAL REACTIONS OF RADICALS IN THE LIQUID PHASE

1. Nitroxy-Radicals

Nitroxy-radicals of the type



(I) (II)

do not react in the ground state with hydrocarbons up to a temperature of about 100°C, but, on being excited with radiation corresponding to the $\pi-\pi^*$ absorption band of the N–O group ($\lambda_{max} = 240$ nm, $\epsilon = 1500$), the radicals are destroyed even at a comparatively low temperature (about 10°C).[121,122] The main photolysis products are hydroxylamine and ether—the product of the recombination of nitroxy- and alkyl radicals[123]. The yields of each of these radicals are the same, amounting to about 50%.

The kinetic mechanism of the destruction of the radical can be represented as follows:

$$\dot{R} \xrightarrow{h\nu} \dot{R}^* \text{ (excitation of the radical)},$$
$$\dot{R}^* \xrightarrow{f} \dot{R} \text{ (radiative deactivation)},$$
$$\dot{R}^* \xrightarrow{d} \dot{R} \text{ (radiationless deactivation)},$$
$$\dot{R}^* + rH \xrightarrow{r} RH + \dot{r} \text{ (destruction of the radical)},$$
$$\dot{R} + \dot{r} \rightarrow Rr \quad .$$

The rate of destruction of radicals for $\bar{\epsilon}[R]l \ll 1$ is defined by the equation

$$-\frac{d[\dot{R}]}{dt} = \frac{2r[rH]\,n_0\bar{\epsilon}l}{f+d+r[rH]}[\dot{R}]$$

or

$$\lg\frac{[\dot{R}]_0}{[\dot{R}]} = \frac{0{,}87r[rH]\,n_0\epsilon l}{f+d+r[rH]} \quad ,$$

where n_0 is the number of incident photochemically active quanta and $\bar{\epsilon}$ is the effective extinction coefficient.

The quantum yields of the reaction $\gamma = r[rH]/\{f + d + r[rH]\}$ were found from the equation of Bogatyreva et al.[122], and the activation energies for the abstraction of a hydrogen atom from solvents by the electronically excited

radicals (I) were determined from the temperature variation of $(f + d)/r$ (provided that $f + d$ depends only slightly on temperature). These results are listed in Table 3.

The high quantum yields and the low activation energies [the activation energy for the reaction of the radical (I) is 34 kcal mole^{-1} [124]] show that in an electronically excited state the radical (I) is highly reactive.

Table 3. The quantum yields and activation energies E for reactions involving the abstraction of a hydrogen atom by the electronically excited radical (I).[122]

Solvent	10° C	18° C	25° C	E, kcal mole^{-1}
Heptane	0.32	0.37	0.42	2.3
Toluene	0.51	0.61	0.68	2.5
Cyclohexane	0.30	0.37	0.42	3.0
Water	0.16	0.31	0.42	9.1

The quenching of the electronically excited state of the radical (I) by oxygen in heptane and water and by nitric oxide in heptane[122] obeys the Stern–Volmer equation, from which the values of $k_q\tau$ were found, k_q being the quenching rate constant and τ the lifetime of the radical. The constant k_q was assumed equal to the rate constant for the diffusional encounters of radicals and was determined from the broadening of the ESR spectra of the radicals in the presence of oxygen and nitric oxide[125]. The observed values of k_q and the calculated τ are listed in Table 4.

Table 4. The values of k_q and τ for the radical (I).

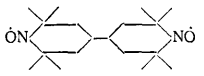
System	k_q, litre mole^{-1} s^{-1}	τ, s
Heptane + O_2	$1.6 \cdot 10^{10}$	$5.7 \cdot 10^{-8}$
Water + O_2	$8.7 \cdot 10^{10}$	$6.3 \cdot 10^{-8}$
Heptane + NO	—	$4.6 \cdot 10^{-3}$

The spectrum of the nitroxy-radical (I) contains two absorption bands corresponding to $\pi-\pi^*$ and $n-\pi^*$ excitations[126]. According to molecular spectroscopic data, the lowest excited state is the most stable and long-lived and the radiationless transitions from the highest electronic and vibrational levels to the lowest excited level take place at a high rate[127]. The radical (I) has the $n-\pi^*$ low-excited state. The dipole moment of the radical (I) in the excited state has been determined from the shifts of the $n-\pi^*$ absorption band in different solvents[122]. It was found that, on excitation of the radical, its dipole moment decreases from 3.14 D in the ground state[128] to 1.0 ± 0.8 D in the excited state. On $n-\pi^*$ excitation, there is probably a partial charge transfer from the oxygen atom (from the lone electron pair) to the delocalised π^* orbital. As a result, there is a deficiency of electrons at the reaction centre, which must be the cause of the high reactivity of the radical (I) in the electronically excited state.

Furthermore, this state must be comparatively long-lived, because an activation energy is required for the reaction of the excited radical. These considerations are consistent with experimental results. Evidently, reactions involving the abstraction of a hydrogen atom by the excited nitroxy-radicals proceed in the $n-\pi^*$ state.

The photolysis of the radicals (I) in the solid state takes place in accordance with the mechanism discussed for the photolysis of these radicals in the liquid phase[49].

The photochemical behaviour of the biradical



(III)

is of interest, because it contains two reaction centres whose unpaired electrons are involved in exchange reactions on intramolecular collisions. It was found that the quantum yield of the reaction of the biradical is the same as the quantum yield of the reactions of monoradicals[121], i.e. the quenching due to intramolecular collisions between the radical centres is insignificant. This implies that the period τ_0 between these collisions is greater than the lifetime of the excited radical τ, i.e. $\tau_0 > 10^{-8}$ s.

It was found in the photolysis of the radical (I) in a dense gas (ethane under a pressure of 50 atm) that the lifetime of the electronically excited radical is greater than in the liquid phase. This fact is probably due to the decreased rate of deactivation $(f + d)$ of the radical in the gas phase compared with the liquid phase.

2. Diphenylpicrylhydrazyl (DPPH)

The electronic spectrum of DPPH contains two bands corresponding to the $\pi-\pi^*$ and $n-\pi^*$ transitions with λ_{max} = 330 and 528 nm.[125] As in nitroxy-radicals, the $n-\pi^*$ state is responsible for the photochemical activity of DPPH.

Presumably, on $n-\pi^*$ excitation a possible mechanism of the photochemical destruction of DPPH is one involving the abstraction of hydrogen from solvent molecules. This hypothesis has been confirmed by a series of investigations. Thus, on photolysis of DPPH in methyl methacrylate (MMA) and in MMA solution in benzene in the absence of oxygen, the radical is quantitatively converted into the corresponding hydrazine[129]. The reaction kinetics obey the first-order equation with respect to the radical and MMA and can be described schematically as follows:

$$\text{DPPH} \xrightarrow{h\nu} (\text{DPPH})^*$$

$$\text{DPPH}^* \xrightarrow{f+d} \text{DPPH (deactivation)},$$

$$\text{DPPH}^* + \text{M} \xrightarrow{r} \text{DPPH} - \text{H} + \text{M(P)} \text{ (reaction)},$$

$$\text{DPPH} + \dot{\text{M}}(\dot{\text{P}}) \xrightarrow{k} \text{DPPH} - \text{H} + \text{products (disproportionation)}.$$

Here $\dot{P}$ is the macroradical obtained by the addition of the $\dot{M}$ radical to the monomer. At 25°C $(f + d)/r = 2.3 \pm 1.1$ M, i.e. the quantum yield of the reaction and the reactivity of the excited radical are high.

In the presence of O_2 the reaction kinetics are more complicated: DPPH is destroyed in a zero-order reaction and hydrazine is formed only in small amounts; radical oxidation and decomposition products have been found. Evidently in the presence of oxygen the reactions of DPPH involving MMA peroxy-radicals play a significant role[129].

The photolysis of DPPH in various hydrocarbons has been investigated[130]. The destruction of the radical in the absence of oxygen obeys first-order kinetics and only light corresponding to the 330 nm bond is photochemically active. The rate constant ratio $(f + d)/r$ and the quantum

yields (φ) at 25°C are presented in Table 5. Evidently the quantum yields are fairly high; there is also a correlation between the quantum yield and the energy of the C–H bond dissociated in the hydrocarbons. The rate-limiting stage of the reaction is the abstraction of a hydrogen atom by the excited radical.

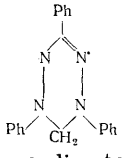
Table 5. The quantum yields of the photochemical destruction of DPPH.[130]

Solvent	$(f+d)/r$	Φ
Hexane	4.71	0.18
Toluene	3.16	0.24
Cyclohexane	2.70	0.27
Methylcyclohexane	1.77	0.36
Cumene	0.66	0.59

DPPH-H is also formed on irradiation of DPPH with light corresponding to the long-wavelength absorption band in acetic acid, in an ethanol–acetone mixture[131], in carbon tetrachloride, and in benzene[132].

3. Triphenylverdazyl

The triphenylverdazyl (TPV) radical



is excited by light corresponding to the absorption bands with λ_{max} = 400 and 710 nm. Both bands are intense ($\epsilon \simeq 10^4$ litre mole^{-1} cm^{-1}); being displaced towards the red in polar solvents, they probably correspond to $\pi-\pi^*$ transitions[133]. The lowest $\pi-\pi^*$ state is probably responsible for the photochemical activity of TPV. The dipole moment of TPV in the excited state, determined from the spectroscopic shifts of the 400 nm band in various solvents, is 9 D, i.e. on photoexcitation the dipole moment of the radical increases by about 6 D.[133,134]

The principal pathways for the photochemical destruction of TPV involve the abstraction of a hydrogen atom from the solvent with formation of the corresponding leuco-base and also the dissociation of the N–N bond with formation of the five-membered ring of 1,3-diphenyl-1,2,4-triazole and aniline.

It has been established that concentration-dependent quenching of the radicals takes place, i.e. the higher the concentration of the radical the slower the photochemical reaction. The quantity $k_q\tau \simeq 5 \times 10^3$ litre mole^{-1} was determined from the kinetic curves for the destruction of the radicals at their different concentrations. The rate constant for the diffusional encounters of radicals can be determined from the concentration-dependent broadening of the ESR line. It is caused by the exchange interaction of the electrons of the colliding radicals[125]. The rate constant for the collisions found from the exchange broadening of the ESR lines is 1×10^9 litre mole^{-1} s^{-1}, i.e. is close to the rate constant for diffusional collisions. If it is assumed that this constant is identical with the quenching constant k_q, then the lifetime of the excited state of the radical is found to be unduly long: $\tau = 5 \times 10^{-6}$ s. On the other hand, if it is assumed that the lifetime of the excited radical is 10^{-7}–10^{-8} s, then k_q is found to be 10^{10}–10^{11} litre mole^{-1} s^{-1}, i.e. exceeds by two–three orders of magnitude the value corresponding to the diffusion-controlled process. Possibly the concentration-dependent quenching is not associated with the diffusion of radicals, but proceeds via an inductive-resonance mechanism. However, an unambiguous choice between these two situations is impossible on the basis of the data quoted above.

4. The Perchlorotriphenylmethyl Radical (TPM)

The stable radical $(C_6Cl_5)_3\dot{C}$ has an absorption spectrum consisting of four bands with maxima at 220 nm ($\epsilon = 1 \times 10^5$), 293 nm ($\epsilon = 7 \times 10^3$), 382 nm ($\epsilon = 7 \times 10^4$), and 510 and 562 nm ($\epsilon = 10^3$ litre mole^{-1} cm^{-1}). Each band is photochemically active[135].

The principal pathway to the photochemical destruction of the radical involves the abstraction of a hydrogen atom from solvent molecules with formation of the corresponding triphenylmethane. The effective rate constants for the destruction of the radical in various solvents are different; there is an approximate correlation between the energies of the C–H bonds dissociated in the solvents and the radical destruction rate constants.

In the photolysis of TPM in the presence of aromatic additives the electronically-excited state of the radical is found to be quenched by these additives. This can occur via two mechanisms: firstly in a charge-transfer complex (since all the additives are effective electron donors) and secondly via energy transfer.

5. π-Complexes and Hydrogen Bonds Involving Electronically Excited Radicals

Data have been obtained for the π-complexes of excited radicals and for hydrogen-bonded complexes[136]. The difference between their heats of formation of the ground (ΔH_g) and excited (ΔH_e) states can be obtained from a thermodynamic cycle involving the excited radical[137]:

$$\Delta H_g - \Delta H_e = h(\nu_0 - \nu_s),$$

where ν_0 and ν_s are the frequencies at the maxima of the electronic bands of the radical in inert and solvating solvents.

The solvation mechanism is as follows:

$$\dot{R} + S \overset{K_g}{\rightleftarrows} \dot{R}_s \quad ,$$
$$\dot{R}^* + S \overset{K_e}{\rightleftarrows} \dot{R}_s^* \quad ,$$

where K_g and K_e are the equilibrium constants for the solvation of the radical in the ground and excited states.

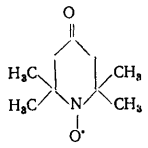
Then

$$\ln K_e/K_g = \frac{\Delta H_e - \Delta H_g}{RT} = \frac{h(\nu_0 - \nu_s)}{RT} \quad , \qquad (27)$$

provided that the entropies of the ground and excited states are identical. The ratio of the equilibrium constants for the solvation of the ground and excited states and the difference between the activation energies for the decomposition of the solvated states can be determined from the spectral shifts by Eqn. (27).

It was found that the formation of a π-complex by the dianisylnitroxy-radical with benzene causes a bathochromic shift of the absorption band in the electronic spectrum of the radical (λ_{max} = 329 nm in heptane and λ_{max} = 336 nm in benzene). $\Delta H_e - \Delta H_g$ = 1.3 kcal mole^{-1} can be found from the shift by Eqn. (27). Thus the π-complex of the excited radical (excimer) is more stable to the extent of 1.3 kcal mole^{-1} than the π-complex of the radical in the ground state[136].

Analysis of the hypsochromic shifts of the $n-\pi^*$ absorption band of aliphatic nitroxy-radicals permits the calculation by Eqn. (27) of the equilibrium constant for association via hydrogen bonding in the excited $n-\pi^*$ state of the radical. It was found that for the radical



$K_e/K_g = 2.9 \times 10^{-3}$ in methanol and $K_e/K_g = 2.5 \times 10^{-4}$ in acetic acid (at 22°C). Thus the equilibrium constant for solvation in the excited $n-\pi^*$ state of the radical is much smaller than in the ground state; accordingly, the solvate of the ground state is much more stable than that of the excited state.

Thus electron transfer from the n orbital of oxygen to the excited π^* molecular orbital weakens the donor–acceptor interaction in the hydrogen-bonded complex and displaces the solvation equilibrium towards the free radicals. Since the lifetime of the excited state is much longer than the vibration period of the nuclei in the hydrogen bond bridge, on excitation the radical may be involved in further reactions as a free non-associated species. This result is of significant importance for the kinetics of the reactions of radicals in the electronically excited state.

IV. THE QUENCHING OF EXCITED STATES BY RADICALS

The deactivation of electronically excited states of molecules by paramagnetic species is of considerable interest to spectroscopists and photochemists; because in the presence of paramagnetic quenching agents different quenching mechanisms operate from those of quenching by diamagnetic molecules; this is caused by the removal of the spin prohibition of electronic transitions in the excited molecule in the presence of paramagnetic species. For example, oxygen is known to be an excellent quenching agent for excited singlet and triplet states. Nitric oxide possesses similar properties. Since for the majority of organic molecules energy transfer to NO is impossible, evidently effective quenching of this molecule involves a reorientation of the electron spin in the excited molecule, but the total spin of the system is retained:

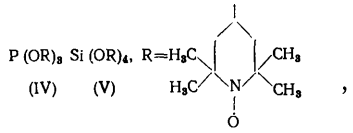
$$^3M(\uparrow\uparrow) + {}^2NO(\uparrow) \rightarrow {}^1M(\downarrow\uparrow) + {}^2NO(\downarrow),$$

where ^3M denotes the triplet state of the molecule, ^1M the ground singlet state, and the arrows indicate the orientations of the electron spins. This mechanism was first proposed by Porter and Wright[138].

However, oxygen and nitric oxide are not always suitable quenching agents, since they are frequently actively involved in chemical reactions and alter their mechanisms. This naturally led to interest in other paramagnetic quenching agents (metal ions and complexes and organic, especially stable, radicals). In this section the quenching of excited states by organic radicals will be considered.

1. The Quenching of Excited States in a Liquid

The quenching of the fluorescence of 2,5-diphenyloxazole, anthracene, 1,2-benzanthracene, and naphthacene in cyclohexane by the radical (I) and the polyradicals (IV) and (V),



was observed by Buchachenko et al.[139] The kinetics of the quenching process obeyed the Stern–Volmer equation and the ratio of the quenching constants for the radical (I) (k_q) and oxygen (k_{O_2}) was 0.53, 0.57, 0.53, and 0.73 respectively for the above electron donors. Evidently, the rate of quenching of excited singlet states is limited by the diffusion of the species. The fluorescence of rubrene and rhodamine B, where the position of the excited singlet level coincides with that of the radicals, was not quenched. Hence it was concluded that the quenching of the excited singlet state of donors occurs only if this state is above the lowest excited level of the quenching radical, i.e., in other words, the quenching by radicals involves energy transfer via an exchange-resonance mechanism.

However, in a later study[140] the quenching of fluorescence by di-t-butylnitrogen oxide (t-$C_4H_9)_2NO$ (VI) was investigated in methylcyclohexane and measurements were made of the lifetime of the excited singlet states and the quenching rate constant; it was shown that both rubrene and rhodamine B are quenched almost as effectively as other donors with high singlet levels. The energies of the excited singlet states and the quenching rate constants are listed in Table 6.

Table 6. The energies of the excited singlet levels and the rate constants for quenching by the radical (V) and oxygen.

Donor	$10^3 E_S$, cm^{-1}	$10^{-9} k_q$, litre mole^{-1} s^{-1}	k_q/k_{O_2}
Naphthalene	32.2	8.2	—
Chrysene	27.7	8.5	3.9
Pyrene	26.9	7.8	3.2
Anthracene	26.7	12.9	2.4
1,2-Benzanthracene	26.0	8.0	3.5
9,10-Diphenylanthracene	25.5	9.2	3.5
Perylene	23.0	12.0	2.4
Naphthacene	21.2	6.4	3.8
Rubrene	18.5	2.1	5.6
Rhodamine B	17.5	4.7	—

Clearly the rate of quenching is diffusion limited and there is no unambiguous relation between the energy of the singlet level (E_S) and the quenching constant k_q. Hence it follows that energy transfer is not the principal quenching mechanism, i.e. the conclusion of Buchachenko

et al.[139] was incorrect. (They did not measure the lifetime of the singlet states τ_S; possibly the quenching of the fluorescence of rubrene and rhodamine B could not be observed owing to the short lifetimes of the excited donors.) One must also rule out quenching due to energy transfer via an inductive-resonance mechanism, since the efficiency of quenching is independent of the overlapping of the absorption bands of the donor and acceptor.

The mechanism of the quenching of excited singlet states $^1M^*$ as a result of a chemical electron transfer reaction with formation of ion pairs is possible:

$$^1M^* + \dot{R} \rightarrow (M^{\cdot-}\dot{R}) \rightarrow {}^1M_0 + \dot{R} \ .$$

Quenching by amines usually involves this mechanism, the quenching efficiency depending strongly on solvent polarity. The quenching has been found to depend[140] only on the viscosity of the solvent, i.e. quenching by the radicals (VI) does not take place via the charge transfer mechanism.

The most probable quenching mechanism involves the removal of spin prohibition in the contact complex ($^1M^*...\ ^2R$), which results in the induction of $S-T$ transitions in the excited molecule and relaxation of the excess energy in the vibrational degrees of freedom (this mechanism will be discussed in detail a little later).

The quenching of the singlet states of fluorenone by the radical (VI) with a diffusional rate constant was observed in a study of the photocycloaddition of fluorenone to ketenimine[141].

The radical (VI) also quenches the fluorescence of pyrene monomers and excimers in benzene solution with nearly diffusional rate constants: 8.4×10^9 and 4.1×10^9 litre mole^{-1} s^{-1} for the monomer and excimer respectively[142]. The rate constants for the quenching of the excited singlets of substituted benzenes by nitric oxides are also the same as the collision rate constants and hardly differ from the constants for the quenching by oxygen[143].

We shall now consider the quenching of triplet states by radicals. Yang and Murov[144] observed that the ketyl radicals formed in solutions in the photochemical reduction of benzophenone behave as quenching agents for triplet states. In a study of photocycloaddition of fluorenone and aromatic aldehydes to olefins and ketenimine[145,146] it was found that the radical (VI) quenches both the singlet and triplet states of fluorenone with a diffusional rate constant. The quenching of triplet exciplexes by the radical (VI) has been observed in a study[147] of the photoaddition of 2-cyclohexenes to 1.1-dimethoxyethylene. In the radiolysis of mixtures of benzene and but-2-ene in the presence of the stable galvinoxyl radical (a phenoxy-radical) excited benzene triplet molecules are quenched[148]. $k_q\tau = 4.8 \times 10^2$, where k_q is the quenching rate constant, close to a diffusional constant (about 5×10^9 litre mole^{-1} s^{-1}) and τ is the lifetime of the triplet benzene molecule. It has been shown[149] that the *NNN'N'*-tetramethyl-*p*-phenylenediamine radical-cation (Wurster's cation) is an effective quenching agent for the triplet states of anthracene molecules. Thus the lifetime of the triplet state of anthracene in methylene chloride solution is 2.8×10^{-6} s in the presence of 1.8×10^{-7} M cation and 6.4×10^{-6} s in the absence of the cation.

It is interesting that in a magnetic field (up to 7000 G) the rate of quenching falls, i.e. the magnetic field inhibits the quenching of the triplet states of molecules by radicals. This inhibition also explains the increase in the intensity of the phosphorescence of the triplet molecules of aromatic hydrocarbons obtained in electrochemical reactions[150]. In this case the electrochemically generated hydrocarbon radical-anions are oxidised by Wurster's radical-cation with formation of triplet states of aromatic molecules. With increase of the magnetic field strength, the electroluminescence intensity rises; this effect can be explained by the fact that the magnetic field inhibits the quenching of the triplets by Wurster's cation.

Incidentally, the influence of the magnetic field on the efficiency of the quenching of the triplets is evidence that the quenching does not occur in every collision between the excited molecule and the quenching agent, i.e. that the rate of quenching is lower than the rate of diffusional collisions. This conclusion was confirmed quantitatively in two investigations[151,152]. The quenching of benzophenone and stilbene triplets by the radical (VI) takes place with a rate constant close to the diffusional value ($\sim 3 \times 10^9$ litre mole^{-1} s^{-1}), while the triplet state of naphthalene is quenched much more slowly (6×10^8 litre mole^{-1} s^{-1}). The perdeuteronaphthalene triplet is quenched still more slowly (3.7×10^8 litre mole^{-1} s^{-1}).[151] Thus the probability of quenching on collision with a paramagnetic species also depends significantly on the probability of the intramolecular radiationless degradation of the excitation energy (cf. naphthalene and deuteronaphthalene).

An interesting dependence of the rate constants for the quenching of triplets of aromatic molecules by the radical (VI) and nitric oxide on the energy of the triplet levels has been observed[152]. With increase in the energy of the triplet level, the rate constants initially decrease and then rapidly increase; the constant has a minimum corresponding to the energy $\sim 14 \times 10^3$ cm^{-1}. Both quenching agents behave in exactly the same way, although the energies of their lowest excited levels differ markedly. The observed relations have been explained by the hypothesis that quenching takes place in charge-transfer collision complexes; however, this hypothesis involves certain difficulties, since it does not explain the identical efficiencies of both quenching agents and is not consistent with the effect of the dielectric constant on the quenching efficiency.

Table 7. The quenching rate constants and the energies of the triplet levels of donors.

Donor	$10^{-8}k_q$, litre mole^{-1} s^{-1}	E_T, kcal mole^{-1}
Stilbene	50	48
Diacetyl	37	55
Benzophenone	26	69
Fluorenone	15	53
Biphenyl	7	69
Phenanthrene	6.4	62
Naphthalene	6.3	61
3-Acetylphenanthrene	6.0	59
1-Bromonaphthalene	5.2	59
Naphthalene-d_8	3.7	60

The quenching of triplets by the radicals (VI) has been investigated in detail[153]. Table 7 presents the quenching rate constants and the energies of the triplet levels. Evidently there is no unambiguous relation between the constants k_q and the position of the triplet level. However, there is a definite tendency as regards quenching efficiency: stilbene is quenched most effectively, $(n-\pi^*)$-excited triplets of ketones are quenched less effectively,

and the efficiency of the quenching of the $\pi-\pi^*$ triplets of aromatic hydrocarbons is lowest. This trend and the absence of a correlation between k_q and E_T constitute powerful evidence against the quenching mechanism involving energy transfer.

The exchange-induced quenching mechanism appears to be the most likely. It involves the removal of spin prohibition and the induction of the reorientation of the electron spin in the excited triplet in the contact complex of the excited molecule and the radical $^3M...R$ as a result of the exchange interaction of the electrons:

$$^3M^* + \dot{R} \rightarrow (^3M\cdots\dot{R}) \rightarrow {}^1M_0 + \dot{R} \ .$$

This process can be called exchange-induced vibrational relaxation rather than energy exchange, since the energy remains in the same initial molecule and is then degraded via its vibrational levels[154]. Evidently the probability of such vibrational relaxation depends on the exchange interactions in the contact complex $^3M...R$ and must be sensitive to the details of the electronic interactions in the complex and to the nature of the electron orbitals involved in complex formation.

The physical validity of this quenching mechanism was recently confirmed from completely different standpoints. In a study of the NMR of various organic molecules in the presence of stable radicals it was observed that even in the ground state all the molecules are involved in complex formation with the radicals[155]. In these short-lived complexes the unpaired electron of the radical is transferred to the orbitals of the molecules involved in the complex, i.e. there is partial merging of the electron shells and formation of common molecular orbitals. The nature of the complexes is extremely varied, but they can be classified in terms of the type of orbitals involved in complex formation ($n-\sigma$, $\pi-\sigma$, $\pi-\pi$, $\pi-n$, etc.) Here n, σ, and π are the orbitals of the lone pairs and σ bonds and π orbitals.

There is no doubt that radicals form complexes of this type with excited molecules and the electronic interactions in these complexes determine the efficiency of the quenching by radicals of excited states such as singlet and triplet states.

2. The Quenching of Excited States in the Solid Phase

Ern and Merrifield[156] showed that the triplet excitons of anthracene are quenched by the radicals formed when crystalline anthracene is irradiated by X-rays. The quenching of the phosphorescence of tetrahydrocarbazole and benzophenone by the radicals (I) in mixtures of alcohol and ether frozen at 77 K has been observed[157]. In the presence of the radicals there was merely a decrease of the intensity of the phosphorescence, while the kinetics of the decrease did not change after switching on the exciting light, i.e. the lifetime of the triplet state was independent of the presence of the quenching radicals and of their concentration. This shows that the quenching proceeds via the mechanism proposed by Perren[158], who suggested that the molecule of the quenching agent creates around itself a sphere of action of specific volume, so that the excited molecule is instantaneously quenched when it enters this sphere; on the other hand, when the molecule is outside the sphere of action of the quenching agent, it luminesces as an unperturbed molecule, i.e. in the same way as in the absence of the quenching agent.

This model yields the following expression for the dependence of the intensity (or quantum yield) of the phosphorescence on the concentration of the quenching agent c:

$$I/I_0 = \exp(-vNc) = \exp(-\alpha c),$$

where I_0 is the phosphorescence at $c = 0$ and $N = 6 \times 10^{20}$ mol. cm^{-3} (when v is expressed in cm^3 and the concentration is on the molar scale). Having determined experimentally the variation of I with c, it is possible to find from this equation the volume v of the sphere of action of the quenching agent.

The radius of the sphere where tetrahydracarbazole is quenched by the radical in alcohol–ether mixtures, determined in this manner, is 10 ± 1 Å, the value for benzophenone being 12.9 ± 0.8 Å. Thus the Perren radii for the quenching of the triplet states of electron donors by nitroxy-radicals are close to the radii corresponding to quenching by the usual molecules[157].

The radiolysis of the stable nitroxy-radical 2,2,6,6-tetramethyl-1-piperidinyloxy-radical has been investigated[159] in a pure form (in the absence of extraneous molecules) and in solid solutions of the radicals in isopropyl alcohol.

After the irradiation of individual radicals in the temperature range 100–300 K, the latter are destroyed by a first-order reaction with a rate constant k proportional to the dose rate γ:

$$N = N_0 e^{-kt} = N_0 e^{-k_1 \gamma t} = N_0 e^{-k_1 D},$$

where D is the radiation dose. The constant k_1 obeys the Arrhenius relation with an activation energy of about 0.4 kcal $mole^{-1}$; the values of k_1 are 4×10^{-4} Mrad at 100 K and 1.4×10^{-3} $Mrad^{-1}$ at 300 K.

In the radiolysis of radicals in solid solutions in isopropyl alcohol (at a concentration of 2.4×10^{19}–2.5×10^{20} radicals g^{-1}) the constant k_1 is much higher, amounting to 4×10^{-2} $Mrad^{-1}$. Thus in solid solutions the radicals are destroyed by radiation with a high radiation yield—about 240 radicals are destroyed for 100 eV of the energy absorbed by the radicals; the radiation yield of the destruction of the radicals derived from isopropyl alcohol is much lower: 2–3 radicals for 100 eV. The high efficiency of the radiolytic destruction of stable radicals shows that in the solid state the radicals behave as powerful acceptors of the energy of excited states arising on γ-irradiation. However, the physical causes of such quenching remain unknown.

The influence of radicals on the quenching of excited singlet and triplet states of aromatic amines (diphenylamine, triphenylamine, and carbazole) in solutions frozen at 77 K has been studied[160]. If the radicals in the matrix were obtained photochemically, then an increase of the radical concentration entailed a parallel decrease of the intensity of both the fluorescence and phosphorescence of the amines. Hence it was concluded that the radicals quench the excited singlet states. If the radicals were obtained by the radiolysis of solid solutions, then the quenching efficiency was an order of magnitude lower. In other words, in order to quench the phosphorescence of amines to the same extent, the concentration of the radicals generated by radiation must exceed by an order of magnitude the concentration of the photochemically generated radicals.

This interesting effect was explained[160] by the characteristics of the distribution of the radicals: in photolysis the radicals are generated and located near amine molecules, i.e. there is a high local concentration of the

quenching agent near the molecules being excited, while in radiolysis the distribution of radicals is much more uniform. Nevertheless, even in radiolysis it is not ideally uniform. Indeed, when the Perren radii for quenching by "radiation" radicals are determined, they are found to be about 30–35 Å. They are physically unreal, since the overlapping of the absorption bands of the electron donor and the quenching agent is weak and the inductive-resonance mechanism cannot ensure such effective quenching. The distribution of radicals in space during radiolysis is probably also non-uniform[160].

Table 8. The types of excitation and chemical reactions of radicals.

Excitation	Radicals	Type of reaction	Excitation	Radicals	Type of reaction
$\pi-\sigma^*$	Alkyl	Decomposition	$\sigma-\pi^*$	$R\dot{C}O$	Decomposition
$\pi-\pi^*$ (?)	Alkyl	Substitution (?), isomerisation	$\pi-\pi^*$	Allyl	Substitution
				Polyenyl	»
$\pi-\sigma^*$	$\dot{C}H_2OH$	Decomposition		Triphenylverdazyl	»
	$R\dot{C}HOMe$	»		Perchloro-triphenylmethyl	»
	$\dot{C}H_2COMe$	»	$n-\pi^*$	Nitroxyl	»
	$\dot{C}H_2C(=O)OH$	»		Diphenylpicryl-hydrazyl	»
	$\dot{C}H_2C(=O)OC(=O)CH_3$	»		$R\dot{O}_2$	Substitution, decomp. (?)
	$MeC\dot{H}N(C_2H_5)_2$	»	$n-\pi^*$	Perchlorotriphenyl-methyl	Electron transfer
			$\pi-\pi^*$	Wurster's cation	ditto

Thus radicals are effective quenching agents for excited singlet and triplet states also in the solid phase. The quenching mechanism is probably the same as in the liquid and consists in the exchange-induced removal of spin prohibition and the subsequent vibrational relaxation of the energy of the excited molecule.

V. CONCLUSION

Despite a number of difficulties and ambiguities in the interpretation of the results of experimental studies on the reactions of excited radicals, definite advances have been made in the development of this field. Thus a definite relation has been noted between the nature and type of excitation of the radical and the mode of its reaction; it can be observed in the analysis of the compilation in Table 8.

It is readily seen that the radicals with $\pi-\sigma^*$ or $\sigma-\pi^*$ excitation mainly decompose (alkyl radicals, radicals derived from alcohols, ethers, ketones, carboxylic acids, their anhydrides, and amides, acyl radicals, etc.). In all these cases the σ orbitals of the radicals are involved in excitation; decomposition at the β-bond (for example, $\dot{C}H_2OH \rightarrow CH_2O + H^{\cdot}$) or at the α-bond (for example, the decomposition of acyl radicals and probably alkyl radicals) is most characteristic under these conditions.

The radicals with $\pi-\pi^*$ or $n-\pi^*$ excitation are mainly involved in reactions with transfer of a hydrogen atom (allyl, polyenyl, peroxy, and nitroxy-radicals, DPPH, etc.). Finally, radicals with a low ionisation potential (perchlorotriphenylmethyl) are involved in electron transfer on excitation.

Admittedly the relations noted above are only approximate and qualitative, but they nevertheless show that the transformations of excited radicals are not unduly varied and that there is a definite system in their behaviour. In many instances quantitative characteristics were also found: the quantum yields of the reactions have been determined and the lifetimes of the excited radicals and the quenching constants have been measured; the changes in the dipole moments of a number of radicals on excitation, due to the rearrangement of the electron shell, have been determined.

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