Translated from *Uspekhi Khimii*, 51 925-949 (1982) U.D.C. 541.14+547.21+547.31+678.742

The Mechanism of the Photolysis of Certain Hydrocarbons by Vacuum Ultraviolet Radiation

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The results of studies of the photolysis by vacuum ultraviolet radiation of saturated hydrocarbons and hydrocarbons containing individual double bonds are examined and characteristics of the photolysis of these classes of substances are discussed as a function of the molecular structure, the phase state of the given substance, and the wavelength of the radiation.
The bibliography includes 104 references.

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I. INTRODUCTION

The study of the photochemical reactions of hydrocarbons under the influence of vacuum ultraviolet radiation constitutes a branch of chemistry which has been vigorously developing in the last 15–20 years. The interest in this field is due to a number of causes.

Firstly, vacuum ultraviolet radiation constitutes an appreciable proportion of the solar radiation spectrum in the upper layers of the Earth's atmosphere and outside its limits. In particular, it is responsible for the ionisation and dissociation of atmospheric gases and for photochemical reactions involving the molecules of atmospheric contaminants. Changes in the composition of the atmospheres of other planets of the solar system also occur under the influence of vacuum ultraviolet radiation, since molecules of greatest geochemical interest absorb only this light (for example, methane, an important component of the atmosphere of Jupiter, absorbs light with $\lambda < 143$ nm [1]). Evidently, this radiation can influence significantly the physicochemical surface characteristics of the materials of flying machines in the upper layer of the atmosphere and in space; therefore the determination of the general characteristics of the effect of vacuum ultraviolet radiation on polymers is of considerable interest from the standpoint of the development of the scientific foundations of materials science.

Secondly, vacuum ultraviolet radiation is one of the significant factors acting on matter when materials, including polymers, are treated in a plasma[2].

Thirdly and finally, the study of the chemical consequences of the action of vacuum ultraviolet radiation is important for high-energy chemistry in general. Depending on the wavelength of the active light, various electronic states of molecules are excited and at shorter wavelengths (with photon energy in excess of 10–15 eV) the substance is photoionised; studies of the reactions occurring under these conditions permit inferences about the properties of the photochemical reactions of various neutral electronically excited states and ionised states of molecules. Such information is of interest for many branches of high-energy chemistry, for example, for plasma chemistry and radiation chemistry.

The aim of the present review is to examine the fundamental features of the photolysis of paraffinic and olefinic hydrocarbons in the vacuum ultraviolet region i.e. in the spectral region corresponding to intrinsic absorption by these substances. Particular attention has been concentrated on the comparative study of the photolysis of gaseous, liquid, and solid hydrocarbons.

II. CHARACTERISTIC FEATURES OF THE EXPERIMENT

Active research in the vacuum ultraviolet region has been prosecuted only during the last two decades because only comparatively recently the necessary optical materials, transparent in the wavelength range 105–160 nm, sufficiently powerful light sources in this region, and the corresponding spectroscopic apparatus have become available for experiments[3].

Optical Materials

The optical components of apparatus designed for research in the vacuum ultraviolet region must be made of substances transparent to this type of radiation. Such substances are LiF, CaF_2, MgF_2, BaF_2, SrF_2, LiO, BeO, and sapphire[3,4]. However, these substances are opaque to light with $\lambda < 105$ nm so that studies in the above spectral region are still more difficult. However, the use of various substances in the form of thin film permits experiments also at $\lambda < 105$ nm. The choice of substances suitable for the preparation of thin transparent films which can be used to make windows in photochemical cuvettes or filters depends on their absorption coefficients in the experimental region and also on their mechanical properties. The films are obtained from organic substances or metals[4].

Light Sources

The main requirement which must be met by photochemical light sources is high radiation intensity (not less than 10^{13} to 10^{14} quanta s^{-1}), which is dictated by the sensitivity of modern analytical methods and the limited amount of time available. It is desirable to have a monochromatic light source, which permits the generation in the test specimen of quite definite excited electronic or ionic states. Various monochromatic radiation sources in the vacuum ultraviolet region, operating on the basis of various types of electric

discharge (ultrahigh frequency, high frequency, arc, spark, and glow discharges) in the inert gases (Xe, Kr, Ar, Ne, and He) and in molecular gases (Br_2, I_2, N_2, etc.) have now been developed and used.

Electrodeless resonance lamps, in which the discharge is maintained with the aid of a decimetre wave generator, have been most widely used in the last decade[1,5,6]. Xenon and krypton arc discharge resonance lamps (of types of KSR-1, KSR-2A, KRR-2A) are manufactured in the USSR.[7,8] In addition, synchrotron radiation, i.e. the electromagnetic radiation of electrons moving in a circular orbit with a velocity close to that of light, can be employed as the source of vacuum ultraviolet radiation[4,9]. The continuous spectrum of synchrotron radiation extends from the near infrared to hard X-rays. The intensity of the radiation is stable and is calculated in absolute units, which permits its employment as a standard light source. The radiation is polarised (degree of polarisation approximately 85%; the electric vector lies in the plane of the electron orbit). In order to isolate monochromatic light, monochromators are used; the intensity of the vacuum ultraviolet radiation, for example, that of the DEZI synchrotron (Hamburg, Federal Republic of Germany) at the outlet slit of the monochromator then reaches ~10^{12} quanta s^{-1} nm^{-1}.[9]

Detectors of Vacuum Ultraviolet Radiation

A whole series of detectors are used to detect vacuum ultraviolet radiation: photoelectric detectors, thermophosphors, photographic plates, and ionisation chambers[4]. Photochemical actinometry is also widely used. One of the easiest and commonest methods of measuring the absolute radiation intensities is photochemical gas actinometry, i.e. the determination of the intensity of the light generated by the source from the known yield of gaseous products of photochemical reactions. The following actinometric systems may be noted: the decomposition of carbon dioxide[4,10] or hexafluoroacetone[11] with formation of CO; the formation of O_3 in the photolysis of O_2,[12] the formation of H_2 and C_2H_2 in the photolysis of C_2H_4,[13] the formation of NO in the photolysis of N_2O,[14] the formation of H_2 on irradiation of HBr,[15] etc.[1,4,15].

Analytical Methods for the Products of Photochemical Reactions

The analysis of the products of the photolysis of hydrocarbons by vacuum ultraviolet radiation requires the application of extremely sensitive analytical methods, particularly in the photolysis of solids. On the one hand, this can be accounted for by the low intensity of the radiation from the existing light sources (~10^{14}–10^{15} quanta s^{-1}). On the other hand, the changes in polymeric materials lead to the accumulation of products in a very thin layer (~100 to 200 nm [16,17]) even after long photolysis times, and even high concentrations of these products can be detected only with the aid of sensitive methods. Gas and liquid chromatography, mass spectrometry, optical absorption spectroscopy in the vacuum ultraviolet region, multiple diffuse total internal reflection infrared spectroscopy, and EPR are used nowadays for the qualitative and quantitative detection of the products of the vacuum ultraviolet photolysis of hydrocarbons[5,16–21].

III. PHOTOLYSIS OF SATURATED HYDROCARBONS

1. Optical Spectroscopy

The threshold in the absorption of light by saturated hydrocarbons is near 7–8 eV. With increase of the number of carbon atoms in linear alkanes, the light absorption threshold shifts from ~143 nm for methane[1,22] towards longer wavelengths (Fig. 1). The absorption threshold for polyethylene (Fig. 2) is observed at 160–165 nm [23,24] (at longer wavelengths the optical density is mainly due to light scattering[23]). It is believed[22] that the first absorption band of alkanes is due to the $\sigma \rightarrow \sigma^*$ excitation of the electrons of the C–C bond, while the C–H bond begins to absorb light with $\lambda \lesssim 143$ nm. However, it has been suggested[26,27] that the first absorption band is due to Rydberg transitions to 3*s* and 3*p* orbitals. The transition takes place from two close molecular orbitals: $1e_g$ and $3a_g$ (Sandorfy[27]); the $1e_g$ molecular orbital is strongly bonding for the C–H bond and is antibonding for the C–C bond, while the $3a_{1g}$ orbital is weakly C–H bonding and is strongly C–C bonding. Mulliken[26] believes that the difference between the Rydberg transitions and the transitions of the valence shell electrons is in this case merely semantic and in reality these two types of transitions are coupled.

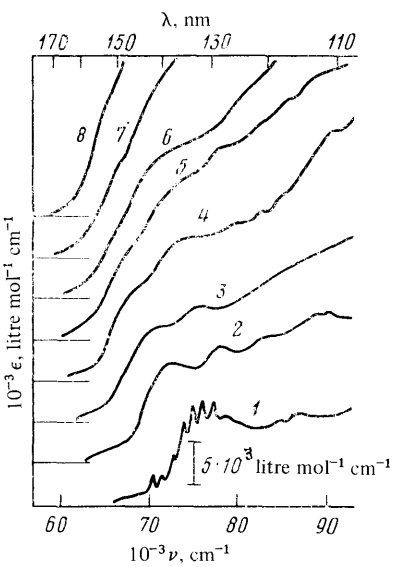


Figure 1. Absorption spectra of linear alkanes in the gas phase[22]: *1*) C_2H_6; *2*) C_3H_8; *3*) C_4H_{10}; *4*) C_5H_{12}; *5*) C_6H_{14}; *6*) C_7H_{16}; *7*) C_8H_{18}; *8*) C_9H_{20}.

The study[25] (Fig. 2) of the absorption spectra of polyethylene (PE) and the normal paraffins $C_{28}H_{58}$ and $C_{42}H_{86}$ at 4.2 K led to the discovery of a peak with $\lambda_{max} \cong 148$ nm, which is not observed at room temperature. The authors[25] assigned it to a transition due to a Vanier exciton. Partridge[23,28–31] believes that the entire PE absorption band is due to the exciton interaction. On irradiation with $\lambda \cong 125$–100 nm light, the C_1–C_8 alkanes begin to ionise in

the gas phase. For photon energies near the ionisation threshold, the ionisation quantum yield is low, but, with increase of the photon energy, it rises and, for low-molecular-weight alkanes and light with $\lambda \cong 83-78$ nm, it is unity[32]. In the absorption spectra this region has the form of a broad maximum at the above wavelengths (~80 nm). The absorption intensity then falls monotonically to ~28 nm.[26]

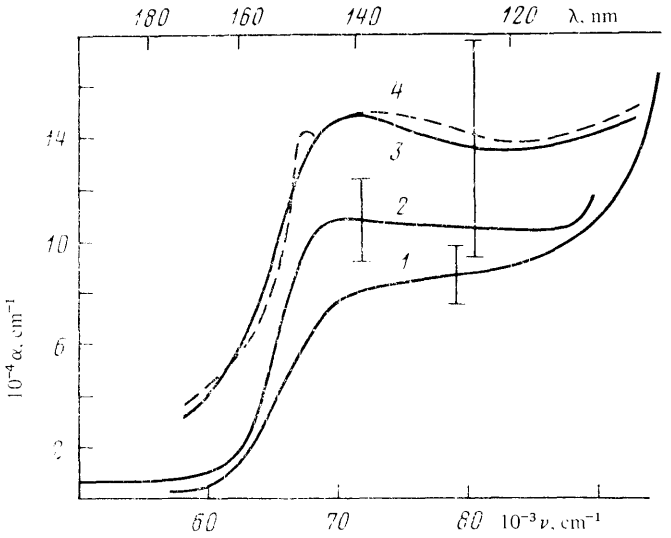


Figure 2. Absorption spectra of polyethylene: *1*)–*3*) at room temperature (data from Refs. 23–25 respectively); *4*) at 4.2 K;[25] α = decadic absorption coefficient.

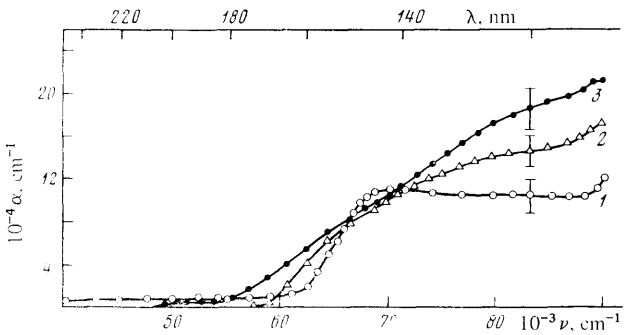


Figure 3. Absorption spectra: *1*) polyethylene; *2*) polypropylene; *3*) polyisobutylene[24]; α = decadic absorption coefficient.

The spectra of highly branched saturated hydrocarbons exhibit a bathochromic shift of the edge of the absorption band relative to the spectra of linear hydrocarbons owing to the decreased energy of the first excited state[33].

In the theory of the absorption spectra of branched alkanes in the gas phase it is assumed that the excited states are degenerate[22], but in reality this degeneracy is removed. For example, for isobutane two transitions are observed instead of one transition (as for propane), the two transitions being symmetrically displaced relative to the transition frequency in propane; for neopentane, three transitions are observed instead of one[22].

Analogous changes have been observed also on comparing the absorption spectra of polymers: PE, polypropylene (PP), and polyisobutylene (PIB) [24] (Fig. 3). To account for this, Raymonda and Simpson[22] and Dorofeev and Skurat[24] resorted to the Jahn–Teller theorem, according to which the degeneracy of the excited state is removed when the molecular symmetry is disturbed. As a result, one observes states with higher and lower energies than those observed for linear saturated hydrocarbons.

Cycloalkanes and highly branched alkanes absorb at longer wavelengths than the corresponding linear alkanes. Thus it has been established[22] that the C_3–C_8 cycloalkanes begin to absorb light at a wavelength of ~175 nm.

The fluorescence of saturated hydrocarbons on excitation with light corresponding to the intrinsic absorption band has been investigated in a number of studies[29–32]. The observed luminescence is monomeric and not excimeric, as suggested by Antonova et al.[21], because the luminescence spectra of hydrocarbons in the vapour phase and the pure liquid hardly differ[34,36]. Furthermore, the emission does not change even in dilute solutions of hydrocarbons in various solvents frozen at 77 K.[36]

The fluorescence of hydrocarbons is characterised by the following features. The spectral distribution of the fluorescence exhibits a Gaussian dependence of the intensity on the wavenumber[37]. On excitation of the fluorescence with light at different wavelengths, its spectrum remains unaltered but the quantum yield decreases with decrease of the wavelength of the exciting light. The fluorescence spectra of saturated hydrocarbons are displaced relative to their absorption spectra by approximately 0.7–1.8 eV;[37] such a large Stokes shift indicates appreciable nuclear perturbations in the excited emitting state[36,37]; under these conditions, the position of the maximum remains unaltered as the number of carbon atoms (N_C) increases, but the fluorescence quantum yield increases (Table 1). The increase of the fluorescence quantum yield is believed[35–37] to be due to a significant decrease in the rates of certain non-radiative processes.

Table 1. The lifetimes of the excited states and the fluorescence quantum yields (liquid phase, 147 nm).[34–37]

Compound	$10^9 t$, s	$10^4 \cdot \Phi_f$	Compound	$10^4 \cdot \Phi_f$
n-Pentane	0.3	0.6	2-Methylpentane	0.001
n-Heptane	6	7	3-Methylhexane	0.007
n-Nonane	15	15	4-Methylnonane	0.028
n-Undecane		28	2-Methylundecane	0.036
n-Hexadecane	50	44		

This influence of N_C can be explained by the fact that its increase entails an increase of the lifetime of the excited states as a consequence of the delocalisation of the electronic excitation over a long chain. The potential surfaces of the ground and excited states approach one another with increase of N_C, diminishing the excitation amplitude, which reduces the probability of non-radiative transitions (including chemical processes). This explanation is consistent with the

fact that the first absorption transition of n-alkanes undergoes a bathochromic shift with increase of N_C, while the energy of the fluorescence transition remains unaltered[35-37]. After the introduction of branches into n-alkanes, the emission spectrum undergoes a bathochromic shift. Thus all the n-alkanes investigated emit light at ~207 nm, 2-methylbutane emits at 233 nm, 2-methylhexane emits at 223 nm, 2-methyloctane emits at 217 nm, etc.[37]. As mentioned above, the wavelength of the first absorption transition also increases under these conditions, but the wavelengths of the emitted light increases to a greater extent, implying that branching increases the changes in the internuclear distances in the excited state, which leads to an increase of the rate of nonradiative transitions and to a corresponding decrease of the fluorescence quantum yield (Table 1).[35,36] The fluorescence of unsubstituted cycloalkanes is observed only for cyclohexane[35,37] (at 201 nm with quantum yields of 8.8×10^{-3} and 3.5×10^{-3} on excitation with light at 165 and 147 nm respectively).

Table 2. The quantum yields of the products of primary processes in the photolysis of fully deuterated n-butane (n-C_4D_{10}).[38]

Product	147 nm	123.6 nm
$CD_4 + C_3D_6$	0.009	0.04
$\dot{C}D_2 + C_3D_8$	0.005	0.018
$C_2D_4 + C_2D_6$	0.21	0.28
$\dot{C}_2D_5 + \dot{C}_2D_5$	0.15±0.01	0.17±0.02
$\dot{C}_2D_7 + \dot{C}D_3$	0.04	0.07
$\dot{C}_4D_9 + \dot{D}$	0.05	0.06
$C_4D_8 + D_2$	0.55±0.05	0.40±0.05

2. Photolysis of Low-Molecular-Weight Hydrocarbons

The gas phase. The photolysis of alkanes in the gas phase has been studied in greatest detail for photon energies below the ionisation threshold: the yields of the products of photochemical reactions have been determined and the mechanisms of the formation of a number of substances have been deduced. Table 2 lists the products of the primary photolytic reactions of n-butane under the influence of light at 147 and 123.6 nm in the gas phase with an indication of their quantum yield. The processes and yields presented in Table 2 are typical for the photolysis of linear alkanes in the gas phase[1,32,38]. The main process in the photolysis of linear alkanes by light below the ionisation threshold involves the removal of a hydrogen molecule on decomposition of an electronically excited molecule. In addition to the elimination of a hydrogen molecule, for ethane the elimination of two hydrogen atoms has been noted:

$$CH_3CH_3 + h\nu \begin{cases} \longrightarrow H_2 + CH_3\ddot{C}H^{\neq} \\ \longrightarrow 2\dot{H} + CH_2{=}CH_2^{\neq} \end{cases}.$$

Acetylene is formed in the decomposition of excited $C_2H_4^{\neq}$:

$$C_2H_4^{\neq} \rightsquigarrow H_2 + CH \equiv CH \quad .$$

Decomposition side reactions have been noted[1] also for propane and butane.

The study of the isotopic composition of hydrogen in the photolysis of mixtures of the normal and deuterated alkanes and also of partly deuterated alkanes has shown (Table 3) that H_2 can be eliminated from both two neighbouring carbon atoms and from the same carbon atom, for example[1]:

$$CH_3CD_2CH_3 + h\nu \begin{cases} \longrightarrow H_2 + CH_3CD_2\ddot{C}H^{\neq} \\ \longrightarrow D_2 + CH_3\ddot{C}CH_3^{\neq} \\ \longrightarrow HD + CH_3\dot{C}D\dot{C}H_2^{\neq} \end{cases}.$$

In the photolysis with light at 147 nm a hydrogen atom is eliminated with a probability smaller by a factor of ~10; in the photolysis by light at shorter wavelengths the process probability increases. Overall, a decrease of the wavelength of the photolysing light entails a decrease of the overall yield of hydrogen: for example, the quantum yield of hydrogen from ethane[46] changes from 0.85 (147 nm) to 0.4 (123.6 nm). The decrease is compensated by an increase of the yields of other primary processes, for example, the dissociation of the C–C bond.

Table 3. The isotope composition (mole %) of the hydrogen formed on irradiation of partly deuterated hydrocarbons and 1 : 1 mixtures of the usual and fully deuterated hydrocarbons.

Hydrocarbon	λ, nm	H_2	HD	D_2	Refs.
CH_4+CD_4	123.6	47.3	10.5	42.2	[39]
CH_4+CD_4	*	47.4	26.4	26.2	[39]
$C_3H_6+C_3D_6$	147	58.16	3.3	38.5	[1]
$C_3H_6+C_3D_6$	*	48	24.6	27.4	[40]
CH_3CD_3	147	58.5	16.9	24.6	[1]
$C_3H_8+C_3D_8$	147	56.7	5.4	37.9	[1]
$C_3H_8+C_3D_8$	123.6	45.7	19.4	34.9	[1]
$C_3H_8+C_3D_8$	*	67.6	22.1	10.3	[41]
$CH_3CD_2CH_3$	147	24.6	22.6	52.8	[1]
$CH_3CD_2CH_3$	123.6	51.3	28.7	20.0	[1]
$C_4H_{10}+C_4D_{10}$	147	62.3	6.3	31.6	[1]
$C_4H_{10}+C_4D_{10}$	123.6	49.8	16.4	33.8	[1]
iso-C_4H_{10}+ iso-C_4D_{10}	147	56	27.3	16.7	[1]
iso-C_4H_{10}+ iso-C_4D_{10}	123.6	50.2	30.9	9.9	[1]
$(CH_3)_3CD$	147	41.6	55.5	2.9	[1]
$(CH_3)_3CD$	123.6	64.7	32.1	3.2	[1]
$(CH_3)_2CHCH_2CH_3+(CD_3)_2CDCD_2CD_3$	147	63.0	2.0	35.0	[42]
$(CH_3)_2CHCH_2CH_3+(CD_3)_2CDCD_2CD_3$	123.6	67.6	5.5	26.5	[42]
$(CH_3)_2CHCH_2CH_3+(CD_3)_2CDCD_2CD_3$	104.8—106.7	71.8	17.4	10.7	[42]
$(CH_3)_2CHCH_2CH_3+(CD_3)_2CDCD_2CD_3$	**	57.2	28.8	14.0	[42]
PE + DPE	156	79	5.2	15.8	[43]
PE + DPE	147	68.4	6.7	24.9	[43]
PE + DPE	123.6	62.8	8.9	28.3	[43]
PE + DPE	*	57.5	23.9	18.6	[44]
C_2H_4-C_2D_4 copolymer	147	67	16	17	[45]
C_2H_4-C_2D_4 copolymer	123.6	67	18	15	[45]
Cyclo-C_3H_6+ cyclo-C_3D_6	147	52.3	20.5	26.3	[1]

*Irradiation with fast electrons. **Irradiation with ^{60}Co γ-rays.

The dissociation of the C–C bond can occur with formation of both molecular and radical hydrocarbon products, for example[1]:

$$CH_3CH_2CH_3 + h\nu \begin{cases} \longrightarrow CH_4 + C_2H_4 \\ \longrightarrow \dot{C}H_3 + \dot{C}H_2CH_3 \end{cases}.$$

However, the probability of the dissociation of the C–C bond with formation of molecular hydrocarbons is greater than for the process involving the formation of radical products[1,32,38]. It is noteworthy that the dissociation of the C–C bond with formation of molecular products involves the transfer of a hydrogen atom. Experiments with partly deuterated hydrocarbons permit a determination of the relative probability of the transfer of primary, secondary, and tertiary hydrogen atoms (Table 4).

With increase of the branching of the alkanes, the yields of processes involving the dissociation of the C–C bond increase, while the yield of hydrogen falls (Tables 5–7); the fraction of HD in the hydrogen produced increases (Table 3). For cyclopropane and cyclobutane, hydrogen is formed with a low quantum yield (Table 5), as for branched alkanes, while the fraction of atomic hydrogen eliminated increases (Table 3); on the other hand, the main process is one involving the dissociation of the C–C bond:[1,38]

$$\text{cyclo-}C_3H_6 + h\nu \rightarrow C_2H_4 + \ddot{C}H_2 \ .$$

However, in the case of cyclopentane and cyclohexane the main processes involve (as for linear alkanes) the elimination of molecular hydrogen (Table 5).[38]

Table 4. The form in which alkanes are formed in the photolysis of branched alkanes $CH_3CX_2CYCZ_3$ by 147 nm light[38].

Product	Relative probabilities of formation	
	R=CH_3	R-CH_2CH_3
RY	1.0	1.0
RX	1.3	1.0
RZ	0.15	0.17

Note. X, Y, and Z denote hydrogen and/or deuterium atoms in various partly deuterated compounds. No correction was applied for the isotope effect.

Table 5. The quantum yields of hydrogen in the gas-phase photolysis of alkanes by 147 nm light[38].

Compound	Φ	Compound	Φ
CH_3CH_3	0.85	$(CH_3)_4C$	<0.05
$CH_3CH_2CH_3$	0.70	cyclo-C_3H_6	<0.02
$CH_3CH_2CH_2CH_3$	0.59	cyclo-C_4H_8	<0.02
$CH_3CH_2CH_2CH_2CH_3$	0.65	cyclo-C_5H_{10}	0.7±0.1
$(CH_3)_2CHCH_3$	~0.22	cyclo-C_6H_{12}	0.7±0.1
$(CH_3)_2CHCH_2CH_3$	~0.24		

Overall the molecular decomposition reactions of electronically excited alkanes (linear, branched, and cyclic) predominate. The decomposition quantum yields are then close to unity.

The liquid phase. A number of studies have been made on the photolysis of linear and branched alkanes in the liquid phase[5,20,21,47–49]. It has been established that the primary processes are similar to those observed in the gas phase (Tables 6 and 7). However, the secondary fragmentation of the excited molecules formed in the primary process is less important than in the gas phase. For example, in the photolysis of ethane at the temperature of liquid nitrogen, excited ethylene molecules are formed. The decomposition of these excited molecules with formation of acetylene, which plays an important role in the gas-phase photolysis, is in this case inhibited by deactivating collisions in solution[50]. As in the gas phase, the formation of hydrogen is unimportant for branched alkanes in the liquid phase (Table 7); the yields of processes involving the dissociation of the C–C bond and the formation of molecular hydrocarbon products are higher in the liquid phase than in the gas phase but the relative probabilities of these processes are approximately the same in the two cases (Table 7).

Table 6. The quantum yields of the primary products in the photolysis of n-pentane (n-C_5H_{12}) on irradiation with 147 nm light in the gas and liquid phases[20,38].

Product	Gas	Liquid
CH_4	0.01	0.01
C_2H_6	0.048	0.05
C_3H_8	0.053	0.06
H_2	0.65±0.1	0.70

Table 7. The quantum yields of the primary molecular hydrocarbon products in the photolysis of 2,2,4-trimethylpentane (iso-C_8H_{18}) in the gas and liquid phases[20,32,38].

Product	Gas		Liquid
	147 nm	123.6 nm	147 nm
CH_4	0.063	0.066	0.17
iso-C_4H_{10}	0.190	0.225	0.36
neo-C_5H_{12}	0.029	0.34	0.05
H_2	~0.1		

Overall, the different primary decomposition reactions of excited alkane molecules persist and their quantum efficiency remains high also in the liquid phase. For example, in the photolysis of liquid cyclohexane, on irradiation with light at 147 nm, the quantum yield of hydrogen is close to unity, as in the gas phase[51,52]. In the study of the photolysis of isooctane by light at 147 and 160–180 nm in the condensed phase over the temperature range 173–373 K, it was established[49] that the ratio of the yields of the photolysis products hardly changes with increase of temperature but the overall quantum yield becomes greater than unity.

3. The Photolysis of Polyolefins

Polyethylene. The photolysis of PE by light at the wavelengths corresponding to the intrinsic absorption band has been investigated in a series of studies[16,17,43,45,53–57]. It was established that the main gaseous product (and virtually the only product) of the photolysis of PE on irradiation with light at 147 nm is hydrogen[43,57]. Its initial quantum yield is 0.4 ± 0.1.[43] Hydrogen can be eliminated in the form of a molecule accompanied by the formation of a *trans*-vinylene double bond[16] (hydrogen can then be eliminated from one carbon atom or two neighbouring atoms[45]):

$$M + h\nu \xrightarrow{\Phi \simeq 0.31} H_2 + \sim CH{=}CH \sim \ ,$$

and also on elimination of the $\dot{H}$ atom[17,43,56]:

$$M + h\nu \xrightarrow{\Phi \simeq 0.06} \dot{H} + \sim \dot{C}H{-}CH_2 \sim \ .$$

The relative probability of the elimination of atomic hydrogen

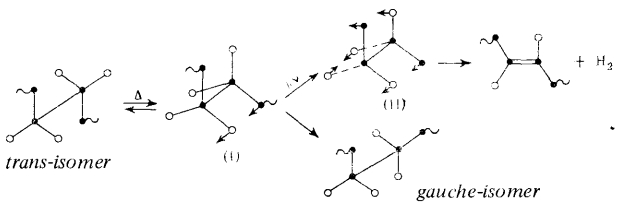
is approximately the same for solid PE as for low-molecular-weight alkanes in the gas phase. This is also indicated by a comparison of the isotopic compositions of the hydrogen formed in the photolysis of mixtures of the usual and deuterated hydrocarbons (Table 3). However, in contrast to the photolysis of simple alkanes in the gaseous and liquid phases, where $\Phi(H_2) \cong 1$, in the photolysis of solid PE pathways leading to the deactivation of the excited state of molecules without the formation of hydrogen predominate[43]. According to the authors[43], the factors responsible for the decrease of the quantum yield of hydrogen must be both transition to the solid phase, facilitating the deactivation of the electronically excited states, and the large size of the polymeric molecules, promoting the delocalisation of the excitation.

Table 8. Temperature dependence of the quantum yields of hydrogen in the photolysis of deuteropolyethylene[43,54].

t, °C	23	100	120	150	175	200	220	250
$\Phi(D_2+HD)$	0.2—0.25	0.4	0.5	0.65	0.75	0.8	0.9	0.9

The influence of temperature above room temperature on the quantum yield of hydrogen (Table 8) has also been observed[43,54], the greatest increase of the yield being noted at high temperatures even in a polymer melt. It is believed[54] that this temperature dependence indicates the elimination of molecular hydrogen from the vibrationally excited states. Presumably, the fraction of polymeric molecules having a conformation favourable for the elimination of molecular hydrogen increases with increase of temperature.

The relation between the effect of temperature in the photolysis of PE and the conformational kinetics has been explained[58] on the assumption that the transient configurations in the rotational-isomeric transition (I) and in the elimination of molecular hydrogen (II) in the $\sim CH_2-CH_2\sim$ unit in the electronically excited state are similar. In this case, the hydrogen atoms approach one another most closely and the steric conditions are most favourable for the elimination of an H_2 molecule:



According to selection rules, the probability of the absorption of a photon is a maximum for excitation of symmetrical vibrations of the unit (in the scheme above the directions of the vibrations are indicated by arrows). The planar disposition of the H—C—C—H bonds occurring in the *trans*—*gauche* transitions is therefore most favourable for the elimination of H_2, the transhybridisation $sp^3 \rightarrow sp^2 + p$ of carbon atoms, and the formation of a double bond. As a consequence of this stereospecificity of the process, the kinetics of slow conformational transitions partly determine (since the hydrogen molecule is also eliminated with a high probability from the same carbon atom and not only from two neighbouring carbon atoms[45]) the unusual temperature dependence of the quantum yield of hydrogen in the rapid photolysis of PE.

In the photolysis of PE by light at 147 nm, a C—C bond is also ruptured with formation of a vinyl double bond[16,17]:

$$M + h\nu \xrightarrow{\Phi \cong 0.0} \sim CH_2-CH_3 + CH_2=CH-CH_2\sim \quad .$$

It has been observed[43,45] that the hydrogen formed in the photolysis of mixtures of PE and deuterated polyethylene (DPE) is characterised by a higher [H]/[D] ratio than the mixture of polymers. This effect is due to the intermolecular transfer of excitation energy from the deuterated PE molecules to the normal molecules. Judging from the isotopic composition of the hydrogen formed, in the 1 : 1 copolymer of C_2H_4 and C_2D_4 the energy transfer from the C_2D_4 units to C_2H_4 units via the polymer chain takes place with a greater efficiency than the intermolecular transfer in the mixture of PE and DPE.

The radius of energy transfer from methylene units to *trans*-vinylene double bonds, amounting to 0.3—0.7 nm, has been calculated[57]. In the course of photolysis the quantum yields of the main products diminish: the double bonds attain a limiting concentration (4×10^{-3} mol g^{-1}), while hydrogen continuously evolves with a low (~0.02), slowly decreasing quantum yield. The observed sharp diminution of the quantum yield of hydrogen at the beginning of the photolysis is due to the transfer of excitation energy to double bonds.

The photolysis of PE is also accompanied by a cross-linking process[56,57] as a result of the recombination of the radicals formed in the course of the elimination of a hydrogen atom H and

$$\dot{H} + \sim CH_2-\dot{C}H-CH_2\sim \rightarrow H_2 + \sim \dot{C}H-CH_2\sim \quad .$$

As double bonds accumulate, they are also hydrogenated by atomic hydrogen:

$$\dot{H} + \sim CH=CH\sim \rightarrow \sim \dot{C}H-CH_2\sim \quad .$$

Furthermore, double bonds are consumed in the intramolecular cross-linking reaction, which leads to the attainment of their limiting concentration[17,56,59].

Polypropylene (PP). It has been established[17,60] that the photolysis of PP by light at 147 nm results in the formation of individual bonds and hydrogen in the main primary processes. The double bonds are produced on elimination of a hydrogen molecule and on degradation of the main polymer chain into molecular products:

$$M + h\nu \xrightarrow{\Phi \leq 0.25} H_2 + \sim \underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}-CH\sim \quad ,$$

$$M + h\nu \xrightarrow{\Phi \cong 0.25} \begin{cases} \sim CH_2CH_2CH_3 + CH_2=\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}\sim \\ \sim CH_2CH=CH_2 + CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}\sim \end{cases} \quad .$$

Processes involving the elimination of a hydrogen atom,

$$M + h\nu \rightarrow \dot{H} + R$$

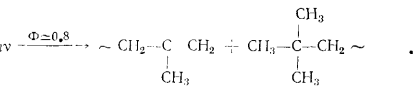
and the formation of methane,

$$M + h\nu \xrightarrow{\Phi \cong 0.025} CH_4 \quad ,$$

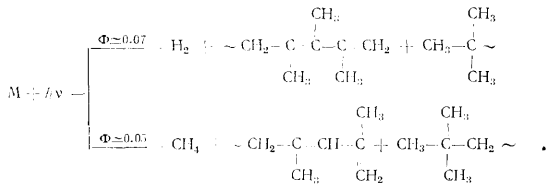
also occur. 2-Methylpropane and propene are formed in still lower yields.

In the course of its photolysis, PP undergoes cross-linking, apparently by the recombination of radicals in reactions similar to those in the photolysis of PE. However, in contrast to PE, in PP the cross-linking process is accompanied by a highly efficient degradation process, which is indicated by the decrease of the thickness of PP films during photolysis.

Polyisobutylene (PIB). In the photolysis of PIB by light at 147 nm, mainly individual double bonds and conjugated diene double bonds are formed in the primary stage[17,24]. Individual double bonds are produced on degradation of the main polymer chain:



The conjugated diene double bonds are formed in the primary process with elimination of H_2 or CH_4 and the degradation of the main polymer chain:



In the secondary stages of photolysis, gaseous hydrocarbon products are formed (2,4,4-trimethylenepentane, 2,4,4-trimethylpent-1-ene, and isobutene) with increasing quantum yields, which leads to the conversion of the surface layer of the polymer into a viscous liquid and to a decrease of the thickness of the specimen.

4. Excited States of Saturated Hydrocarbons and Their Decomposition Products

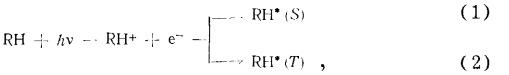
According to optical selection rules[61], in the photolysis of hydrocarbons virtually only singlet states are excited (the probability of the excitation by light of the triplet states of organic molecules without heavy atoms is $\sim 10^{-5}$).[61] However, on the basis of theoretical calculations, it has been claimed[62,63] that the rate of the intersystem crossing for alkanes, particularly in a condensed phase, is high ($\sim 10^{10}$ to 10^{11} s^{-1}). It follows from studies on the fluorescence of alkanes[34-37], examined above, that the radiative deactivation of the excited singlet state is accompanied by non-radiative deactivation processes (including chemical processes), the overall rate constant for which decreases almost linearly with increasing chain length. This suggests that the intersystem crossing cannot be very significant in long-chain alkanes.

Liquid iso-octane has been photolysed[48] by 147 nm light in the presence of 1,3-cyclohexadiene (it is known[64] that 1,3-cyclohexadiene, which is an acceptor of the donor triplet state, undergoes photochemical dimerisation in the triplet state). The 1,3-cyclohexadiene dimer was then detected and identified, but its quantum yield did not exceed 0.005, indicating that the probability of the intersystem crossing in hydrocarbons (linear and branched) is low.

The effects involving a decrease of the quantum yields of the iso-octane photolysis products as a result of combination with radicals and transfer of excitation energy to the molecules of additives (CCl_4, $C_6H_{13}Cl$, C_6F_{16}, O_2, cyclo-C_6H_8) suggest[21,48] the presence of two excited states of iso-octane, leading to the same products via mechanisms involving the molecular and radical decomposition of iso-octane molecules.

The presence of at least two electronically excited states of n-hexane, from which hydrogen is formed, is also indicated by a decrease of the quantum yield of hydrogen to a constant value of 0.65 following the addition of SF_6, compared with that observed in the photolysis of pure n-hexane[47]. It has been established that in the photolysis of hydrocarbons hydrogen is split off in the form of a molecule or atom.

Theoretical studies[62,63] have led to the conclusion that excited singlet states of alkanes are capable of decomposing with elimination of molecular hydrogen directly in the primary step, while triplet states give rise to atomic hydrogen and a free radical via a predissociation mechanism. To test this hypothesis (the elimination of atomic hydrogen from the triplet state), a study was made[55] of the isotope composition of the hydrogen formed in the photolysis of the 1:1 copolymer of C_2H_4 and C_2D_4 at 77 K by 147 and 123.6 nm light. It was established that, in the photolysis at 77 K, ~30 and 37% of the hydrogen formed is evolved directly in the course of elimination (for 147 and 123.6 nm light respectively). The residual hydrogen is evolved only in the course of heating the specimen to room temperature. It has been observed (Table 9) that the fraction of HD in the hydrogen evolved on warming the copolymer irradiated at 77 K is greater than in the hydrogen evolved directly during photolysis. Since the photoionisation of PE takes place preferentially with formation of charged pairs, like that of any other solid organic compound with a low dielectric constant, i.e.



(1)

(2)

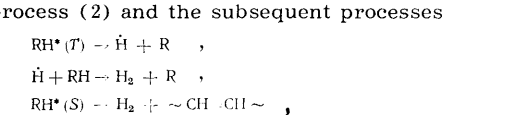
the above processes proceed via a mechanism involving the recombination of charged pairs. In this case, the ratio of the yields of reactions (1) and (2) depends on the average lifetime τ of the ion pairs relative to the recombination process[65]. For low values of τ (less than the spin relaxation time of the electron, which is $\sim 10^{-6}$ s), the charged pair recombines only via mechanism (1), while for large τ ($>10^{-6}$ s), the statistical ratio of the yields of reactions (1) and (2), amounting to 1:3, is attained[55,65].

Table 9. The isotope composition of the hydrogen (H_2:HD:D_2) evolved in the photolysis of specimens I–IV at 77 K and after photolysis on heating the specimens to room temperature[55].

Specimen	Photolysis			Heating		
	H_2:HD:D_2	HD/H_2	HD/D_2	H_2:HD:D_2	HD/H_2	HD/D_2
I	72:16:12	0.22	1.3	69:19:12	0.28	1.6
II	82:9.6:8.4	0.12	1.1	64:22:14	0.34	1.6
III	73:7:20	0.096	0.35	74:9:14	0.12	0.53
IV	0:19:81	—	0.23	0:18:82	—	0.22

Notation: I—1:1 C_2H_4–C_2D_4 copolymer (irradiation with 147 nm light); II—1:1 C_2H_4–C_2D_4 copolymer (123.6 nm); III—1:1 polyethylene–deuteropolyethylene mixture (147 nm); IV—deuteropolyethylene (147 nm).

Thus at 77 K process (2) and the subsequent processes



take place on heating PE containing captured charges with $\tau \gg 10^{-6}$ s (with a probability of 0.75). The hydrogen evolved in the course of photolysis is formed via a non-ionic mechanism or via rapid ($\tau < 10^{-6}$ s) recombination of "close" charged pairs in process (1), which does not give rise to HD. The fraction of HD in this hydrogen is therefore reduced. This explanation is supported also by the finding that the increase of the HD content in the retained hydrogen is particularly high on photolysis by light at $\lambda = 123.6$ nm (10 eV), compared with photolysis at 147 nm (8.4 eV).

However, the authors of a later review[66] believe that the triplet states of alkanes can decompose also with elimination of molecular hydrogen. Indeed, it has been shown[67] that the formation of fairly excited triplet states of 1,2-diphenylethane entails, together with the elimination of atomic hydrogen, also the elimination of molecular hydrogen with a quantum yield of 10^{-2}. Unfortunately, the yield in the elimination of atomic hydrogen was not determined in the above studies, which precludes the determination of the relative probabilities of these two processes involving the formation of hydrogen from the triplet state. However, comparison of the yields of double bonds and radicals and also of the isotope composition of hydrogen (Table 3) in the photolysis of linear hydrocarbons and in their radiolysis shows that, whereas the yields of atomic and molecular hydrogen elimination reactions in radiolysis are approximately identical[17,57,68], the elimination of molecular hydrogen predominates in photolysis[17,43,56,57].

This difference is due to the fact that, as a consequence of prohibition rules, virtually only the singlet state is excited in photolysis, whereas in radiolysis, where the main active factor is secondary radicals with an energy below 100 eV, such prohibition rules are missing (particularly for resonance energies of the electrons) and triplet states should be formed with a high probability already in the primary process and also in the ion recombination process. On the basis of this comparison, one may claim that the dominant process in the decomposition of the electronically excited triplet state is the elimination of atomic hydrogen with formation of a free radical.

According to Raymonda and Simpson[22], the 147 nm light excites only C–C bond electrons in hydrocarbons. On this basis, Holroyd[20] suggests that the elimination of molecular hydrogen should be attributed to the excitation of the electrons of the above bonds. However, it has been assumed[32] that the ^1E_u state, produced by the excitation of the C–H bonding electron, is responsible for the elimination of molecular hydrogen.

The decrease of the yield of hydrogen with increasing branching of hydrocarbons (Tables 4 and 8) has been explained[17,24], on the one hand, by the decrease of the number of CH_2 and CH–CH groups (molecular hydrogen is eliminated from these groups[45]) and, on the other hand, by the more effective consumption of the absorbed energy in processes involving the dissociation of the C–C bond.

The observed increase of the yield of processes involving the dissociation of the C–C bond with increasing branching of compounds is due to the weakening of the C–C bond near the branching point (for example, in the case of polymers, which is indicated by the decrease of the heat of polymerisation of the corresponding monomers, which amounts to 92, 69, and 54.5 kJ mol^{-1} for PE, PP, and PIB respectively[69]). It is noteworthy that the high yield in the dissociation of the C–C bonds of polymers is believed[70] to be caused (according to theoretical calculations of adiabatic potential curves) by the low activation energy for this process in the excited state and the correlation between the yields of C–C bond dissociation processes involving polymers and the corresponding heats of polymerisation is justified if the adiabatic potential curve in the ground state for a given bond characterises the potential curve in the excited state.

According to calculations[70], such a correspondence obtains for PE and PIB. However, in the case of polytetrafluoroethylene (which undergoes degradation on radiolysis) a high heat of polymerisation (165 kJ mol^{-1}) corresponds to a low activation energy in the excited state[70]. Such weakening of the C–C bond is caused by steric strain in the ground and excited states as a consequence of the presence of side groups; it leads to a decrease of the dissociative lifetime for the C–C bond dissociation reaction (this is indicated by the decrease of the fluorescence quantum yield of alkanes with increase of the degree of branching—see Table 1 and Refs. 34 and 37) and hence to an increase of the yield of processes involving the dissociation of this bond.

It is noteworthy that the dissociation of the C–C bond is observed mainly near the branching point and in hydrocarbons containing methyl side groups the C–C bonds of the main chain are largely dissociated (in the PP and PIB polymers the yield of the bond branching reactions involving the main polymer chain is approximately ten times higher than the yield corresponding to the methyl side groups[17,24,57,60]). Apart from the features examined above, in PE, PI, and PIB there is an increase of the overall quantum yield of the photodecomposition of the polymers (Table 10). It has been noted[17,24] that, with increased degree of branching in the above series of compounds, the efficiency of the deactivation of the electronically excited states diminishes with a simultaneous increase of the contribution of processes involving the dissociation of the C–C bonds in the main polymer chain. On the basis of the results of studies[34–37] of the fluorescence of saturated hydrocarbons, this effect has been explained by the increase of the lifetime of the excited states with increase of the number of carbon atoms in linear alkanes (Table 1) accompanied by an increase of the fluorescence quantum yield. Therefore, on the basis of the data in Table 1 for PE, one may expect still higher lifetimes of the excited singlet states, which would promote their effective deactivation, particularly in the solid phase. Such increase of the lifetime of excited states has been explained[34–37] by the diminution of the changes in the internuclear distances in the excited state (as a consequence of the delocalisation of the electronic excitation over a long chain), which diminishes the probability of non-radiative transitions (for example, chemical processes). This explanation is confirmed by the finding that the first absorption transition of normal alkanes undergoes a bathochromic shift with increasing number of carbon atoms, while the energy of the fluorescence transition remains unaltered[34–37]. This is one of the possible causes[43] of the low quantum yield of the photodecomposition of PE compared with that observed in the photolysis of the lower linear alkanes, where the photodecomposition quantum yield is close to unity[1,32,38].

It has been established (see Table 1 and Refs. 35–37) that the luminescence quantum yield or branched alkanes is appreciably lower than for normal alkanes (by a factor of approximately 10). It is suggested that the emitting state is characterised by a high degree of localisation of the electronic excitation near the branching point. The localisation of the electronic excitation is accompanied by a large change in internuclear distances and this induces an increase of the rates of certain non-radiative processes, i.e. polymer chain degradation processes. Another possible explanation

involves a diminution of matrix effects hindering the photodecomposition of polymer molecules on transition to the amorphous PIB polymer[24].

Table 10. The quantum yields of the primary photolytic processes involving PE, PP, and PIB on irradiation with 147 nm light[17,24].

Process	PE	PP	PIB
Elimination of hydrogen molecule	~0.3	⩽0.25	⩽0.07
Degradation with formation of terminal double bonds	0.03	~0.25	0.8

It is interesting to compare certain predictions of the molecular exciton theory for σ-bonds of alkanes, examined in a number of studies[23,28–31], with the results of experiments on the photolysis of PE by 147 nm light. In the first place one should note that the light quantum with $\lambda = 147$ nm has an energy of 8.4 eV, which is apparently sufficient for the formation of an exciton (according to some data[23,28–31], the formation of an exciton requires an energy of ~7.5–9.5 eV). According to the above investigations[23,28–31], the excitation energy of linear alkanes can be divided into two parts, one of which is localised at the C–H bonds of the $\sim CH_2\sim$ group and the other migrates from one C–C bond to another. Only localised excitation of carbon–hydrogen bonds can lead to the formation of a hydrogen atom or an H_2 molecule as a result of their separation from the $\sim CH_2\sim$ group.

However, the results of experiments on the photolysis of PE conflict with this postulate of the theory of singlet σ-bond excitons. The results are as follows. An H_2 molecule is eliminated not only from a single carbon atom but also from two neighbouring atoms[45] and there is excitation energy transfer from deuterated units to the usual units on photolysis of the C_2D_4–C_2H_4 copolymer[45]; the double bonds formed on photolysis hinder the formation of hydrogen[17,57], the quantum yield of hydrogen increasing with temperature and approaching unity (see Table 8 and Refs. 43 and 44).

IV. PHOTOLYSIS OF HYDROCARBONS CONTAINING INDIVIDUAL DOUBLE BONDS

1. Optical Spectroscopy

Absorption by ethylene is observed at $\lambda \cong 200$ nm [71,72] (Fig. 4). At $\lambda \cong 175$ nm, a series of sharp intense peaks are observed and are superimposed on the absorption continuum with a maximum at ~164 nm. A new series of sharp bands are observed at ~142 nm and are superimposed on another continuum with maximum absorption at ~130 nm. It is believed to be established[71] that the long-wavelength absorption and the first continuum are due to the singlet excitation of the electron from the bonding molecular π orbital $1b_{2u}$ with transition to the antibonding π orbital $1b_{3g}$. The sharp absorption bands at 175 nm are due to Rydberg transitions; the lowest Rydberg transition $N \rightarrow 3s$ is observed at 174.4 nm. Rydberg transitions ($\pi \rightarrow 3p$, $\pi \rightarrow 3d$) [71] have also been noted in the range 154–118 nm. It is believed that the second absorption continuum of ethylene at 125 nm is due to the $\sigma \rightarrow \sigma^*$ transition. The ionisation of ethylene begins at 128 nm.[71] It has been suggested[71,73] that the ethylene molecule in the lowest Rydberg state has been "twisted" by an angle of 30° relative to the geometrical plane in the ground state. The geometry of the ethylene molecule in the singlet π^* state has not been established, while in the triplet state the molecule has been "twisted" by an angle of 90°.

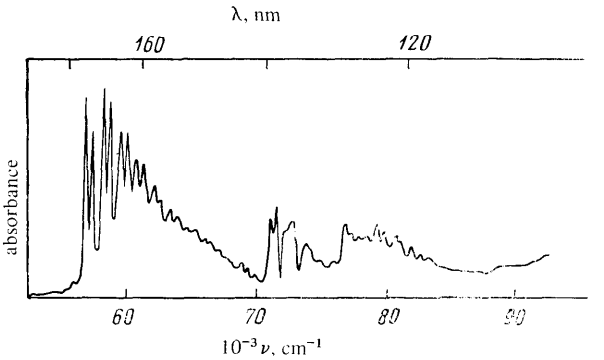


Figure 4. Absorption spectrum of gaseous ethylene in the vacuum ultraviolet region[72].

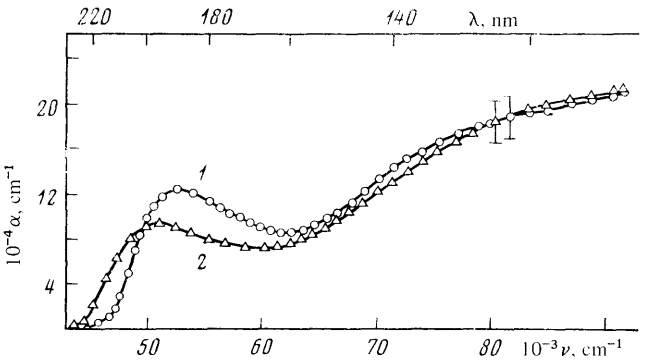


Figure 5. Absorption spectra: *1*) polybutadiene; *2*) polyisoprene[59]; α = decadic absorption coefficient.

As for ethylene, the first intense band in the absorption spectra of alkylolefins is due to the $\pi \rightarrow \pi^*$ transition and the fine structure superimposed on this band is less well resolved than for ethylene. It has been noted[71] that, with increase of the number of alkyl groups at the double bond, the absorption band undergoes a bathochromic shift (Fig. 5). The literature data on the oscillator strengths of various substances at the wavelength of the absorption band of carbon–carbon double bond ($\pi \rightarrow \pi^*$ transition) have been compiled in a monograph[71]. These data show that the oscillator strengths of compounds of different types are in the range from 0.26 to 0.59.

The fluorescence of mono-olefins irradiated with light corresponding to the absorption band of the double bonds has been studied[37,73]. On excitation by 184.9 nm light, a weak emission by gases at a pressure of 1 atm is observed (propene has a fluorescence band maximum at $\lambda_f \cong 223$ nm and *cis*- and *trans*-but-2-enes have $\lambda_f \cong 223$–227 nm). The fluorescence quantum yields for these substances are ~(1–2) × 10^{-6}. A similar luminescence has been observed also for pure liquids: hex-1-ene ($\lambda_f \cong 236$ nm), *cis*-hex-2-ene ($\lambda_f \cong 238$ nm), and *trans*-hex-2-ene ($\lambda_f \cong 235$ nm). The luminescence quantum yields for these substances are (5–7) × 10^{-6}. With increase of the degree of branching, the fluorescence undergoes a bathochromic shift and its quantum yield increases[37,73]. Thus the fluorescence of liquid tetramethylethylene is observed at $\lambda_f \cong 258$ nm with a quantum yield of 1.5 × 10^{-4}.

2. Photolysis of Mono-olefins

The photolysis of ethylene has been studied in greatest detail. For photons with energies ranging from 6.1 to 11.8 eV, the elimination of H_2 is the main process[38,74,75] [$\Phi(H_2) \cong 0.45 \pm 0.05$ in the range of photon energies 8.4–6.4 eV [38,74]]. Experiments on the photolysis of CH_2CD_2 by 147 and 123.6 nm light have shown[38] that the elimination of H_2 and D_2 from a single carbon atom is more probable than the elimination of HD from two carbon atoms. Furthermore, it has been established that the relative probabilities of the formation of H_2, D_2, and HD are independent, within the limits of experimental error, of the wavelength and the phase state of ethylene[76]. However, it has been stated that the probability of the competing process

$$C_2H_4 + h\nu \rightarrow \ddot{C}_2H_3\,(C_2H_2 + \dot{H}) + \dot{H}$$

increases with increase of the photon energy from 8.4 to 11.6–11.8 eV. In addition the following process has also been observed:

$$C_2H_4 + h\nu \rightarrow 2\ddot{C}H_2 \quad .$$

It has been suggested that there should be at least three different electronic states of ethylene in order to account for the photodecomposition processes in the range of photon energies from 6.4 to 8.4 eV.

The photolysis of ethylene by 104.8–106.7 nm light[38,77] entails ionisation and the formation of superexcited states:

$$C_2H_4 + h\nu \begin{cases} \rightarrow (C_2H_4^{\neq})^+ + e^- \\ \rightarrow C_2H_4^{**} \rightarrow (C_2H_4^{\neq})^+ + e^- \end{cases} .$$

The superexcited ethylene molecule ($C_2H_4^{**}$) can also decompose in the following processes:

$$C_2H_4^{**} \begin{cases} \rightarrow C_2H_2 + H_2 \\ \rightarrow C_2H_2 + 2\dot{H} \end{cases} .$$

It is believed[77] that, on collision with an ethylene molecule, $C_2H_4^+$ gives rise to a vibrationally excited ion:

$$C_2H_4^+ + C_2H_4 \rightarrow (C_4H_8^{\neq})^+ \quad .$$

In the absence of deactivating collisions, the $(C_4H_8^{\neq})^+$ ion decomposes:

$$(C_4H_8^{\neq})^+ \begin{cases} \rightarrow C_3H_5^+ + \dot{C}H_3 \\ \rightarrow C_4H_7^+ + \dot{H} \end{cases} .$$

Ethylene has been photolysed[76] in the condensed phase at 20 K by photons with energies from 8.4 to 21.2 eV. It has been established that, for higher photon energies, the relative yields of the products are comparable to the yields in the decomposition of solid ethylene. The relative yields of acetylene and cyclobutane (these are not the main products in the photolysis by photons with an energy of 8.4 eV) increase by an order of magnitude for higher photon energies, where the ions play a significant role.

Table 11. The composition of the products of the gas-phase photolysis of propene[78].

Product	147 nm	123.6 nm	Product	147 nm	123.6 nm
Hydrogen	7.6	14.7	Allene	7.4	6.8
Methane	3.4	3.8	Isobutane	11.4	8.6
Acetylene	38.0	34.9	Isobutene + but-1-ene	3.5	4.8
Ethylene	12.2	18.2	*trans*-But-2-ene	7.2	4.8
Ethane	7.4	4.1	*cis*-But-2-ene	1.9	0.0

The products of the photolysis of propene by 147 and 123.6 nm light are presented in Table 11.[78,79] The hydrogen formed in the photolysis is split off mainly in molecular processes:

$$CH_3CH{=}CD_2^{\neq} \begin{cases} \rightarrow H_2 + \ddot{C}HCH{=}CD_2 \\ \rightarrow H_2 + CH_2{=}C{=}CD_2 \end{cases} .$$

Acetylene is formed as a result of the rapid consecutive dissociation of two bonds:

$$CH_3CH{=}CH_2 \rightarrow \dot{C}H_3 + \dot{C}H{=}CH_2^{\neq} \quad ,$$

$$\dot{C}H{=}CH_2^{\neq} \rightarrow CH{\equiv}CH + \dot{H} \quad .$$

In the photolysis of the $C_3H_6 + C_3D_6$ mixture the yield of C_2H_4 is higher than that of C_2D_3H. Hence it follows that ethylene is partly formed via a molecular pathway:

$$CH_3CH{=}CH_2 + h\nu \rightarrow \ddot{C}H_2 + CH_2{=}CH_2 \quad .$$

Another process is also possible:

$$\dot{H} + C_3H_6 \rightarrow \dot{C}_3H_7 \rightarrow \dot{C}H_3 + C_2H_4 \quad .$$

The photolysis of propene by 123.6 nm light entails ionisation with a quantum yield of 0.197. Direct ionisation and self-ionisation in the superexcited state are observed. The $C_3H_6^+$ ions formed are involved in ion–molecule reactions:

$$C_3H_6^+ + C_3H_6 \rightarrow C_6H_{12}^+ \quad ,$$

$$C_6H_{12}^+ + C_3H_6 \rightarrow C_6H_{10}^+ + C_3H_8 \quad .$$

The process

$$C_6H_{12}^+ + C_3H_6 \rightarrow C_9H_{18}^+ ,$$

is possible but with a much lower probability.

In the photolysis of but-1-ene by 184.9, 147, 123.6, and 104.8–106.7 nm light, the main products are formed on fragmentation of the excited molecule[80]. Allene, buta-1,3- and buta-1,2-dienes, ethylene, and acetylene are formed (Table 12). When a hydrogen atom interacts with a double bond, the butyl radical is formed. On photolysis of trimethylethylene by 147 and 123.6 nm light, the following main products are formed: isopropene, buta-1,3-diene, propyne, allene, and ethylene[81] (Table 13).

It follows from Tables 12 and 13 and the results of a series of investigations[80–97] that, in the photolysis of linear olefins by light corresponding to the absorption band of double

bonds, the main process is the dissociation of the C–C β-bond if such is present and a C–H bond if there is no C–C bond in the β-position:

$$C_4H_8\text{-}1 + h\nu \xrightarrow{\Phi=0.71} \dot{C}H_3 + \dot{C}H_2{-}CH{=}CH_2 \ ,$$

$$C_4H_8\text{-}2 + h\nu \xrightarrow{\Phi=0.6} \dot{H} + \dot{C}H_2{-}CH{=}CH{-}CH_3 \ .$$

Analogous processes occur also in the photolysis of hex-2-ene and but-2-ene by 202.6 and 206.2 nm light:

$$C_6H_{12}\text{-}2 + h\nu \rightarrow CH_3CH{=}CH\dot{C}H_2 + \dot{C}H_2CH_3 \ ,$$

$$C_4H_8\text{-}2 + h\nu \rightarrow CH_3CH{=}CH{-}\dot{C}H_2 + \dot{H} \ .$$

In branched olefins the methyl side groups promote the dissociation of the C–C bonds in the α-position:

$$\text{iso-}C_4H_8 + h\nu \rightarrow \begin{cases} \xrightarrow{\Phi\geq 0.78} CH_3{-}\dot{C}{=}CH_2 + \dot{C}H_3 \\ \xrightarrow{\Phi\geq 0.25} \dot{C}H_2{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2 + \dot{H} \end{cases} .$$

Table 12. The quantum yields of the primary processes in the decomposition of the excited state of but-1-ene (C_4H_8-1) in photolysis by light corresponding to the intrinsic absorption band[80].

Product	184.9 nm	147 nm	123.6 nm	104.8–106.7 nm
$C_3H_4+\dot{C}H_3+\dot{H}(CH_4)$	0.04	0.38	0.23	0.16
$C_4H_6+2\dot{H}(H_2)$	—	0.32	0.36	0.17
$2C_2H_4$	0.09	0.04	0.05	0.2
$\dot{C}_2H_3+C_2H_5+\dot{H}$	—	0.04	0.05	
$C_2H_2+\dot{C}_2H_5+\dot{H}$	—	0.16	0.12	
$C_2H_2+C_2H_6$	0.1	0.03	0.02	0.33
$C_2H_2+2\dot{C}H_3$	—	0.04	0.05	
$C_3H_6+\dot{C}H_2$	—	0.03	0.04	0.05
$\dot{C}_4H_7+\dot{H}$	0.12	≤0.05	≤0.05	≤0.05
$\dot{C}_3H_5+\dot{C}H_3$	0.71	0.0	0.0	0.0

Table 13. The quantum yields of the decomposition processes involving the excited state of the trimethylethylene (C_5H_{10}) molecule[81].

Product	147 nm	123.6 nm	Product	147 nm	123.6 nm
$\dot{C}_5H_8+2\dot{H}(H_2)$	0.33	0.28	$[C_5H_{10}^+]^*+e^-$	0.00	0.22
$C_3H_4+2\dot{C}H_3$	0.27	0.2	$\dot{C}_5H_9+\dot{H}$	0.15	0.12
$C_4H_6+\dot{C}H_3+\dot{H}(CH_4)$	0.15	0.1	Other products	0.09	0.08

In the photolysis by light at $\lambda \leq 145$–150 nm decomposition processes involving the formation of three species, namely a hydrogen molecule and two radical species ($\dot{H}$ and the hydrocarbon radical or $2\dot{H}$), begin to predominate. A decrease of the yields of certain products with increase of pressure has been noted in the photolysis of olefins by light corresponding to the absorption band of double bonds[81,84,85,89,90,93,96]. The influence of pressure is due to the following sequence of processes:

$$M + h\nu \rightarrow M^{**} \ ,$$

$$M^{**} \rightarrow R^* + R_1 \ ,$$

$$R^* \rightarrow m + \dot{H} \text{ (or } \dot{C}H_3) \ ,$$

where m is a molecule containing an acetylenic or cumulated bond[84,93,94]. The influence of pressure is due to the stabilisation of the excited radical R* in the process

$$R^* + M \rightarrow R + M \ .$$

A similar mechanism of the effect of pressure has been considered also in the photolysis of hex-2-ene and but-2-ene by 202.6 and 206.2 nm light[92]:

$$C_6H_{12}\text{-}2 + h\nu \rightarrow C_6H_{12}\text{-}2^{**} \ ,$$

$$C_6H_{12}\text{-}2^{**} \rightarrow C_6H_{12}\text{-}1^{**} \ ,$$

$$C_6H_{12}\text{-}2^{**} \rightarrow C_6H_{12}\text{-}2^* \ ,$$

$$C_6H_{12}\text{-}2^{**} \rightarrow CH_3CH{=}CH\dot{C}H_2 + \dot{C}H_2CH_3 \ ,$$

$$C_6H_{12}\text{-}2^* + M \rightarrow C_6H_{12}\text{-}2 + M \ .$$

The absence of an influence of pressure on the yields of various products in photolysis by short-wavelength light has been explained[88] by the faster decomposition of excited radicals and molecules owing to their higher excess energy. The photolysis of olefins by 123.6 and 104.8–106.7 nm light involves the ionisation of double bonds with a quantum yield of ~0.2–0.3.[81,87,88,97]. The ions formed participate in ion-molecule reactions leading to the formation of saturated hydrocarbons as well as hydrocarbons containing a larger number of carbon atoms than the initial olefin.

3. Photolysis of Diene Polymers

Polybutadiene (PB) and polyisoprene (PI). The photolysis of polymers containing individual double bonds (PB and PI) on irradiation with 147 and 123.6 nm light has been investigated[17,56,59,98]. It has been established that the main processes involve the consumption of double bonds and their *cis–trans* isomerisation. In addition, hydrogen and intermolecular cross-links are produced (Table 14) as well as unidentified hydrocarbon products. The formation of these hydrocarbons entails a decrease of the thickness of PB and PI film by 30–50 nm on photolysis by 147 and 123.6 nm light with a dose of $(1–2) \times 10^{18}$ quanta cm^{-2}. It is believed that mainly electronically excited states of the polymer molecules arise in this instance as in the photolysis of olefins in the gas phase:

$$M + h\nu \rightarrow M^* \ .$$

The decomposition of M* involves the elimination of atomic hydrogen:

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

However, the photolysis of PB and PI differs significantly from the photolysis of olefins in the gas phase by the fact that the overall yield of diene, cumulated, and acetylenic bonds (~0.06) is approximately ten times lower than in the gas-phase photolysis of butenes and pentenes, where the yield of the above bonds is ~0.5.[80,81,87,94]. The difference is believed[17,59] to be caused by the transition to the condensed phase, which suppresses the secondary decomposition reactions of the excited radicals leading to the formation of these bonds:

$$M^* \rightarrow \begin{cases} R^* + \dot{C}H_2{-}CH{=}CH{\sim} \\ \rightarrow m + \dot{H} \end{cases} .$$

The hydrogen detected is formed in the molecular elimination reaction

$$M^* \rightarrow \begin{cases} \rightarrow H_2 + \sim CH{=}CH{-}CH{=}CH{-}CH{=}CH \sim \\ \rightarrow H_2 + \sim CH{=}C{=}CH{-}CH_2 \sim \end{cases} .$$

C–C bond dissociation reactions involving the main polymer chain take place:

$$M^* \rightarrow \begin{cases} \rightarrow \sim CH{=}CH{-}\dot{C}H_2 + \dot{C}H_2{-}CH{=}CH \sim & (3) \\ \rightarrow \sim CH{=}\dot{C}H + \dot{C}H_2{-}CH_2{-}CH{=}CH \sim & (4) \end{cases} .$$

It is believed[17,59] that the probability of process (3) is higher than that of process (4) owing to the fact that the C–C bond in the β-position is weaker (~231 kJ mol^{-1}). The strength of this bond is appreciably lower than that of the usual C–C bond (~374 kJ mol^{-1}) owing to the resonance stabilisation of the two allyl radicals formed on dissociation of the main polymer chain[99].

It is thought possible that the double bond migrates with formation of a conjugated diene double bond[59]:

$$M + h\nu \rightarrow \sim \dot{C}H{=}CH{-}CH_2{-}CH{=}CH \sim + h\nu \rightarrow \sim CH{=}CH{-}CH{=}CH \sim .$$

The primary process can also be the formation of cyclopropane groups:

$$M + h\nu \rightarrow \sim CH_2{-}\dot{C}H{-}\dot{C}H{-}CH_2 \sim \rightarrow \sim CH_2{-}\dot{C}H{-}CH_2{-}\dot{C}H_2 \sim \rightarrow \quad (5)$$
$$\rightarrow \sim CH_2{-}\underset{\displaystyle CH_2}{\overset{\displaystyle CH}{\diagdown\!\diagup}}{-}CH \sim .$$

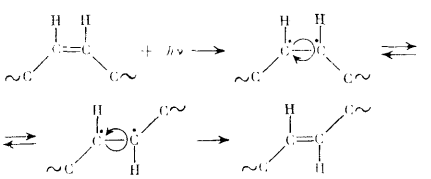
This process occurs in the photolysis of PB and PI by 253.7 nm light, assumed to proceed via the triplet state[98,100], and in the triplet sensitisation of but-1-ene in the gas phase by mercury atoms[15]. Cyclopropane groups can also be formed in the isomerisation of the allyl radical:

$$\sim CH_2{-}CH{=}CH{-}\dot{C}H_2 \rightarrow \sim CH_2{-}\underset{\displaystyle CH_2}{\overset{\displaystyle CH}{\diagdown\!\diagup}}{-}\dot{C}H \quad . \quad (6)$$

Cross-links are formed mainly in radical recombination processes and possibly also in the interaction of radicals with double bonds:

$$R + \sim CH{=}CH \sim \rightarrow \text{cross-link} + R' .$$

It has been established[98] that *cis–trans* isomerisation takes place in the photolysis of PB by 123.6 nm light. It has been suggested that this process proceeds as follows: when a light quantum is absorbed, the π-electrons are transferred to the antibonding orbital, whereupon there is a possibility of free rotation leading to a change in the steric configuration[99]:



A similar process should apparently be observed also in photolysis by light at 147 nm, since it has been noted[100] that *cis–trans* isomerisation proceeds also in the photolysis of PB and PI by light at λ = 253.7 nm with a quantum yield of ~0.04.

The difference between the yields of reactions involving the consumption of double bonds in photolysis by 147 and 123.6 nm light is striking (Table 14). It is believed to be caused by the ionisation of double bonds by 123.6 nm light, in contrast to 147 nm irradiation. The ion–molecule mechanism of the cross-linking of PB and PI in photolysis by light at λ = 123.6 nm has been considered:

$$M + h\nu \rightarrow \sim CH_2{-}\dot{C}H{-}\overset{+}{C}H \sim + e^- ,$$
$$\sim \dot{C}H{-}\overset{+}{C}H \sim + M \rightarrow \sim CH_2{-}\overset{+}{C}H \sim + R ,$$
$$\sim CH_2{-}\overset{+}{C}H \sim + \sim CH{=}CH \sim \rightarrow \sim CH_2{-}\underset{\displaystyle \sim \overset{+}{C}H{-}CH \sim}{\overset{\displaystyle |}{CH}} \sim .$$

This is followed by further chain propagation.

Table 14. The quantum yields of the main processes in the photolysis of polybutadiene and polyisoprene on irradiation with 147 and 123.6 nm light.

Process	Polybutadiene		Polyisoprene	
	147 nm	123.6 nm	147 nm	123.6 nm
Consumption of individual double bonds	0.28 [59]	1.3 [59]; 1.53 [98]	0.24 [59]	1.3 [59]
cis–trans-Isomerisation	—	0.25 [98]	—	—
Formation of H_2	0.019 [59]	0.023 [59]	0.015 [59]	0.022 [59]
Formation of intermolecular cross-links	0.012–0.024 [56]	0.027–0.056 [56]	0.008–0.03 [56]	0.048–0.063 [56]

Note. The numbers in square brackets denote references (Ed.of Translation).

It has been postulated[56] that the free-radical mechanism of cross-linking determines the formation of a gel in photolysis by 147 nm light, while in photolysis by 123.6 nm light the ion–molecule cross-linking mechanism should play a decisive role. The large difference between the yields of the cross-linking and double bond consumption reactions is striking, although, according to both the free-radical and ion–molecule mechanisms, these quantities should be similar. The higher overall quantum yield (>1)† (Table 13) in photolysis by 123.6 nm light indicates a chain mechanism of the destruction of double bonds.

The yields of the cross-linking reaction are much lower than these values, which makes it necessary to seek additional double bond destruction processes apart from intermolecular cross-linking. It has been suggested[17,56,59] that there exist two types of such processes: intermolecular cross-linking with formation of cyclopropane groups [processes (5) and (6)] and the formation of multiple intermolecular cross-links in the same pair of macromolecules, which should be promoted by chain processes due to the migration of a charge or a radical. The ratio of the rates of these processes and the number of cross-links in the pair of macromolecules probably depend on the type of active radiation: on passing from photolysis by 147 nm light to photolysis by 123.6 nm light, the yield of the double bond consumption reaction increases by a factor of 5–6 and the yields of the cross-linking reactions increase only by a factor of two.

V. PHOTOCHEMICAL REACTIONS OF CERTAIN POLYMERS INVOLVING OXYGEN

The influence of vacuum ultraviolet light in the wavelength range ~110–220 nm on polymers in the presence of oxygen has been investigated in several studies[101–104].

†Probably >0.1 (Ed.of Translation).

Thus a silicone rubber, poly(vinyl chloride) (PVC), and poly(methyl methacrylate) (PMMA) have been irradiated with the light of a hydrogen discharge[102]. During photolysis by radiation *in vacuo* in the course of approximately 100 h, no changes in the irradiated films were detected by infrared spectroscopy. However, during photolysis the films changed colour, particularly the PVC films, and ceased to dissolve in solvents, which indicates the formation of intermolecular cross-links. After the addition of small amounts of oxygen to the photochemical cuvette, the absorption band due to carbonyl groups appeared in the infrared spectra.

PVC, PMMA, polystyrene (PS), and polycarbonate (PC) films 100–150 nm thick have been irradiated with light at λ = 110–200 nm in an atmosphere of nitrogen[101]. It was established that, on irradiation, the optical densities of the PVC and PMMA specimens decrease fairly appreciably in the first 15 min and then, having attained ~50% of the initial value, no longer change. The optical densities of PS and PC change very insignificantly during irradiation for 1.5 h. The irradiated sections of all four polymers become insoluble in solvents which are effective for the initial non-cross-linked polymers.

Table 15. Some parameters of the decomposition of polymers [rate of decomposition v (nm min^{-1}), quantum yield Φ, and consumption of O_2 molecules in the decomposition of one unit n] on irradiation with light at $\lambda \cong$ 100–200 nm in an atmosphere of oxygen[103].

Polymer	v, nm min^{-1}	Φ	n
PVC	16	0.32	1
PMMA	10	0.24	1
PS	1.6	0.01	10
PC	1.5	0.005	20
PTFE	2.5	0.1	2

The kinetics of the decomposition of polymer films by light at 110–200 nm have been investigated[101,103] in an oxygen-containing medium. Table 15 presents the results of measurements of the rates of decomposition of PVC, PMMA, PS, PC, and polytetrafluoroethylene (PTFE). The following stable decomposition products of PVC, PMMA, PS, and PC were detected: CO_2, CO, and H_2O. A more involved mass spectrum containing the following ions was obtained for PTFE: F^+, CO^+, CO_2^+, COF^+, COF_2^+, CF_3^+, $C_2F_4^+$, $C_2F_5^+$, and $C_2F_4O_2^+$; other ions with a mass number m/e > 180 were also detected. The absence of a signal due to fragments resulting from the decomposition of the polymer chain in the mass spectra of polymers without fluorine and the low consumption of oxygen are apparently due to the activity of the decomposition products of these polymers: they settle on the walls of the reactor in the form of solid deposits. It has been suggested that the stable radicals $\sim CF_2CF(\dot{O}_2)CF_2\sim$ and $\sim CF_2CF_2\dot{O}_2$ participate in the PTFE decomposition reactions. The formation of such radicals on irradiation of PTFE with vacuum ultraviolet light (~120–160 nm) with subsequent exposure of the specimen to air has been detected by EPR.[104] The authors[104] believe that the peroxy-radicals detected are formed from central ($\sim CF_2\dot{C}FCF_2\sim$) and terminal ($\sim CF_2-\dot{C}F_2$) radicals under the influence of vacuum ultraviolet light.

VI. CONCLUSION

Thus the photolysis of two classes of hydrocarbons (including polymers) by vacuum ultraviolet radiation, mainly in the wavelength range 105–200 nm, results in the formation of electronically excited states due to the transitions $\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, and $n \rightarrow \pi^*$, Rydberg states are excited, and ionisation takes place.

In the photolysis of the compounds examined, both molecular and free-radical products can be formed in the photochemical process. The formation of primary products in an excited state is characteristic of olefins, which can lead to their subsequent dissociation in secondary processes. It has been noted for a number of substances that secondary fragmentation can be suppressed by increasing the pressure in the gas phase, by conversion into the liquid phase, and particularly by conversion into the condensed phase (polymers). A decrease of the yield of primary processes has also been noted for PE owing to the transition to the condensed phase and the formation of long-chain molecules.

Comparison of primary processes involving low-molecular-weight substances in the gas phase and polymers with a similar structure in the condensed phase shows that the primary processes are as a rule the same in both cases. This makes it possible to predict the photochemical processes in polymers on the basis of the results of the photolysis of low-molecular-weight substances in the gas phase. However, the analogy is not complete. Thus PIB gives rise to the formation of conjugated diene double bonds, which has not been noted for low-molecular-weight branched alkanes. This feature is apparently due to the regularity of the structure of the PIB macromolecules.

It is of interest to compare certain characteristics of the photolysis of polymers by vacuum ultraviolet light, i.e. by light corresponding to the intrinsic absorption band, and light at $\lambda \gtrsim$ 200 nm, when absorption is due to impurities or anomalies in the structure of the real macromolecule. In photolysis by light at $\lambda \lesssim$ 200 nm the quantum yields of products derived from the polymers investigated are in the range ~0.1–1, while in the photolysis of the same polymers by light at $\lambda \gtrsim$ 200 nm the quantum yields are lower by a factor greater than ten[99]. Whereas the photolysis of PE, PP, and PBI by vacuum ultraviolet radiation involves the occurrence of molecular processes, in photolysis by light at $\lambda \gtrsim$ 200 nm free-radical processes take place. Since the absorption coefficients of polymers in the vacuum ultraviolet region are high (~10^3–10^6 cm^{-1}), the photochemical reactions take place under the influence of this light in a thin surface layer (~0.1–100 μm) and the energy absorbed in this layer is high, which leads to high degrees of conversion. As a result of this, a non-trivial phenomenon has been observed for a series of polymers (PP, PIB, PB, and PI): photo-etching of the surface layer, particularly in the presence of oxygen.

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