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Photochemical Reactions of Free Radicals in the Solid Phase

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The photochemical reactions of free radicals of different classes in the solid phase (solids, low-molecular-weight organic compounds, and polymers) are examined and data characterising the absorption spectra of the radicals are presented. The role of free radicals in processes involving the breakdown of substances under the action of light is discussed. The bibliography includes 299 references.

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I. INTRODUCTION

The photochemical reactions of free radicals are varied and numerous published reports have presented experimental evidence confirming their occurrence. However, their mechanism is in many instances still unestablished.

The study of the general features of the photochemical reactions of free radicals is important for the determination of the relation between the nature of the excited state and the mode of chemical reactions, and also in connection with the role which these processes play in the breakdown of substances under the action of light.

The absorption spectra of free radicals formed in solid-phase photolysis and radiolysis at relatively high concentrations are characterised by a bathochromic shift relative to the spectra of the initial compounds and fairly high extinction coefficients. On irradiation, more active species are formed from the radicals, unstable under these conditions and regenerating the initial radicals in reactions with water molecules. As a result, radical photochemical chain processes arise in the system and lead to an appreciable decomposition of the medium:

$$\dot{\text{C}}\!-\!\Phi \xrightarrow{h\nu} \text{M}_1 + \dot{\text{R}}$$

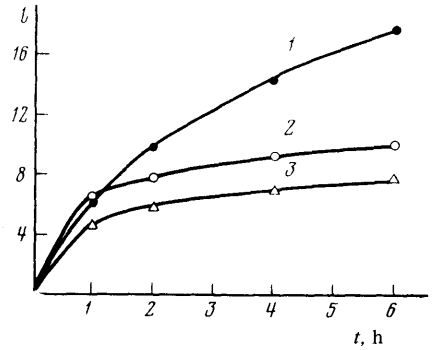
$$\dot{\text{R}} + \text{M}_0 \rightarrow \text{M}_2 + \dot{\text{C}}\!-\!\Phi,$$

where Φ is a functional group, M_0 a molecule of the medium and M_1 and M_2 are reaction products. The Figure presents experimental relations characterising the development of photochemical radical chains in methylamine, ethanol, and acetic anhydride. The average photochemical radical chain length $l = [M_1]/[\dot{C}\!-\!\Phi]_0 = [M_2]/[\dot{C}\!-\!\Phi]_0$ in the test systems did not exceed 20 and the main factor limiting it is radical recombination processes.

In order to determine the mechanisms of photochemical reactions, studies were made on the nature and kinetics of the formation of free radicals in the solid phase by ultraviolet and infrared spectroscopy, etc., and also on the nature of the stable reaction products—by gas–liquid chromatography, mass spectrometry, etc.

Reviews have been published recently in which the optical properties of free radicals are discussed[2], the available information about the photochemical reactions involving them is compiled[3-5], and attempts are made at a general survey and the determination of several general characteristics of these processes[6,7].

In the present review we confined ourselves to an examination of the photochemical reactions of certain free radicals and their role in solid-phase photolytic processes.



Variation of the photoradical chain length l in the photolysis of radicals by light at a wavelength $\lambda \geq 300$ nm at 77 K in different solvents: 1) methylamine; 2) ethanol; 3) acetic anhydride[1].

II. PHOTOCHEMICAL REACTIONS OF ALKYL RADICALS

ESR data have shown that the unpaired electron in alkyl radicals is in the p_z orbital of the carbon atom. Alkyl radicals are formed in a chemically excited state as a result of the transfer of the unpaired electron from the p_z orbital to an antibonding σ-orbital and from a bonding σ-orbital to a non-bonding orbital ($\sigma-\pi^*$ transition). These transitions are symmetry-forbidden, but analysis of literature data nevertheless shows that alkyl radicals absorb light at wavelengths $\lambda \leq 300$ nm and have fairly high extinction coefficients. A short-wavelength absorption corresponds to $\pi-\sigma^*$

transition. The absorption associated with the $\sigma-\pi^*$ transition could not be observed experimentally. It follows from the analysis of the vibrational structure of the absorption spectra of methyl radicals in the gas phase that, on transition to an electronically excited state[8], the geometry of the methyl radical does not change significantly.

Table 1 presents the available literature data for the absorption spectra of alkyl radicals.

Table 1. Absorption spectra of alkyl radicals.

Radical	λ_{max}	$10^{-3}\varepsilon_{\lambda max}$, litre mol^{-1} cm^{-1}	Conditions of generation*	Refs.
$\dot{C}H_3$	216	—	f.p. of $Hg(CH_3)_2$ and $(CH_3)_2O$	9,10
$\dot{C}H_3$	216	—	p. of $(CH_3)_2O$, 1180 K	11
$\dot{C}H_3$	215.8	—	py of $(CH_3)_2N_2$	12
$\dot{C}H_3$	216.4	—	py of CH_4	13
$\dot{C}H_3$	—	$\varepsilon_{210}=0.85$	p.r. of CH_4 in H_2O	14
$\dot{C}H_3$	217	εG ** $=14$	proton p.r. of CH_4	15
$\dot{C}H_3$	216	—	f.p. of but-1-ene and hexa-1,5-diene, 298 K	16
$\dot{C}H_3$	215.8; 216.4	—	f.p. of acetaldazine	17
$\dot{C}H_3$	216	1.01 ± 0.07	f.p. of acetone, 298 K	18
$\dot{C}H_3$	213 ± 2	1.6	p.r. of CH_4 in H_2O, 298 K	19
$\dot{C}H_3$	216.5	—	p. of azomethane	20
$\dot{C}H_3$	216	—	f.p. of CH_3Hal and alkyl nitrates	21
$\dot{C}H_3$	216	1.6	f.p. of azomethane in H_2O	22
$\dot{C}H_3$	216.4	—	f.p. of azomethane	23
$\dot{C}D_3$	214	—	f.p. of CD_3I	24
$\dot{C}D_3$	214—215	—	p. of $(CD_3)_2N_2$	25
$\dot{C}_2H_5$	227	$\varepsilon G=22$	proton p.r. of C_2H_6	15
$\dot{C}_2H_5$	200	$\varepsilon_{210}=0.74$	p.r. of C_2H_6 in H_2O	19
$\dot{C}_2H_5$	248	0.75 ± 0.18	p. of azoethane	20
$\dot{C}_2H_5$	222—224.2	—	py of $(C_2H_5)_2O$ and C_2H_6	26
$\dot{C}_2H_5$	206 ± 1	—	p. of $H_2+C_2H_4$ and $H_2+C_2H_6$	27
n-$\dot{C}_3H_7$	225	$\varepsilon G=23$	proton p.r. of C_3H_8	15
iso-$\dot{C}_3H_7$	260	—	r- of $(CH_3)_2CHBr$ in 3-MP, 77 K	28
iso-$\dot{C}_3H_7$	233	2.34 ± 0.6	p. of azoisopropane	20
n-$\dot{C}_4H_9$	232	$\varepsilon G=19$	proton p.r. of C_4H_{10}	15
t-$\dot{C}_4H_9$	229	3.1	p. of 2,2-azoisobutane	29
t-$\dot{C}_4H_9$	229	4.8	p. of 2,2-azoisobutane	20
t-$\dot{C}_4H_9$	230	$\varepsilon_{254}=0.8\pm0.3$	r. of $(CH_3)_3CCl$ in 3-MP, 77 K	30
n-$\dot{C}_5H_{11}$	234	1.7	p.r. of C_5H_{12}, 297 K	31
n $\dot{C}_5H_{11}$	234	1.1	p.r. of C_5H_{12} in H_2O, 297 K	31
n-$\dot{C}_5H_{11}$	245	$\varepsilon G=22$	proton p.r. of C_5H_{12}	15
n-$\dot{C}_6H_{13}$	240	2.1 ± 0.4	p.r. of C_6H_{14}, 293 K	32
$\dot{C}_6H_{13}$	230	1.0 ± 0.3	r. of 2,3-dimethylbutane, 77 K	30
$\dot{C}_6H_{13}$	218	—	r. of 2-methylpentane in adamantane, 298 K	33
$\dot{C}_6H_{13}$	250	—	r. of 3-MP, 77K	34
$\dot{C}_6H_{13}$	240	1.8 ± 0.6	r. of 3-MP, 77 K	35,36
$\dot{C}_7H_{15}$	240	1.6 ± 0.6	r. of 3-ethylpentane, 77 K	36
$\dot{C}_8H_{17}$	245	1.4 ± 0.5	r. of 3-methylheptane, 77 K	36
C_8H_{17}	245	1.4 ± 0.5	r. of 4-methylheptane, 77 K	36
cyclo-$\dot{C}_5H_9$	—	$\varepsilon_{250}=0.43$	p.r. of cyclopentane in H_2O, 293 K	37
cyclo-$\dot{C}_5H_9$	—	$\varepsilon_{215}=1$	p.r. of cyclopentane in H_2O, 293 K	38
cyclo-$\dot{C}_5H_9$	235	$\varepsilon_{248}=0.48$	p.r. of cyclopentane, 77 K	39
cyclo-$\dot{C}_6H_{11}$	235	1.4 ± 0.3	p.r. of cyclohexane, 293 K	32
cyclo-$\dot{C}_6H_{11}$	255	0.34	p.r. of cyclohexane, 293 K	40
cyclo-$\dot{C}_6H_{11}$	240	1.5	p.r. of cyclohexane, 293 K	41
cyclo-$\dot{C}_6H_{11}$	240	$\varepsilon_{250}=0.92$	p.r. of cyclohexane in H_2O	38
cyclo-$\dot{C}_6H_{11}$	210, 245	—	proton p.r. of cyclohexane	15
$-CH_3$	245	1.4 ± 0.2	p.r. of methylcyclohexane, 293 K	42
$\sim CH_2\dot{C}HCH_2\sim$	250	1.5	r. of polyethylene, 103 K	43
$\sim CH_2\dot{C}HCH_2\sim$	215	1.8 ± 0.3	r. of polyethylene, 77 K	44
$\sim CH_2\dot{C}HCH_2\sim$	216	—	r. of polyethylene, 77K	45
$\sim CD_2\dot{C}DCD_2\sim$	216	—	r. of deuteropolyethylene, 77 K	46
$\dot{C}Cl_3$	230	2.3 ± 0.45	f.p. of CCl_4 in H_2O, 293 K	47
$\dot{C}_2Cl_5$	250	—	f.p. of $C_2Cl_4+Cl_2$, 300 K	48
$\sim CF_2\dot{C}(CF_3)CF_2\sim$	265	—	r. of TFE-hexafluoropropene copolymer, 77 K	49

*Notation: f.p. = flash photolysis; p.r. = pulse radiolysis; p. = photolysis; r = radiolysis; py = pyrolysis (flame).
**G = radiation-chemical yield.

Excited alkyl radicals can be involved in reactions of various types: isomerisation, substitution, and dissociation. We shall examine a number of specific examples of such reactions. Following irradiation at $\lambda = 260$ nm of t-butyl radicals, obtained in isobutyl bromide γ-irradiated at 77 K, the 10-line ESR spectrum of the t-butyl radical with a binomial distribution of intensities and a splitting of 23 G is transformed into a 5-line spectrum with intensity ratios 1 : 2 : 2 : 2 : 1 and a splitting of 21 G, which is due to the isobutyl radical[50]. The reaction is reversible and the reverse process occurs in various systems after the latter have been kept for a long time at 77 K:[51-54]

$$CH_3-\dot{C}(CH_3)_2 \overset{h\nu}{\rightleftarrows} \dot{C}H_2-CH(CH_3)_2.$$

The action of the total radiation of a high-pressure mercury lamp on t-butyl radicals obtained in isobutene γ-irradiated at 77 K leads to the formation of isobutyl and methylallyl radicals[54]. The authors attribute the appearance of isobutyl radicals to the possibility of isomerisation reactions, the dissociation of t-butyl radicals, or their reactions with the molecules of the medium.

Analogous photochemical processes take place under the influence of ultraviolet radiation in γ-irradiated n-, s-, iso-, and t-butyl chlorides, where the conversion of s-butyl radicals into n-butyl radicals and of t-butyl radicals into isobutyl radicals was observed by ESR.[55] When isotactic polypropylene (PP) γ-irradiated at 77 K is acted upon by radiation with $\lambda = 253.7$ nm, the resolution of the ESR spectrum is improved and a 4-line spectrum with the intensity ratios 1 : 3 : 3 : 1 and a splitting of 25.5 G appears. It has been attributed[56,57] to the isomerisation reaction

$$\sim CH_2-\dot{C}CH_3-CH_2\sim \overset{h\nu}{\rightleftarrows} \sim CH_2-CH(\dot{C}H_2)-CH_2\sim.$$

At the same time, a singlet line with $\Delta H \cong 17$ G was noted in the ESR spectra when deuteropolypropylene (DPP) was γ-irradiated at 77 K. The absence of hyperfine structure (HFS) components from the ESR spectrum of DPP suggested that the singlet spectrum is due to allyl radicals. Subsequent exposure to ultraviolet radiation leads to the disappearance of the singlet line and the appearance of an ESR spectrum consisting of 15 HFS lines with a splitting of 3.7 G, corresponding to the radical $\sim CD_2-\dot{C}(CD_3)-CD_2\sim$. These radicals are stable with respect to irradiation and do not undergo further photochemical reactions. The data obtained by Klinshpont et al.[58] suggest that the changes observed by Iwasaki et al.[56] are associated with the reactions of allyl and not alkyl radicals.

The action of ultraviolet radiation on the radical $\sim CF_2-\dot{C}(CF_3)-CF_2\sim$, obtained in the tetrafluoroethylene (TFE)–hexafluoropropylene copolymer γ-irradiated at 77 K, leads to the formation of the radicals $\sim CF_2-\underset{\dot{C}F_2}{CF}-CF_2\sim$, detected by their characteristic ESR spectrum[49].

Following γ-irradiation of polyisobutylene (PIB) at 77 K, a doublet with a splitting of 22 G was recorded in the ESR spectrum and was assigned to the radical $\sim C(CH_3)_2-\dot{C}H-C(CH_3)_2\sim$. When the specimens are heated to 213 K for 5 min, cooled to 77 K, and exposed to light with $\lambda \leqslant 303$ nm, the initial doublet is rapidly converted into a spectrum consisting of 15 lines[59]. These changes can be explained by the isomerisation

$$\sim \dot{C}H-CH(CH_3)_2 \overset{h\nu}{\rightleftarrows} \sim CH_2-\dot{C}(CH_3)_2.$$

On the basis of the change in the ESR spectra, it has been suggested that, after exposure to radiation with $\lambda = 253.7$ nm, the alkyl (n-propyl and t-butyl) radicals, formed on γ-irradiation of propene and isobutene at 77 K in an argon matrix,

may be converted into the corresponding allyl radicals[60,61]:

$$CH_3-CH_2-\dot{C}H_2 \xrightarrow{h\nu} CH_2 \cdots CH \cdots CH_2 + 2H(H_2) \ .$$

However, the absence of an analysis of the stable reaction products makes this hypothesis questionable. We believe that the mechanism proposed by Shamonina and Krotov[54] and involving the reaction of the excited alkyl radical with a molecule of the unsaturated compounds, for example

$$CH_3CH_2\dot{C}H_2 + CH_3CH=CH_2 \xrightarrow{h\nu} C_3H_8 + CH_2 \cdots CH \cdots CH_2 \ ,$$

is more probable.

It is important to note that the yields of the majority of the radicals quoted above are based solely on the analysis of the changes in the ESR spectra, which involves serious difficulties under the conditions of the solid-phase photolysis and radiolysis, particularly in polymeric matrices. Furthermore, in radiolysis there is a possibility of the formation of allyl radicals, whose photochemical reactions, which have been examined in detail in a number of reviews[3,6,7], can mask the reactions of alkyl radicals, as shown for DPP.[58]

When 0.01 M solutions of t-butyl chloride in 3-methylpentane (3-MP), γ-irradiated at 77 K, were irradiated in the wavelength range $240 \leq \lambda \leq 270$ nm, t-butyl radicals disappeared and 3-methylpentyl radicals appeared. The total number of free valences does not change under these conditions. The quantum yield Φ of the reaction in 3-MP was determined as 0.5 ± 0.15 from the initial sections of the kinetic curves for the disappearance of t-butyl radicals[30]. In this case there is apparently a reaction between the excited t-butyl radicals and the matrix molecules. The isomerisation of alkyl radicals in γ-irradiated frozen alkyl halides and other systems, observed previously[49,50,55,60,61], can also be explained by the reactions of excited alkyl radicals with matrix molecules:

$$\dot{R}^* + R_1-X \rightarrow R-X + \dot{R}_1 .$$

The formation of 3-methylpentyl radicals when alkyl radicals, obtained on γ-irradiation of 1 M solutions of alkyl chlorides in 3-MP, are exposed to radiation with $\lambda = 253.7$ nm at 77 K, was observed also in another study[62]. The fact that t-butyl radicals are partly converted into isobutyl radicals in solutions of t-butyl chloride in 3-MP is apparently associated with the high concentration of the solutions and the possibility of reactions involving associated species. According to Burbo's results[63], the formation of associated species from alkyl halide molecules in hydrocarbon matrices is observed at concentrations above 0.01 M.

By analysing the reaction products and the changes in the ESR spectra, it has been shown in a number of studies that alkyl radicals can dissociate on excitation. Thus, after photolysis of a solid solution of n-butyl iodide in argon at 4 K by radiation with $\lambda = 246$ nm, methyl radicals and hydrogen atoms appear, which the authors attribute to the dissociation of n-butyl radicals[64]. The rate constant for the abstraction of a hydrogen atom from the electronically excited radicals can reach approximately 10^9 s^{-1}:[65]

$$CH_3CH_2CH_2CH_2 \xrightarrow{h\nu} \begin{cases} \rightarrow CH_3CH_2CH=CH_2 + H \\ \rightarrow \underline{-CH_2CH_2CH_2-} + \dot{C}H_3 \end{cases} .$$

The formation of methyl radicals when isobutyl vinyl ether γ-irradiated at 77 K was exposed to ultraviolet light was recorded by ESR:[66]

$$\dot{C}H_2CH(CH_3)CH_2OCH=CH_2 \xrightarrow{h\nu} \dot{C}H_3 + CH_2=CHCH_2OCH=CH_2 \ .$$

The study of the kinetics of the accumulation of gaseous products in the photolysis of isotactic PP by the total radiation of the high-pressure mercury lamp showed[67] that the observed rates of gas evolution in photolysis are greater by 3–5 orders of magnitude than the rates which would be expected if the macroradicals underwent thermal decomposition. According to the authors[67], this implies that the macroradicals are to a large extent decomposed on electronic excitation. The study of the kinetics of the accumulation of gaseous products of the photolysis of PP in the presence of 2,2′,6,6′-tetramethylpiperidine 1-oxide showed that the yield of methane then increases almost by a factor of 250, while the yield of the remaining photolysis products hardly changes. Since methyl radicals and hence methane could not be formed from nitroxy-radicals, it was suggested[68] that the vigorous formation of methane is a consequence of the photochemical decomposition of the central PP macroradicals, arising in the reaction of excited nitroxy-radicals with the macromolecules:

$$\dot{R}^* + \sim CH_2-CH(CH_3)-CH_2\sim \rightarrow RH + \sim CH_2-\dot{C}(CH_3)-CH_2\sim \ ,$$
$$\sim CH_2-\dot{C}(CH_3)-CH_2\sim \xrightarrow{h\nu} \dot{C}H_3 + \sim CH_2\sim\ddot{C}-CH_2\sim \ .$$

The biradicals arising in the photolysis react with the polymer, which leads to the regeneration of the central PP macroradicals.

Irradiation of PP in the presence of an added aromatic sensitiser (hexahydropyrene) at 77 K by light at wavelengths in the range $260 \leq \lambda \leq 380$ nm, corresponding to the sensitiser absorption band, leads to the appearance of a 4-line ESR spectrum with nearly binomial intensity ratios, which was assigned to the radical $\sim CH(CH_3)\dot{C}HCH(CH_3)\sim$. On subsequent irradiation of the same specimens with radiation at wavelengths in the range $240 \leq \lambda \leq 270$ nm, which is hardly absorbed by the sensitiser so that there is virtually no sensitised radical formation, components due to the methyl radical are clearly manifested in the ESR spectrum. The action of light at wavelengths of $240 \leq \lambda \leq 270$ nm on the radicals $\sim CMe_2-\dot{C}H-CMe_2\sim$, formed in PIB on photolysis and radiolysis sensitised by aromatic compounds at 77 K, also leads to the formation of methyl radicals. These processes in PP and PIB take place without a change of the total number of free valences. The formation of methyl radicals under the influence of ultraviolet radiation on the macroradicals in PP and PIB apparently proceeds via the reactions[69,70]

$$\sim CH(CH_3)\dot{C}HCH(CH_3)\sim \xrightarrow{h\nu} \sim CH(CH_3)CH=CHCH_2\sim + \dot{C}H_3 \ ,$$
$$\sim C(CH_3)_2\dot{C}HC(CH_3)_2\sim \xrightarrow{h\nu} \sim C(CH_3)_2CH=C(CH_3)\sim + \dot{C}H_3 \ .$$

The numerous instances of the formation of methyl radicals when PP is exposed to radiation with $\lambda \leq 300$ nm can in fact be accounted for by the photolysis of alkyl macroradicals[71–77]. It has been shown that the additional action of radiation at wavelengths in the range $240 \leq \lambda \leq 270$ nm does not entail significant changes in the molecular weight of PP and PIB. Evidently the reactions

$$\sim CH(CH_3)\dot{C}HCH(CH_3)\sim \rightarrow \sim CHCH_3-CH=CHCH_3 + \dot{C}H_2CH(CH_3)CH_2\sim \ ,$$
$$\sim C(CH_3)_2\dot{C}HC(CH_3)_2\sim \rightarrow \sim (CH_3)_2CH=C(CH_3)_2 + \dot{C}H_2C(CH_3)_2CH_2\sim$$

which lead to the dissociation of the polymer chain, take place with low quantum yields if at all and do not cause an appreciable change in molecular weight[69,70].

At the same time, analysis of the composition of the products (methane, ethane, and ethylene), resulting from the exposure to light of alkyl radicals in γ-irradiated polyethylene (PE) at 77 K, led to the following reaction mechanism[78]:

$$\sim CH_2-\dot{C}H-CH_2\sim \xrightarrow{h\nu} \sim CH_2-\dot{C}H-CH_3 + CH_2=CH\sim \ ,$$
$$\sim CH_2-\dot{C}H-CH_3 \xrightarrow{h\nu} \begin{cases} \rightarrow \sim CH=CH_2 + \dot{C}H_3 \\ \rightarrow \sim CH_2-\dot{C}H-CH_3 + C_2H_4 \end{cases} ,$$

incorporating processes leading to the decomposition of the main polymer chain.

Significant changes occur in the ESR spectra of γ-irradiated branched aliphatic hydrocarbons at 77 K, following exposure to short-wavelength ultraviolet radiation. Thus the action of ultraviolet radiation on 3-MP γ-irradiated at 77 K leads, according to the authors[79,80], to the formation of methyl radicals:

$$C_2H_5\dot{C}(CH_3)C_2H_5 \xrightarrow{h\nu} C_2H_5C(CH_3)=CH_2 + \dot{C}H_3 \ .$$

However, one should note that the study of the structure of the radicals in branched aliphatic hydrocarbons γ-irradiated at 77 K established[81-84] that in this case the radicals $CH_3\dot{C}HR$, arising on dissociation of a secondary C–H bond, are formed preferentially. The mechanism of the formation of methyl radicals, proposed in the studies mentioned above[79,80], therefore requires revision. Analogous changes in the ESR spectra of 3-MP and deuterated 3-MP γ-irradiated at 77 K, have been observed after irradiation in another investigation[85].

Analysis of the changes in the ESR spectra occurring under the influence of radiation at wavelengths in the range $240 \leq \lambda \leq 270$ nm on 3-MP and 3-ethylpentane γ-irradiated at 77 K suggested that the photolysis of the corresponding hydrocarbon radicals proceeds with formation of ethyl radicals[35,36]. Ethane was detected among the gaseous reaction products, which constitutes additional confirmation of this conclusion:

$$CH_3\dot{C}HCH(CH_3)C_2H_5 \xrightarrow{h\nu} \dot{C}_2H_5 + CH_3CH=CHCH_3 \ .$$

When hydrogen sulphide and alkanethiols are photolysed in a 2-MP matrix at 77 K by radiation with $\lambda = 253.7$ nm, the changes in the ESR spectrum of 3-methylpentyl radicals are evidently associated with the appearance of small amounts of ethyl radicals as a result of the photolysis of the 3-methylpentyl radicals[86].

Table 2. Absorption spectra of alkoxy-radicals.

Radical	λ_{max}	$10^{-3}\varepsilon_{\lambda max}$, litre mol^{-1} cm^{-1}	Conditions of generation*	Refs
ȮH	280	—	r. of ice, 77 K	98,99
ȮH	280±10	0.45±0.14	r. of ice, 77 K	100
ȮH	280±5	0.56±0.05	p.r. of ice, 143-217 K	101
ȮH	230	—	f.p. of H_2O, 297 K	102
ȮH	<200	$\varepsilon_{200}=0.509$, $\varepsilon_{220}=0.523$, $\varepsilon_{230}=0.543$, $\varepsilon_{250}=0.463$	p.r. of $HClO_4$ in H_2O, 296-298 K	103
ȮH	—	$\varepsilon_{260}=0.37$	p.r. of $HClO_4$ in H_2O	104
ȮH	250—260	0.2	p.r. of H_2O	105
ȮH	260	—	p.r. of H_2O_2 in H_2O	106
ȮH	—	0.41±0.05	p.r. of H_2O_2 in H_2O	107
ȮH	230	0.543	p.r. of HCN in H_2O	108
ȮH	230	0.6	p.r. of NaCl in H_2O	109
ȮD	235	0.55	p.r. of $DClO_4$ in H_2O	110
$CH_3\dot{O}$	199.9; 203.6, 206.4	—	f.p. of methyl nitrite	111,112

*The notation is the same as in Table 1.

The exposure to radiation with $\lambda = 254$ nm of γ-irradiated polycrystalline n-hexane[87], 3-methylheptane, and 4-methylheptane[36] at 77 K led to the observation of changes in the ESR spectra, which could be attributed to the isomerisation of alkyl radicals:

$$\sim CH_2\dot{C}HCH_2\sim \xrightarrow{h\nu} \sim CH_2\dot{C}HCH_3 \ .$$

At the same time the observed reactions can be accounted for fully by the reaction of the excited alkyl radicals with matrix molecules.

Table 3. Absorption spectra of peroxy-radicals.

Radical	λ_{max}	$10^{-3}\varepsilon_{\lambda max}$, litre mol^{-1} cm^{-1}	Conditions of generation*	Refs.
$H\dot{O}_2$	230	$\varepsilon_{254}=0.83\pm0.125$	p.r. of $HClO_4$ in H_2O	115
$H\dot{O}_2$	230	—	p.r. of H_2SO_4 in H_2O, 298 K	116
$H\dot{O}_2$	243	$\varepsilon_{260}=0.34$	p.r. of H_2SO_4 in H_2O	117
$H\dot{O}_2$	240	1.15	r. of ice, 77 K	101
$H\dot{O}_2$	210	1.20	p. of H_2O_2, 298 K	118
$H\dot{O}_2$	230	1.07	p.r. of $HClO_4$ in H_2O	119
$H\dot{O}_2$	240	1.15	p.r. of H_2O_2 in H_2O	120
$H\dot{O}_2$	<220	$\varepsilon_{230}=0.66$	decomp. of H_2O_2, 1000 K	121
$H\dot{O}_2$	240	1.00	f.p. of H_2O_2 in $HClO_4$	122
$H\dot{O}_2$	200—210	—	decomp. of H_2O_2 in shock wave, 900-1500 K	123
$H\dot{O}_2$	205	1.77±0.15	f.p. of H_2O	124
$H\dot{O}_2$	205	0.82	decomp. of H_2O_2, 1100 K	125
$CH_3\dot{O}_2$	235	2.64	p. of azomethane	11
$CH_3\dot{O}_2$	250	1.2	p.r. of CH_4 in H_2O, 298 K	19
$CH_3\dot{O}_2$	235	0.81	f.p. of azomethane	22
$C_2H_5\dot{O}_2$	240	2.64	p. of azoethane	11
$C_2H_5\dot{O}_2$	250	1.25	p.r. of ethane in H_2O 298 K	19
$C_5H_{11}\dot{O}_2$	270	3.2±0.9	p.r. of isopentane in soln.	126
$C_5H_{11}\dot{O}_2$	260	3.2±0.6	r. of isopentane, 77 K	127
$C_5H_{11}\dot{O}_2$	250	$\varepsilon_{280}=0.91\pm0.05$	p.r. of pentane, 298 K	31
$C_6H_{13}\dot{O}_2$	255	1.9	p.r. of hexane, 295 K	41
$C_7H_{15}\dot{O}_2$	270	3.2±0.9	p.r. of heptane, 300 K	126
$C_8H_{17}\dot{O}_2$	270	3.2±0.9	p.r. of isooctane, 300 K	126
$C_9H_{19}\dot{O}_2$	260	3.4±0.7	r. of 2,3,5-trimethylhexane, 77 K	127
$C_5H_9\dot{O}_2$	270	1.45±0.15	p.r. of cyclopentane in H_2O, 293 K	39
$C_6H_{11}\dot{O}_2$	275	2.0±0.4	p.r. of cyclohexane	128—130
$C_6H_{11}\dot{O}_2$	260	2.9±0.9	r. of 3-methylpent-1-ene, 77 K	126
$C_6H_{11}\dot{O}_2$	260	2.7±0.6	r. of 3-methylpent-1-ene, 77 K	127
$C_6H_{11}\dot{O}_2$	260	3.0±0.9	r. of 3-methylpent-2-ene, 77 K	126
$C_6H_{11}\dot{O}_2$	260	2.7±0.6	r. of 3-methylpent-2-ene, 77 K	127
$C_6H_{11}\dot{O}_2$	260	2.9±0.9	r. of 2-methylpent-2-ene, 77 K	126
$C_7H_{13}\dot{O}_2$	260	2.9±0.9	r. of hept-1-ene, 77 K	126
$C_7H_{13}\dot{O}_2$	260	2.8±0.6	r. of hept-1-ene, 77 K	131
$C_7H_{13}\dot{O}_2$	270	2.9±0.9	p.r. of hept-1-ene, 300 K	131
$C_7H_{13}\dot{O}_2$	260	2.8±0.6	r. of hept-1-ene, 77 K	127
$C_6H_9\dot{O}_2$	260	—	p.r. of cyclohexene in H_2O, 298 K	132
$HOCH_2\dot{O}_2$	255	0.7	p.r. of methanol in H_2O, 298 K	132
$HOCH_2\dot{O}_2$	≤230	$\varepsilon_{248}=1.07$	p.r. of methanol in H_2O, 298 K	133
$HOCH(\dot{O}_2)CH_3$	255	1	p.r. of ethanol in H_2O, 298 K	132
$HOC(CH_3)_2\dot{O}_2$	250	1.3	p.r. of isopropyl alcohol in H_2O, 198 K	134
$HOC(CH_3)_2\dot{O}_2$	248	1.1±0.1	p.r. of isopropyl alcohol in H_2O	135
$C_6H_{10}OH\dot{O}_2$	280	2.5±0.5	p.r. of benzene in H_2O	136
$C_6H_{11}OH\dot{O}_2$	302	2.3±0.5	p.r. of cyclohexanol	129, 130
$C_2H_5OCH\dot{O}_2CH_3$	245	9	p.r. of $C_2H_5OC_2H_5$ in H_2O, 298 K	132
$R_1R_2C(\dot{O}_2)OH$	240—250	—	p.r. of aqueous solns of acids	137
$\dot{O}_2CH_2COOH$	290	0.9	p.r. of CH_3COOH in H_2O	138
$C_2Cl_5\dot{O}_2$	250	—	f.p. of $C_2Cl_4 + Cl_2$, 300 K	48
$C_2Cl_5\dot{O}_2$	250	$\varepsilon_{268}=0.39\pm0.17$	f.p. of $C_2Cl_4 + Cl_2$, 297 K	139

*The notation is the same as in Table 1.

The reactions of radicals in 3-MP, 3-ethylpentane, and 3-methylheptane γ-irradiated at 77 K, observed after exposure to ultraviolet radiation, were explained by the conformational transitions in the radicals, which take place on local heating of the matrix in consequence of the dissipation

of the energy of the light quantum absorbed by the radical[88]. Estimates based on the data of Vasil'ev and Tal'roze[89] have shown that the temperature rise can reach several tens of degrees.

The study of the photochemical reactions of the radicals $(CH_3)_2\dot{C}CH(CH_3)_2$, formed on γ-irradiation and hexahydropyrene-sensitised photolysis of 2,3-dimethylbutane at 77 K, not only established that the reaction product is methyl radicals but also led to the determination of the quantum yield in the accumulation of methane under the influence of radiation having a wavelength in the range $240 \leqslant \lambda \leqslant 270$ nm, which proved to be 0.01.[30]

Thus it can now be regarded as established that alkyl radicals can undergo photochemical substitution and dissociation reactions. The question of the possible isomerisation and the explanation of the observed changes in the ESR spectra by conformational transitions occurring on local heating of the matrix require further confirmation.

III. PHOTOCHEMICAL REACTIONS OF ALKOXY- AND PEROXY-RADICALS

The alkoxy-radicals RȮ are formed as intermediates when many organic compounds are irradiated, but their high reactivity makes their direct experimental detection extremely difficult. The rate constants for the reactions of RȮ with alcohol, ester, and aldehyde molecules at 20 °C are in the range 10^5–10^6 litre mol^{-1} s^{-1}.[90,91] The RȮ radicals are usually detected by the spin-trapping method, which makes it possible to reach a conclusion, by analysing the ESR spectrum of the resulting radical adduct, concerning the presence or absence of alkoxy-radicals among the reaction products[92].

The ESR spectra of alkoxy-radicals consist of singlet lines with a *g*-factor in the range 2.0065–2.008 [93,94] or 2.015 ± 0.02 [95] and a half-width in the range 3–6 G.[95,96] The ESR spectra of the radicals ȮH and ȮD are well known in the literature[97]. Table 2 shows that the optical absorption spectra of alkoxy-radicals have been studied inadequately.

The observed photochemical reactions have been attributed to alkoxy-radicals in a number of investigations. However, this is a consequence of an inaccurate identification of the singlet ESR spectra (see for example, Lenci and Neubacher[113] and Moan[114]), observed in the course of the low-temperature photolysis and radiolysis, and is as a rule associated with the photochemical reactions of acyl radicals.

On irradiation in the presence of oxygen or on interaction of irradiated substances with oxygen, a characteristic signal, consisting of a single asymmetric line due to peroxy-radicals, appears in the ESR spectra.

Electronically excited states of peroxy-radicals arise as a result of electron transfer from the n-orbital of the oxygen atom to the antibonding π-orbital. Table 3 presents data characterising the absorption regions and the extinction coefficients of peroxy-radicals.

In γ-irradiated PP the peroxy-radicals obtained as a result of the oxidation of alkyl radicals (heating to 173–193 K after γ-irradiation at 77 K) and allyl radicals (irradiation at room temperature) are converted into the corresponding alkyl radicals under the influence of ultraviolet radiation with $\lambda \geqslant 280$ nm.[140] Analogous reactions under the influence of light with $\lambda \leqslant 370$ nm are undergone by the peroxy-radicals obtained as a result of the oxidation of polyene radicals in PP.[141] The action of radiation with $\lambda \geqslant 280$ nm on peroxy-radicals in PP is not accompanied by a change in the total number of free valences. It has been suggested that the excited peroxy-radicals formed under the influence of light react with matrix molecules to form hydroperoxides:

$$R\dot{O}_2^* + RH \rightarrow \dot{R} + ROOH .$$

The decomposition of the hydroperoxide under the influence of radiation with $\lambda \leqslant 280$ nm can lead to the development of a chain process with photochemical chain branching[142]:

$$ROOH \xrightarrow{h\nu} R\dot{O} + \dot{O}H ,$$
$$\dot{O}H + RH \rightarrow \dot{R} + H_2O ,$$
$$R\dot{O} + RH \rightarrow \dot{R} + ROH .$$

A three-fold increase of the number of free valences is then observed.

The time variation of the overall radical concentration under the influence of light on peroxy-radicals, obtained by the oxidation of allyl radicals in PP, is described by the equation

$$[\dot{R}] = \left[1 + 2\left(1 + \frac{I}{\alpha - I} e^{-\alpha\tau} - \frac{\alpha}{\alpha - I} e^{-\tau}\right)\right],$$

where $\alpha = k_2/k_1$, k_1 is the rate constant for the conversion of peroxy-radicals into alkyl radicals, k_2 the rate constant for the decomposition of hydroperoxides, $\tau = k_1 It$, I is the light intensity, and t the irradiation time. The experimental values agree satisfactorily with the curve calculated for $\alpha = 2.1$, determined from linear logarithmic modifications of the curves describing the disappearance of peroxy-radicals on irradiation at wavelength $\lambda \geqslant 280$ nm and the accumulation of radicals on subsequent ultraviolet irradiation light at wavelength $\lambda \leqslant 280$ nm.[141]

However, it was established that the rate of accumulation of radicals in the photolysis of oxidised PP exceeds approximately by a factor of 7 the rate of decomposition of hydroperoxy-groups[143]. The study of the rate of accumulation of 3-methylpentyl radicals under the influence of light at a wavelength in the range $240 \leqslant \lambda \leqslant 270$ nm at 77 K on peroxy-radicals in 3-MP (at a concentration of approximately 0.001 M) and in solutions of t-butyl hydroperoxide in 3-MP at the same concentration showed that in the latter case the rate of accumulation is smaller almost by an order of magnitude[144]. Together with data for the extinction coefficients of the hydroperoxides (for example, $\varepsilon_{260} = 6$, $\varepsilon_{240} = 16$, and $\varepsilon_{200} = 70$ litre mol^{-1} cm^{-1} for t-butyl hydroperoxide[145]), these results show that, under the conditions of simultaneous absorption of radiation by alkyl radicals ($\lambda_{max} = 220$–240 nm, $\varepsilon \approx 10^3$ litre mol^{-1} cm^{-1}) and peroxy radicals [$\lambda_{max} = 250$–260 nm, $\varepsilon \cong (2$–$3) \times 10^3$ litre mol^{-1} cm^{-1}], present at comparable concentrations, the decomposition of hydroperoxide molecules is greatly hindered. Furthermore, one should note that the threefold increase of the number of free valences observed by Klinshpont et al.[141] is difficult to explain by the decomposition of the hydroperoxide formed in the reaction of the electronically excited peroxy-radical with matrix molecules, because "quasi-cage" radical recombination processes and radical recombination processes within the cage should then play a major role. The quantum yield of free radicals in the photolysis of hydrogen peroxide solutions in reactive and inert matrices at 77 K is known to be in the range from 10^{-4} to 0.3,[146,147] i.e. is less than unity.

At the same time, when peroxy-radicals derived from PP are irradiated at a wavelength $\lambda \leqslant 300$ nm in methyl methacrylate (MMA) vapour, the concentration of peroxy-radicals diminishes and the number of radicals of the growing polymeric PMMA chain increases, the overall radical concentration increasing under these conditions by a factor of 2–3.[148,149]

Under the influence of irradiation in the wavelength range $240 \leq \lambda \leq 270$ nm, the dissociation of peroxy-radicals plays an important role in processes involving them[69,144]. Thus the photolysis of peroxy-radicals (77 K), obtained by the γ-irradiation of solutions of butyl chlorides in 3-MP, leads to the formation of 3-methylpentyl radicals from n-, s-, and t-butyl chlorides, while isobutyl chloride gives rise to isobutyl radicals. It is believed that both substitution reactions and peroxy-radical dissociation reactions can occur:

$$R\dot{O}_2 \xrightarrow{h\nu} \dot{R} + O_2 \ .$$

The quantum yields in the consumption of peroxy-radicals, measured in PE, DPE, PP, and DPP, are presented in Table 4. Evidently, with increase of temperature from 77 to 300 K, the quantum yield increases significantly, the increase occurring over a narrow temperature range above 170 K, because, for example, in PP, the rate of the photochemical reaction of peroxy-radicals does not change in the temperature range from 77 to 170 K.[141]

Table 4. The quantum yields of photochemical reactions of peroxy-radicals[150-151] ($R\dot{O}O \rightarrow \dot{R}$).

Polymer	Quantum yield		Polymer	Quantum yield	
	77 K	300 K		77 K	300 K
PE	0.3±0.1	—	PP	0.1±0.03	—
DPE	0.2±0.07	0.7±0.3	DPP	0.04±0.01	0.7±0.3

The ESR spectra of peroxy-radicals in γ-irradiated PTFE, obtained by the reaction with oxygen of the terminal and central macroradicals, are identical and consist of an asymmetric signal with $g_\perp = 2.007$ and $g_\parallel = 2.038$.[152] The action of radiation at a wavelength $\lambda \leq 280$ nm on the central radicals $\sim CF_2C(O\dot{O})FCF_2\sim$ induces their conversion into terminal fluoroalkyl radicals[152-156]. CF_2O and CO were detected among the reaction products by mass spectrometric and infrared spectroscopic methods[152]. It has been suggested that the photolysis proceeds as follows:

$$\sim CF_2\underset{\underset{O\dot{O}}{|}}{CF}CF_2\sim \xrightarrow{h\nu} \sim CF_2\dot{C}F_2 + CF_2O + CO + CF_3{-}CF_2\sim .$$

The action of light on the terminal peroxy-radicals in PTFE at temperatures below 170 K leads to the formation of terminal fluoroalkyl radicals and oxygen[152]:

$$\sim CF_2CF_2O\dot{O} \xrightarrow{h\nu} \sim CF_2\dot{C}F_2 + O_2 \ .$$

The results presented agree satisfactorily with data obtained in the study of the thermal decomposition of peroxy-radicals in PTFE *in vacuo* at 473 K.[157,158] It was observed that the decomposition of the peroxy-radicals obtained from the central and terminal macroradicals leads to the appearance in the ESR spectra of signals due to the central and terminal macroradicals. At the same time, the formation of considerable amounts of CO, CO_2, and CF_2O among the gaseous reaction products has been observed, which indicates the dissociation of the C–C bonds in the polymer chain. It is important to note that the decomposition of the peroxy-radicals obtained from the central macroradicals leads to a significant decrease of the molecular weight, while the decomposition of the peroxy-radicals obtained from the terminal macroradicals hardly changes this quantity.

The photolysis of the peroxy-radical $\sim CF_2\underset{\underset{^{18}O\,^{18}\dot{O}}{|}}{CF}CF_2\sim$, labelled with the ^{18}O isotope, leads to the formation of considerable amounts of $C^{18}OO$ and $C^{18}O$, which the authors[158] attribute to the occurrence of the following reactions:

$$\sim CF_2C(^{18}O\,^{18}\dot{O})FCF_2\sim \xrightarrow{h\nu} [\sim CF_2CF^{18}O\,^{18}OCF_2\sim] \rightarrow \sim CF_2\underset{\underset{^{18}O}{\|}}{CF} + {}^{18}\dot{O}CF_2\sim \ ,$$

$$^{18}\dot{O}CF_2\sim \rightarrow CF_2{}^{18}O + \dot{C}F_2\sim \ ,$$

$$CF_2{}^{18}O + H_2O \rightarrow HF + C^{18}OO \ .$$

At temperatures above 170 K, the photodissociation of the peroxy-radicals obtained from the terminal macroradical proceeds via the reaction

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

In each decomposition step the free valence migrates via the polymer chain over a distance equal to two C–C bond lengths, which leads to the photorecombination of the radicals in the system[149,159]. Analysis of the amounts of fluoride ions obtained by the hydrolysis of the gaseous products evolved on photolysis shows that between 50 and 90 fluoride ions are produced for each disappearing peroxy-radical, which confirms the chain mechanism of the photochemical reactions of peroxy-radicals in PTFE. The quantum yields in the consumption of peroxy-radicals in PTFE are 0.015 ± 0.005 at 77 K and 0.1 ± 0.03 at 300 K.[150]

Thus the mode of photodissociation of peroxy-radicals in PTFE depends on their nature and is accompanied by the dissociation of C–C or C–O bonds. The peroxy-radicals obtained in hydrocarbon matrices can apparently undergo dissociation and substitution reactions.

IV. PHOTOCHEMICAL REACTIONS OF ACYL RADICALS

The study of the mechanisms of the low-temperature photolysis and radiolysis of various classes of oxygen-containing compounds by ESR led to the observation of radicals giving rise to spectral lines with a *g*-factor smaller than for the free electron. The absence of HFS in the ESR spectra made it difficult to explain the nature of the radical species and initially many investigators attributed the singlet line either to alkoxy-radicals $R\dot{O}$ [160-165] or to the radicals $R\dot{C}OO$.[166]

Analysis of the literature data shows that the singlet lines in the EPR spectra with $\Delta H \cong 10$–16 G and $g \cong 2.0010$ are due to the acyl radicals $R\dot{C}O$. In certain cases HFS is observed with a splitting of approximately 5 G,[167-171] which is confirmed by the theoretical calculation for the acetyl radical[172]. Acyl radicals can be formed in photochemical processes either as a result of the photolysis of molecules[173-179] or as a result of secondary photochemical reactions of radicals.[180-182]

Data for the absorption spectra of acyl radicals are presented in Table 5. The unpaired electron is located in acyl radicals in the sp^2-orbital. The absorption in the range 500 to 550 nm is associated with the transfer of the unpaired electron to the π^*-orbital (the C–CO angle then changes from 120° to 180°, i.e. the radical acquires a linear structure). The absorption in the range 450–500 nm is associated with the transfer of the lone electron pair in the *p*-orbital of the oxygen atom to the π^*-orbital[7].

The excitation of acyl radicals leads to their dissociation (the dissociation energies of these radicals are low and are in the range 5.4–11 kcal mol^{-1} [195-197]). The dissociation of acyl radicals with the formation of the corresponding alkyl radicals and carbon monoxide under the influence of radiation at the wavelength corresponding to the absorption band has been observed in many systems (see, for example, Refs.198

to 201). The reverse process, involving the addition of CO to radicals, takes place effectively in the dark.

At the same time it has been noted[178] that the action of ultraviolet radiation on acyl radicals at 77 K in di-n-heptadecyl ketone results in the disappearance of the singlet line with $\Delta H \cong 15$ G from the ESR spectrum and the appearance of a multiplet spectrum with an overall width of approximately 170 G, which the authors assigned to the radical $\sim CH_2\dot{C}HCHO$. These changes were explained by the isomerisation of the acyl radicals:

$$\sim CH_2CH_2\dot{C}O \overset{h\nu}{\rightleftarrows} \sim CH_2\dot{C}HCHO \ .$$

The hypothesis of the isomerisation reactions also served as the basis of an explanation of the results obtained in the photolysis of PE and PP.[176,177]

Table 5. Absorption spectra of acyl radicals.

Radical	λ_{max}	Conditions of generation*	Refs.
$H\dot{C}O$	510; 533; 555; 579; 605; 635; 670	p. of HI in CO, 20 K	183
$H\dot{C}O$	613,8—617,2; 562,4—565,5	f.p. of glyoxal, HCHO, and CH_3CHO	184
$H\dot{C}O$	520	f.p. of acetaldazine	185
$H\dot{C}O$	210—260; 460—860	p. of HCl, H_2O, and CH_4 in argon, 14 K	186
$F\dot{C}O$	220—340, 539	p. of F_2O and F_2CO in CO, 4.2 K	187
$F\dot{C}O$	220—340	f.p. of N_2F_4 and CO	188
$ClC\dot{O}$	532—534	p. of HCl and Cl_2 in CO, 14 K	189
$CH_3\dot{C}O$	340, 500, 540	r. of CH_3COCl in methyltetrahydrofuran (MTHF), 77 K	190
$CH_3\dot{C}O$**	—	p.r. of acetic acid	191
$CH_3\dot{C}O$***	540	r. of C_2H_5OH and $C_2H_5OC_2H_5$, 80 K	180, 192
$CH_3\dot{C}O$	505	r. of acetic anhydride, 80 K	192
$C_2H_5\dot{C}O$	330; 480; 540	r. of C_2H_5COCl in MTHF, 77 K	190
$C_2H_5\dot{C}O$	530	r. of 1-propanol, 77 K	193
$C_2H_5\dot{C}O$	530	r. of C_2H_5OH and $C_2H_5OC_2H_5$	192
$\sim(CH{=}CH)_n{-}\dot{C}O$	375; 400; 500	r. of poly(vinyl alcohol)	194

*The notation is the same as in Table 1.
**$\varepsilon_{260} = 940$ litre mol^{-1} cm^{-1}.
***$\varepsilon_{540} = 40 \pm 15$ litre mol^{-1} cm^{-1}.

Analogous changes in the ESR spectra were observed in the photolysis of acyl radicals in isobutyraldehyde at 77 K. However, mass spectrometric analysis of the gaseous products showed that this entails vigorous formation of CO and the consequent establishment of a rapid sequence of the following reactions[173]:

$$(CH_3)_2CH\dot{C}O \overset{h\nu}{\rightleftarrows} (CH_3)_2\dot{C}H + CO \ ,$$

$$(CH_3)_2\dot{C}H + (CH_3)_2CHCHO \rightarrow \begin{cases} (CH_3)_2CH\dot{C}O \\ (CH_3)_2\dot{C}CHO \end{cases} + (CH_3)_2CH_2 \ .$$

Thus data [176–178] obtained solely on the basis of the analysis of poorly resolved ESR spectra are open to objection and at the present time it can be regarded as established that the principal photochemical process involving acyl radicals is their dissociation.

The formation of acyl radicals in the course of photolysis and radiolysis greatly increases the region of the spectral sensitivity of the materials and promotes their effective decomposition under the influence of light. For example, a study of the mechanism of the photolysis of acetaldehyde at 77 K showed that the rate of accumulation of CO and methane exceeds almost by an order of magnitude the rate of accumulation of the radicals[200]. Since, according to the results of Pariiskii et al.[201], the contribution of the molecular decomposition of acetaldehyde in photolysis by the total radiation of a high-pressure mercury lamp at 77 K is 30%, the high rate of accumulation of gaseous products is associated with the effective dissociation of the acetyl radical:

$$CH_3C\dot{O} \overset{h\nu}{\rightleftarrows} C\dot{H}_3 + CO \ .$$

V. PHOTOCHEMICAL REACTIONS OF RADICALS DERIVED FROM ALCOHOLS AND ETHERS

The radiolysis of alcohols and ethers and their photolysis sensitised or initiated by various additives in the solid phase involve the preferential formation of the radicals $R_1R_2\dot{C}OR_3$ most stable under these conditions, where R_1, R_2, and R_3 are hydrogen atoms or alkyl groups.

The conjugation of the unpaired electron with the electrons of the lone pair of the oxygen atom leads to a bathochromic shift in the absorption spectra of the radicals relative to the spectra of the initial compounds. Table 6 presents the available literature data for the absorption spectra of radicals derived from alcohols and ethers. The excited state of alcohol and ether radicals arises when a π-electron of the carbon atom is transferred to the σ^*-orbital (the transition is forbidden by symmetry rules)[6]. The action of radiation at the wavelengths corresponding to the absorption bands of the alcohol and ether radicals induces photochemical reactions, which have been investigated in a large number of studies[113, 114,160–164,167,168,180,192,193,210–212,218,229,230,233–262].

The photochemical reactions of alcohol and ether radicals were first observed in a study[211] where the changes occurring under the influence of radiation on a series of alcohols and ethers subjected to preliminary γ-irradiation at 77 K were recorded by ESR. For methanol and CH_3OD, a doublet ESR spectrum was observed under these conditions with a splitting of 129 G, but for deuteromethanol (CD_3OD) a doublet spectrum was not noted. The lack of a correct interpretation of the ESR spectra precluded the explanation of the experimental results.

When dilute frozen solutions of acetaldehyde in ethanol were photolysed at 77 K directly in the resonator of the ESR spectrometer, it was observed[233,234] that the alcohol radicals $CH_3\dot{C}HOH$ formed in this system in the course of the photolysis are effectively decomposed by ultraviolet radiation with formation of methyl radicals.

A sharp increase of the yield of gaseous and liquid products was observed[235,236] after the ultraviolet irradiation of alcohols subjected to preliminary γ-radiolysis at 77 K. The increase of the amounts of hydrogen and CO was attributed in the case of methanol to the photolysis of the radicals $\dot{C}H_2OH$:

$$\dot{C}H_2OH \overset{h\nu}{\rightarrow} H\dot{C}O + H_2 \ ,$$

$$H\dot{C}O \overset{h\nu}{\rightarrow} H + CO \ .$$

However, the proposed mechanism did not explain the increase of the yield of the remaining gaseous and liquid products. The authors[235,236] suggested that complexes of the radicals with alcohol molecules are formed, in which the alcohol molecule can be decomposed as a result of the absorption of radiation by the radical.

Table 6. Absorption spectra of radicals derived from alcohols and ethers.

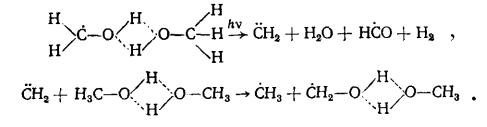
Radical	λ_{max}	$10^{-3}\varepsilon_{\lambda max}$, litre mol^{-1} cm^{-1}	Conditions of generation*	Refs.
$\dot{C}H_2OH$	<230	—	p.r. of methanol	204
$\dot{C}H_2OH$	<210	—	p.r. of methanol in water	204
$\dot{C}H_2OH$	<250	$\varepsilon_{300}G=2.6\pm0.3$	p.r. of methanol	165
$\dot{C}H_2OH$	<260	$\varepsilon_{311}=0.025$	p.r. of methanol in water	205
$\dot{C}H_2OH$	<213	$\varepsilon G=5.89$	r. of methanol, 80 K	206
$\dot{C}H_2OH$	<210	$\varepsilon_{277}=0.978$	r. of methanol, 80 K	207
$\dot{C}H_2OH$	~260	—	p.r. of methanol in water	208
$\dot{C}H_2OH$	~265	—	r. of methanol, 77 K	165
$\dot{C}H_2OH$	290	$\varepsilon G=7.2$	p.r. of methanol	209
$\dot{C}H_2OH$	<204	$\varepsilon G=12.4$	r. of methanol, 77 K	209, 210
$\dot{C}H_2OH$	<220	—	r. of methanol, 77 K	211
$\dot{C}H_2OH$	280	0.6±0.1	p.r. of methanol in water	212
$\dot{C}H_2OH$	270	—	r. of methanol, 77 K	213
$CH_3\dot{C}HOH$	<210	—	p.r. of ethanol	204
$CH_3\dot{C}HOH$	240	0.5±0.05	p.r. of ethanol in water	213
$CH_3\dot{C}HOH$	<250	$\varepsilon_{255}=0.87\pm0.07$	p.r. of ethanol	214
$CH_3\dot{C}HOH$	<210	~1	r. of ethanol, 77 K	215
$CH_3\dot{C}HOH$	<210	$\varepsilon_{230}G=7.63$	r. of ethanol, 80 K	206
$CH_3\dot{C}HOH$	266, 257, 247	$\varepsilon_{297}=0.23\pm0.055$	p.r. of ethanol	216
$CH_3\dot{C}HOH$	~290	—	p.r. of ethanol in water	216
$CH_3\dot{C}HOH$	—	$\varepsilon_{297}=0.24\pm0.045$	p.r. of ethanol in water, 296 K	217
$CH_3\dot{C}HOH$	—	$\varepsilon_{260}=0.23$	r. of ethanol, 77 K	192
$CH_3\dot{C}HOH$	<210	—	p.r. of ethanol in water	204
$CH_3\dot{C}HOH$	<220	—	r. of ethanol, 77 K	211
$CH_3\dot{C}HOH$	—	$\varepsilon_{254}=0.71\pm0.17$	p. of H_2O_2 in ethanol, 77 K	218
$CH_3\dot{C}HOH$	<200	—	r. of ethanol, 77 K	212
$CH_3\dot{C}HOH$	<210	$\varepsilon_{200}=0.1$	r. of ethanol, 77 K	219
$CH_3CH_2\dot{C}HOH$	232	$\varepsilon_{25}G=7.28$	r. of 1-propanol, 80 K	206
$CH_3CH_2\dot{C}HOH$	230	—	p.r. of 1-propanol, 147 and 300 K	220
$(CH_3)_2\dot{C}OH$	330	—	p. of H_2O_2 in isopropyl alcohol, 77 K	221
$(CH_3)_2\dot{C}OH$	<210	—	p.r. of isopropyl alcohol in water	204
$(CH_3)_2\dot{C}OH$	<260	0.87	p.r. of isopropyl alcohol in water	222
$(CH_3)_2\dot{C}OH$	230	—	p.r. of acetone in water, 298 K	223
$(CH_3)_2\dot{C}OH$	<250	—	r. of isopropyl alcohol, 77 K	224
$(CH_3)_2\dot{C}OH$	—	$\varepsilon_{225}=0.38$	f.p. of acetone in hydrocarbons	225
$CH_3(CH_2)_2\dot{C}HOH$	222	~1	p.r. of 1-butanol in water	204
$CH_3(CH_2)_2\dot{C}HOH$	~238	$\varepsilon_{245}G=6.21$	r. of 1-butanol, 80 K	206
$CH_3(CH_2)_2\dot{C}HOH$	<220	—	r. of 1-butanol, 77 K	211
$(CH_3)_2CH\dot{C}HOH$	225	~1	p.r. of isobutyl alcohol in water	204
$(CH_3)_2CH\dot{C}HOH$	220	—	r. of isobutyl alcohol, 77 K	211
$CH_3(CH_3)_2\dot{C}OH$	225	0.9	p.r. of t-butyl alcohol in water	204
n-$C_4H_9\dot{C}HOH$	<256	$\varepsilon_{270}G=4.08$	r. of 1-pentanol, 77 K	206
$(CH_3)_3C\dot{C}HOH$	~238	—	p.r. of neopentyl alcohol in water	204
n-$C_6H_{11}\dot{C}HOH$	<300	$\varepsilon_{313}G=2.7$	r. of 1-hexanol, 77 K	206
$HO\dot{C}HOH$	—	$\varepsilon_{240}=0.2$	p.r. of formaldehyde in water	226
$HO\dot{C}HCH_2OH$	—	$\varepsilon_{250}=0.61$	p.r. of ethylene glycol in water	227
$HO\dot{C}HCH(OH)CH_2OH$ or $HOCH_2\dot{C}(OH)CH_2OH$	250	$\varepsilon_{270}=0.2$	p.r. of glycerol in water	228
cyclo-$\dot{C}_6H_{10}OH$	<290	—	p.r. of cyclohexanol, 298 K	204
cyclo-$\dot{C}_6H_{10}OH$	230	1	p.r. of cyclohexanol in water	204
~$CH_2C(OH)CH_2$~	225—235	1.7±0.5	r. of poly(vinyl) alcohol), 77 K	229, 230
~$CH_2\dot{C}(CH_3)OH$	286	—	r. of poly(propylene oxide), 77 K	231
$CH_3\dot{C}HOC_2H_5$	—	$\varepsilon_{260}=0.39$	r. of $C_2H_5OC_2H_5$, 77 K	218
~$CH_2\dot{C}HO$~	<220	$\varepsilon_{235}=1.5\pm0.1$	p.r. of poly(ethylene oxide) in water	232

*The notation is the same as in Table 1.

The greatest number of studies have been devoted to the photochemical reactions of radicals in methanol, ethanol, and diethyl ether. The benzene-sensitised and hydrogen peroxide-initiated photolysis of methanol and ethanol at 77 K has been investigated[162,237,238] and, on the basis of the study of the kinetics of the accumulation and interconversion of the radicals, a mechanism has been proposed for the photochemical reactions of the alcohol radicals. Under the influence of the ultraviolet radiation of a high-pressure mercury lamp on the $CH_3OH + H_2O_2$ system, the formation of the radicals $\dot{C}H_3$ and $H\dot{C}O$ was recorded by EPR, their concentration rising to a limit. The amount of gaseous photolysis products increased continuously and their composition was independent of the duration of photolysis (57% H_2, 26% CO, and 17% CH_4). At the same time the increase of the concentration of free radicals was accompanied by a decrease of the rate of consumption of hydrogen peroxide, indicating the occurrence of hydrogen peroxide-initiated reactions, which continued for some time even without the participation of the initiator. Two possible mechanisms of the photolysis of alcohol radicals, taking into account the experimental results obtained, have been examined[237]. The first presupposes the formation of the radicals $\dot{C}H_3$ and $H\dot{C}O$ in parallel reactions:

$$\dot{C}H_2OH \xrightarrow{h\nu} \begin{cases} \ddot{C}H_2 + \dot{O}H \xrightarrow{2CH_3OH} \dot{C}H_3 + 2\dot{C}H_2OH + H_2O \\ H\dot{C}O + H_2 \end{cases} \quad (1)$$

The second involves the photolysis of the radicals $\dot{C}H_2OH$ linked by hydrogen bonds to the surrounding alcohol molecules:



(2)

The necessity for hydrogen bonds to permit the formation of the radicals $\dot{C}H_3$ in the photolysis of methanol radicals was confirmed by a study[239] where the authors failed to observe the formation of methyl radicals when methanol radicals were photolysed in a sulphuric acid matrix. Data[162,240], according to which an increase of the concentration of free radicals (to 30%) was observed when the radicals $\dot{C}H_2OH$, obtained by the benzene-sensitised photolysis of methanol at 77 K, were irradiated at wavelengths in the range $290 \leq \lambda \leq 320$ nm and γ-irradiated methanol was exposed to light at wavelengths in the range $240 \leq \lambda \leq 400$ nm, can serve as evidence in support of the possibility of reactions (1) and (2). However, in the majority of studies, for example those[161,180,192,210] where the alcohol radicals were obtained by γ-radiolysis, an increase of the radical concentration was not observed when the radicals $\dot{C}H_2OH$ were exposed to ultraviolet radiation.

An ESR study of the radicals obtained as a result of the irradiation at $\lambda = 253.7$ nm at 77 K of ethanol deuterated in various positions resulted in the measurement of the spectra of the radicals $\dot{C}_2H_5(C_2H_5OH)$, $\dot{C}_2H_5(C_2H_5OD)$, $CD_3\dot{C}H_2(CD_3.CH_2OH)$, and $CH_3\dot{C}D_2(CH_3CD_2OH)$.[241] Evidently, when a quantum of radiation is absorbed by an alcohol radical, ethyl radicals are formed from alcohol molecules linked to the radicals by hydrogen bonds.

The photochemical reactions of radicals in ethanol and diethyl ether in the hydrogen peroxide-initiated and naphthalene-sensitised photolysis have been investigated in detail[171] When light was allowed to act on ethanol and diethyl ether containing added hydrogen peroxide at 77 K, the radicals $\dot{C}H_3$ and $\dot{C}_2H_5$ were detected in the ESR spectra. In the dark, the alkyl radicals were converted into the radicals $CH_3\dot{C}HOR$ ($R = H$ or C_2H_5) and in addition a radical giving rise to a

singlet ESR spectrum appeared. In the naphthalene-sensitised photolysis the ESR spectra revealed the presence of the radicals $\dot{C}H_3$, $\dot{C}_2H_5$, $CH_3\dot{C}HOR$, and, after prolonged photolysis, $CH_3\dot{C}O$, to which a singlet ESR spectrum was assigned. Analysis of the gaseous products, carried out simultaneously with the ESR study of the radicals, showed that in diethyl ether the ratio of the amount of hydrogen to that of ethane diminished with increasing duration of the exposure to radiation, while in ethanol it increased. On this basis, it was concluded that the photolysis of the radicals $CH_3\dot{C}HOH$ results in the formation of hydrogen, while the photolysis of the radicals $C_2H_5O\dot{C}HCH_3$ leads to ethane. The following mechanism has been proposed to account for the results[171]:

$$CH_3\dot{C}HOR \xrightarrow{h\nu} CH_3CHO + \dot{R} \ , \quad (3)$$

$$CH_3\dot{C}H(H)-O-OCH_2CH_3 \xrightarrow{h\nu} CH_3CHO + H_2O + \dot{C}_2H_5 \ , \quad (4)$$

$$CH_3\dot{C}HOR \xrightarrow{h\nu} \dot{C}H_3 + \ddot{C}HOR \ , \quad (5)$$

$$\ddot{C}HOR \xrightarrow{h\nu} CO + RH \ ,$$

$$\ddot{C}HOR \rightarrow RCHO \ ,$$

$$\dot{C}H_3\ (\dot{C}_2H_5) + CH_3CH_2OR \rightarrow CH_4\ (C_2H_6) + CH_3\dot{C}HOR \ ,$$

$$\dot{R} + CH_3CHO \rightarrow RH + CH_3\dot{C}O \ ,$$

$$CH_3\dot{C}O \xrightarrow{h\nu} \dot{C}H_3 + CO \ . \quad (6)$$

This mechanism explained many experimental results; however, the preferential occurrence of reaction (5) compared with reaction (6), which the authors[171] postulated, conflicted with the detection[164] of $\dot{C}_2H_5$ and species giving rise to a singlet ESR spectrum rather than methyl radicals when ethanol radicals $CH_3\dot{C}HOH$ were irradiated at a wavelength in the range $300 \leq \lambda \leq 400$ nm.

The mechanism of the photolysis of alcohol and ether radicals has been studied in greatest detail by Chervonenko and coworkers[180,192]. According to these investigators, the principal reaction of alcohol radicals is their dissociation reaction (3). This mechanism is supported by a number of factors.

1. The main product when alcohol radicals are irradiated is hydrogen.

2. The formation of ethyl radicals is observed in the photolysis of the radicals $\dot{C}H_2OH$ in methanol in the presence of ethylene, which is an effective acceptor of hydrogen atoms, while the rate of consumption of $\dot{C}H_2OH$ radicals increases markedly as a result of the suppression of the process

$$CH_3OH + H \rightarrow \dot{C}H_2OH + H_2 \ .$$

3. Calculation on the $\dot{C}H_2OH$ radical by the CNDO method showed[192] that, after the excitation of the π-electron to the lowest vacant σ-orbital, the O–H bond order diminishes, i.e. the bond is weakened. The dissociation of ether radicals takes place similarly. The quantum yields of reaction (3), determined from the initial linear sections of the kinetic curves for the accumulation of hydrogen in ethanol and of ethane in diethyl ether under the influence of light at a wavelength $\lambda = 310$ nm at 77 K on the corresponding radicals proved to be 0.3 ± 0.2.

The formation of the radicals $R_1R_2\dot{C}H$ in the photolysis of the alcohol radicals $R_1R_2\dot{C}OH$ has been explained[180,192] by reaction (4). The quantum yield of this process, measured in ethanol under the influence of light at a wavelength $\lambda = 310$ nm is 0.03 ± 0.02. Hydrogen bonds play an important role in reaction (4), but one should note that the mechanism proposed requires the transfer of excitation energy over a considerable distance, which imposes severe limitations on the probability of its occurrence. At the same time CNDO calculations for the $\dot{C}H_2OH$ radical showed that the C–O bond is strengthened in the excited state, so that the occurrence of reactions (1) and (2) is unlikely.

Studies have been published recently[114,218,242-244] in which a fundamentally different mechanism is proposed for the formation of the radicals $R_1R_2\dot{C}H$ in the photolysis of alcohol radicals, involving their photoionisation. According to theoretical estimates[245], the ionisation potential of the alcohol radicals $CH_3\dot{C}HOH$ in a solid acetaldehyde matrix can be reduced to 2.5 eV, which corresponds to the energy of a light quantum with a wavelength $\lambda = 495$ nm.

A study of the influence of radiation at a wavelength $\lambda = 253.7$ nm on ethanol radicals, obtained in the photolysis of hydrogen peroxide solutions in ethanol at 77 K in the presence of N_2O, established[218] that the gaseous reaction products contain nitrogen, the formation of which is associated with photoionisation of the alcohol radical:

$$CH_3\dot{C}HOH \xrightarrow{h\nu} CH_3CHOH^+ + e^- \ ,$$

$$e^- + N_2O \rightarrow N_2 + O^- \ .$$

The accumulation of ethyl radicals formed in the photolysis by light at wavelengths in the range $250 \leq \lambda \leq 350$ nm of the alcohol radicals $CH_3\dot{C}HOH$ in γ-irradiated neutral, acid, and alkaline ethanol solutions at 77 K, has been investigated. It has been observed that the initial rate of accumulation of $\dot{C}_2H_5$ is almost independent of the concentration of added acid (H_2SO_4), but decreases sharply with increase of the amount of added alkali (NaOH), At the same time the limiting yield of $\dot{C}_2H_5$ is a maximum in neutral solutions and decreases both with increase of the concentration of alkali and with increase of the concentration of the acid. In order to explain the experimental data obtained, the following reactions have been postulated[242]:

$$CH_3\dot{C}HOH \rightarrow CH_3CHOH^+ + e^- \ ,$$

$$C_2H_5OH + CH_3CHOH^+ \rightarrow CH_3CHO + C_2H_5OH_2^+ \ ,$$

$$e^- + C_2H_5OH_2^+ \rightarrow \dot{C}_2H_5 + H_2O \ .$$

Furthermore, in alkaline media, the reactions

$$C_2H_5O^- + C_2H_5OH_2^+ \rightarrow 2C_2H_5OH \ ,$$

$$OH^- + C_2H_5OH_2^+ \rightarrow C_2H_5OH + H_2O \ ,$$

can occur, while in acid matrices there is a possibility of the reactions

$$e^- + HSO_4^- \rightarrow SO_4^{2-} + H \ ,$$

$$H + C_2H_5OH \rightarrow CH_3\dot{C}HOH + H_2 \ .$$

The possibility of the photoionisation of alcohol radicals has been considered in a number of studies[114,243,244] to explain the results obtained when radicals were u.v. irradiated in water–methanol mixtures, ethylene glycol–water mixtures[243], and ethanol[244] irradiated at 77 K. However, according to the authors[244], it remains obscure why the radicals $R_1R_2\dot{C}H$ are not formed on annealing stabilised electrons in irradiated specimens.

Thus the main process associated with the action of radiation on alcohol and ether radicals is their dissociation. On the other hand, the problem of the mechanism of the formation of the radicals $R_1R_2\dot{C}H$ in the photolysis of alcohol radicals requires additional study.

The occurrence of the photochemical reactions of radicals in poly(vinyl alcohol)[229,230] and poly(ethylene oxide)[246] at 77 K and higher temperatures lead to an effective degradation of the polymers.

VI. PHOTOCHEMICAL REACTIONS OF RADICALS DERIVED FROM ESTERS, ALDEHYDES, KETONES, ACIDS, AND ACID ANHYDRIDES

Data for the absorption spectra of ester, aldehyde, ketone, acid, and acid anhydride radicals are presented in Table 7. The photochemical reactions of ester radicals were first

reported in a study[211] where the appearance of a doublet signal with a splitting of 129 G was observed in the ESR spectra of methyl acetate (γ-irradiated at 77 K) after its exposure to ultraviolet radiation.

Table 7. Absorption spectra of radicals derived from esters, aldehydes, ketones, acids, and acid anhydrides.

Radical	λ_{max}	$10^{-3}\varepsilon_{\lambda max}$, litre mol^{-1} cm^{-1}	Conditions of generation*	Refs.
$\dot{C}H_2COOCH_3$	320	—	p.r. of methyl thioglycolate in water	270
$\dot{C}H_2COOCH_3$	320	0.8	p.r. of chloromethyl acetate in water	271
$\dot{C}H_2COOCH_3$	320	—	p.r. of glycylmethyl acetate in water	271
$\dot{C}H_2COOC_2H_5$	300	—	p.r. of ethyl acetate with N_2O	272
	310	—	p.r. of ethyl acetate	272
$CH_3COO\dot{C}HCH_2OH$	300	1.56	p.r. of 2-hydroxyethyl acetate	263
$\sim CH_2-\dot{C}(COOCH_3)-CH_2\sim$	314	—	r. of poly(methyl methacrylate)	273
$\dot{C}H_2CHO$	~300	0.26	p.r. of ethylene glycol in water	227
$\dot{C}H_2CHO$	—	$\varepsilon_{300}=0.26$	p.r. of 2-hydroxyethyl acetate	263
$\dot{C}H_2COCH_3$	~285	—	r. of acetone, 77 K	264
$\dot{C}H_2COCH_3$	295	0.85±0.15	p.r. of acetone, 293 K	222
$CH_3\dot{C}HCOCH_3$	315	—	r. of ethyl methyl ketone, 77 K	265
$CH_3CO\dot{C}HCH_2OH$	230—350	—	p.r. of methyl vinyl ketone in water	274
$\dot{C}OOH$	250±5	—	p.r. of formic acid	267
$\dot{C}H_2COOH$	320	0.65	p.r. of acetic acid in water	268
$\dot{C}H_2COOH$	240, 365	—	r. of glycine and alanine	269
$\dot{C}H_2COOH$	310	0.31	r. of acetic acid in 10 M H_2SO_4, 80 K	192
$\dot{C}H_2COOH$	320	0.67	p.r. of thioglycolic acid in water	270
$\dot{C}H_2COOH$	300	—	p.r. of acetic acid in water	271
$CH_3\dot{C}HCOOH$	300	0.7	p.r. of propionic acid in water	268
$CH_3CH_2\dot{C}HCOOH$	280	—	p.r. of butyric acid in water	268
$HOOC\dot{C}HCOOH$	340	0.4	p.r. of malonic acid in water	268

*The notation is the same as in Table 1.

The photochemical reactions of the radicals in methyl formate and methyl acetate in the toluene-sensitised or hydrogen peroxide-initiated photolysis at 77 K have been investigated[275]. When the radicals $RCOO\dot{C}H_2$ were irradiated at a wavelength in the range $290 \leq \lambda \leq 380$ nm, the formation of methyl and formyl radicals as well as radicals giving rise to a singlet ESR line was observed. The total number of free valences then increases, which was attributed to the following reactions:

$$RCOO\dot{C}H_2 \xrightarrow{h\nu} \begin{cases} \rightarrow H\dot{C}O + RCHO \\ \rightarrow \ddot{C}H_2 + RCOO\dot{} \end{cases},$$

$$\ddot{C}H_2 + RCOOCH_3 \rightarrow \dot{C}H_2 + RCOO\dot{C}H_2 .$$

The singlet line in the ESR spectra was assigned to radicals of the type $RCOO\dot{}$ (resistant to the action of light according to the authors), $R\dot{O}$, and $RO\dot{C}O$ (which enter into photochemical reactions). This interpretation of the spectra is open to serious objections, because it is known[276] that radicals of type $RCOO\dot{}$ are unstable and decompose spontaneously, while radicals of the type $R\dot{O}$ cannot be stabilised in ester matrices. Analogous changes in the ESR spectra were observed in the photolysis of methyl acetate, sensitised by aromatic compounds, at 77 K.[277]

The photochemical reactions of the free radicals formed in the photolysis sensitised by aromatic compounds and γ-radiolysis of alkyl acetates at 77 K have been studied in detail[182, 278-280]. It was established that the radicals formed as a result of the abstraction of a hydrogen atom from the alcohol moiety of the molecule are effectively photolysed by light at a wavelength $\lambda = 365$ nm, giving rise to acetyl radicals and the molecules of the corresponding aldehydes and ketones;

$$CH_3COO\dot{C}R_1R_2 \xrightarrow{h\nu} CH_3\dot{C}O + O{=}CR_1R_2 .$$

The action of light at a wavelength $\lambda \geq 300$ nm on the radicals arising following the abstraction of a hydrogen atom from the acid moiety of the molecules obtained on γ-irradiation (at 77 K) of α-halogenoacid esters did not lead to an appreciable change of the ESR spectra[280]. Possibly in this case the reaction proceeds via the following mechanism:

$$R_1R_2\dot{C}COOR \rightarrow R_1R_2C{=}C{=}O + \dot{O}R .$$

However the lack of data for the photolysis products precludes a final determination of its mechanism at the present time.

The study of the photochemical reactions of ester radicals in polymeric matrices [poly(vinyl acetate) (PVA), poly(methyl methacrylate) (PMMA), and others] is of considerable interest. It has been established[76,155,281-283] that the action of light at a wavelength $\lambda \leq 380$ nm on the radicals $\sim CH_2\dot{C}(OCOCH_3)CH_2\sim$, which are formed in PVA γ-irradiated at 77 K, leads to the formation of radicals giving rise to a 4-line ESR spectrum with a splitting of 23 G and intensity ratios of 1 : 3 : 3 : 1. When PVA specimens are kept at 77 K, the initial ESR spectrum is restored. The observed reactions of the radicals of PVA were explained by the isomerisation of the macroradicals[76,155,282]:

$$\sim CH_2\dot{C}(OCOCH_3)CH_2\sim \underset{}{\overset{h\nu}{\rightleftarrows}} \sim CH(OCOCH_3)\dot{C}HCH(OCOCH_3)\sim .$$

However, the study of the gaseous products formed in the photolysis of the radicals $\sim CH_2\dot{C}(OCOCH_3)CH_2\sim$ by light at a wavelength $\lambda \geq 360$ nm showed[283] that this involves the accumulation of considerable amounts of methane and carbon monoxide. Consequently macroradicals undergo photodissociation in this instance too:

$$\sim CH_2\dot{C}(OCOCH_3)CH_2\sim \xrightarrow{h\nu} \sim CH_2\overset{\overset{O}{\|}}{C}CH_2\sim + CH_3\dot{C}O ,$$

with subsequent photolysis of the acetyl radicals. Thus the 4-line ESR spectrum observed in a number of studies[76,155,281,282] refers to the methyl radical and not to $\sim CH(OCOCH_3)\dot{C}HCH.(OCOCH_3)\sim$.

When PMMA,[282,284] poly(methyl acrylate), and poly(n-hexyl methacrylate)[284] specimens γ-irradiated at 77 K were exposed to radiation, changes were observed in the ESR spectra, which were explained by the occurrence of a number of photochemical reactions of free radicals. However, the mechanism proposed by the authors[284] for these processes is inaccurate owing to the erroneous interpretation of certain signals in the ESR spectra.

When poly(ethyl acrylate) γ-irradiated at 77 K is exposed to light[285], the radical species giving rise to a singlet ESR spectrum vanishes and ethyl radicals are formed:

$$\sim CH_2-\underset{\dot{O}-\overset{\dot{O}-C_2H_5}{\overset{|}{C}}-C_2H_5}{\overset{|}{CH}}\sim \xrightarrow{h\nu} \dot{C}_2H_5 + \sim CH_2-\underset{C=O}{\overset{|}{CH}}\sim \quad .$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \underset{O-C_2H_5}{\overset{|}{C}}=O$$

However, the observed changes in the ESR spectra are most probably associated either with the photochemical reactions of the acyl radicals or with the photolysis of the corresponding radical-anion, which can be stabilised in the ester matrix on γ-radiolysis[286,287].

The mechanism of the photochemical reactions of radicals in PMMA has been studied in greatest detail by Toptygin and coworkers[198,199,288]. Analysis of the ESR spectra established

that the radicals in PMMA enter into the following photochemical reactions:

$$\sim (CH_3)\,C\,(COOCH_3)\,\dot{C}H\,(CH_3)\,C\,(COOCH_3) \sim \xrightarrow{h\nu} \rightarrow \sim (CH_3)\,C\,(COOCH_3)\,CH{=}C\,(CH_3) + \dot{O}COCH_3 \ .$$

The radicals $O\dot{C}OOCH_3$ dissociate under the influence of light at a wavelength $\lambda \leq 380$ nm with formation of $\dot{C}H_3$ and CO_2 (it has been established[289] that the radicals $O\dot{C}OR$ have an absorption maximum at $\lambda = 330$–335 nm; $\varepsilon \cong 10^3$ litre mol^{-1} cm^{-1}; the quantum yield of photolysis by light at a wavelength $\lambda = 313$ nm at 77 K is 0.24).

The radicals formed as a result of the abstraction of a hydrogen atom from the alcohol moiety in PMMA dissociate under the influence of radiation to form the radicals $H\dot{C}O$:

$$\sim CH_2\,(CH_3)\,C\,(COO\dot{C}H_2)\,CH_2 \sim \xrightarrow{h\nu} [\sim CH_2\,(CH_3)\,C\,(\dot{C}{=}O)\,CH_2 \sim + H_2CO] \rightarrow \rightarrow \sim CH_2\,(CH_3)\,C\,(CHO)\,CH_2 \sim + H\dot{C}O \ .$$

Furthermore, it might have been expected that photochemical reactions of central macroradicals can occur in PMMA with dissociation of the main polymer chain, for example:

$$\sim (CH_3)C(COOCH_3)\,\dot{C}H\,(CH_3)C(COOCH_3) \sim \xrightarrow{h\nu} \dot{C}H_2 \sim (CH_3)C(COOCH_3) \sim + + \sim (CH_3)C(COOCH_3)\,CH{=}(CH_3)C(COOCH_3) \ .$$

The study of the degradation of PMMA in its photolysis initiated by iron(III) chloride and potassium hexacyanoferrate(II) [290,291] and in the direct photolysis and photolysis sensitised by aromatic compounds[287,292,293] showed that the decomposition of the main polymer chain occurs mainly in thermal and not photochemical reactions of radicals.

An ESR study of the photolysis of liquid acetone in the presence of various additives established that, together with the spectrum due to the radical $\dot{C}H_2COCH_3$, there are lines associated with the methyl radical[294]. On this basis, the authors suggested that the following reaction occurs on irradiation:

$$\dot{C}H_2COCH_3 \xrightarrow{h\nu} \dot{C}H_3 + CH_2{=}C{=}O \ . \qquad (7)$$

The action of light at a wavelength $\lambda \leq 340$ nm on the radicals $\dot{C}H_2COCH_3$, stabilised in acetone γ-irradiated at 77 K, led to a decrease of their concentration and to a simultaneous increase of the concentration of methyl radicals $\dot{C}H_3$ and acetyl radicals, giving rise to a singlet ESR spectrum[264]. The rate constants for the destruction of acetonyl radicals and the accumulation of $\dot{C}H_3$ radicals, obtained from the linear sections of the kinetic curves, proved to be approximately equal. These data confirm that the acetonyl radical decomposes via reaction (7). The appearance of the radicals $CH_3\dot{C}O$ may be caused by the photolysis of keten and by the subsequent dark reactions involving CO. Analogous results were obtaineed in a study of the photolysis of acetone in the presence of hydrogen peroxide[295].

The mechanisms of the photolysis of aliphatic aldehydes and ketones at 77 K (acetaldehyde, propionaldehyde, and isobutyraldehyde; ethyl methyl ketone, isopropyl methyl ketone, and diethyl ketone) have been investigated. It has been observed[173,265,296] that, when radicals are irradiated at a wavelength $\lambda \leq 340$ nm in aldehydes and ketones, changes occur in the ESR spectra, associated, according to the authors, with the following reactions:

$$R_1R_2\dot{C}CHO \xrightarrow{h\nu} R_1R_2\dot{C}H + CO \ ,$$
$$R_1R_2\dot{C}COR \xrightarrow{h\nu} R_1R_2\dot{C}H + R'{=}C{=}O \ .$$

It is important to note that the reaction mechanism has been proposed solely on the basis of the analysis of complex ESR spectra and apparently consists of many stages. When solutions of hydrogen peroxide in acetic acid were acted upon by the total radiation of the high-pressure mercury lamp at 77 K, the formation of methyl and formyl radicals as well as species giving rise to a singlet ESR spectrum was observed by ESR. The authors[275] believe that, under the influence of light at a wavelength $\lambda \leq 400$ nm, the $\dot{C}H_2COOH$ radicals undergo a branched-chain photolysis with formation of the radicals $\dot{C}H_3$, $H\dot{C}O$, and $\dot{C}OOH$:

$$\dot{C}H_2COOH \xrightarrow{h\nu} \begin{cases} \rightarrow H\dot{C}O + CH_2O \\ \rightarrow \dot{C}H_3 + \dot{C}OOH \end{cases} , \qquad (8)$$
$$\dot{C}H_3 + CH_3COOH \rightarrow \dot{C}H_3 + \dot{C}H_2COOH \ .$$

The formation of methyl radicals in the photolysis by radiation at a wavelength $\lambda \geq 270$ nm of the radicals $\dot{C}H_2COOH$, obtained by the γ-radiolysis of aqueous acetic acid solutions at 77 K, has been observed[297]. Calculation of the electronic structure of the $\dot{C}H_2COOH$ radicals by the CNDO method showed[192] that, on σ–π^* excitation, the dissociation of the C–OH bond is most probable (bond energy approximately 2.5 eV). The probability of dissociation at the C–C bond diminishes, which throws doubt on the possibility of reaction (8).

The photochemical reactions of monocarboxylic acid radicals have been studied in greatest detail by Chervonenko and Roginskii[192,298], who established that irradiation at a wavelength in the range $300 \leq \lambda \leq 400$ nm of the $R\dot{C}HCOOH$ radicals, formed in γ-irradiated acetic, propionic, butyric, and isovaleric acids, leads to the formation (among other reaction products) of CO_2 and the hydrocarbons RCH_3 in approximately equal yields. The fact that methyl radicals are formed in the CH_3COOD matrix on photolysis of the radicals $\dot{C}H_2COOD$ at 77 K shows that the radicals $R\dot{C}HCOOH$ in the excited state react with the surrounding molecules:

$$R\dot{C}HCOOH + RCH_2COOH \xrightarrow{h\nu} RCH{=}C\,(OH)_2 + RCH_2C\dot{O}O \ , \qquad (9)$$
$$RCH{=}C\,(OH)_2 \rightarrow RCH{=}C{=}O + H_2O \ ,$$
$$RCH_2C\dot{O}O \rightarrow R\dot{C}H_2 + CO_2 \ . \qquad (10)$$

The quantum yield of reaction (9), determined from the initial linear section of the curve for the accumulation of methyl radicals in 10 and 25% acetic acid solutions in 10 M H_2SO_4 on irradiation at a wavelength $\lambda = 310$ nm, proved to be $(4 \pm 2) \times 10^{-3}$.

Apart from reaction (9), the photolysis of the radicals $R\dot{C}HCOOH$ may be expected to involve processes which are difficult to detect by ESR and by analysing stable reaction products, particularly the reaction

$$R\dot{C}HCOOH \xrightarrow{h\nu} RCH{=}C{=}O + \dot{O}H \ . \qquad (11)$$

The study of the photolysis by light at a wavelength $\lambda \geq 360$ nm of the radicals $\dot{C}H_2COOH$, obtained by the γ-irradiation of a 10% monochloroacetic acid solution in 1-propanol at 77 K, showed that 1-propanol radicals then accumulate. The quantum yield of the reaction for light at a wavelength $\lambda = 310$ nm is 0.3 ± 0.2.

When the radicals stabilised on γ-irradiation in acetic, propionic, and butyric anhydrides at 77 K are acted upon by light, the main process is their dissociation[299]:

$$R\dot{C}HCOOCOCH_2R \xrightarrow{h\nu} RCH{=}C{=}O + RCH_2C\dot{O}O \ . \qquad (12)$$

The dissociation is followed by the spontaneous decomposition of $RCH_2C\dot{O}O$ via reaction (10). The quantum yield of reaction (12), determined from the linear section of the kinetic curve for the accumulation of the radicals $\dot{C}H_3$ in acetic anhydride on irradiation at a wavelength $\lambda = 313$ nm at 77 K, is 0.9 ± 0.1.

Thus the main process when ester, aldehyde, ketone, acid, and acid anhydride radicals are acted upon by light at the wavelengths corresponding to their absorption bands is their dissociation.

VII. CONCLUSION

Despite the apparent wide variety of the photochemical reactions of radicals in different systems, there are certain characteristics which make it possible to predict with a particular degree of probability the type of reaction as a function of the type of excitation[6]. Table 8 shows that radicals subjected to $\pi-\sigma^*$ and $\sigma-\pi^*$ excitation undergo virtually only the photodissociation reaction and the quantum yields of these processes are high. Less definite conclusions can be reached concerning the mode of the photochemical reactions with $n-\pi^*$ excitation; here it is necessary to obtain additional experimental and calculated data.

Table 8. Photochemical reactions of free radicals of different types.

Radicals	Excitation	Type of reaction	Quantum yield	Refs.
Alkyl	$\pi \rightarrow \sigma^*$	dissociation	0.01	30
Alkyl	$\pi \rightarrow \sigma^*$	substitution	0.5 ± 0.15	30
Peroxy	$n \rightarrow \pi^*$	dissociation, substitution	$(0.04\pm0.01)\times(0.7\pm0.3)$	150, 151
Acyl	$\sigma \rightarrow \pi^*$	dissociation	—	—
From alcohols	$\pi \rightarrow \sigma^*$	dissociation, ionisation (?)	0.3 ± 0.2	180, 192
From ethers	$\pi \rightarrow \sigma^*$	dissociation	0.3 ± 0.2	180, 192
From esters	$\pi \rightarrow \sigma^*$	dissociation	—	—
From aldehydes	$\pi \rightarrow \sigma^*$	dissociation	—	—
From ketones	$\pi \rightarrow \sigma^*$	dissociation	—	—
From acids	$\pi \rightarrow \sigma^*$	dissociation	0.3 ± 0.2	192, 298
From acid anhydrides	$\pi \rightarrow \sigma^*$	dissociation	0.9 ± 0.1	192, 299

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