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Kinetics of the Photochemical Oxidation of Polyolefins

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The review gives a general and systematic account of data on the kinetics of the thermal and photochemical oxidation of polyolefins and the kinetic parameters obtained by different investigators are compared. The kinetic parameters found at different temperatures and extrapolated to natural conditions are quoted and kinetic curves for the photochemical oxidation of polyolefins are calculated. The curves agree satisfactorily with experimental data on the accumulation of polyolefin photochemical oxidation products.
The bibliography includes 104 references.

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I. INTRODUCTION

Polyolefins are polymers which consist of weakly branched hydrocarbon molecules. The most common and industrially most important examples of this series of polymers are polyethylene (PE) and polypropylene (PP).

On ageing, the mechanical properties of articles made of these polymers are impaired, they become brittle, yellow-coloured, and covered in cracks, their tensile strength falls, etc. The main cause of these changes is oxidative degradation of the polymer[1].

According to modern ideas, the oxidation of polymers is a degenerate branched radical chain process, the principal stages of which are initiation of the oxidation chains, their propagation and termination, the formation of a degenerate-branching agent, and degenerate-branching of the chains by this species. The characteristic features of the mechanisms of each of these stages at high temperatures (120—150°C) have been fairly well investigated. The branching agent is a peroxide formed in the chain propagation step. In air, alkyl radicals are largely converted into peroxy-radicals, which are responsible for the propagation of the oxidation chain. Chain termination occurs in the peroxy-radical disproportionation step with formation of alcohols and carbonyl compounds. The polymeric molecule is ruptured in the chain propagation stage, during the decomposition of the peroxy-radicals, and possibly in the branching stage during the decomposition of the hydroperoxide[2]. In the case of a pure polyolefin, the overall process is satisfactorily interpreted as a degenerate-branched chain reaction with quadratic destruction of active centres[2].

When polymers are used close to room temperature, the rate of chain branching due to the thermal decomposition of the peroxide becomes low due to the high activation energy for this reaction (about 30 kcal mole^{-1}). Under these conditions, the photochemical reactions in the polymer begin to play an important role. The oxidation products of polyolefins absorb light much more effectively than the initial polymeric molecule. Therefore one may expect that the photochemical oxidation of polyolefins is also a degenerate branched chain process in which the initiation and chain branching steps involve light quanta.

At the beginning of the present review, each stage of the process is considered separately and then the results of the treatment are compared with the macroscopic relations observed experimentally.

II. SENSITISED PHOTOCHEMICAL OXIDATION OF POLYOLEFINS

A saturated hydrocarbon molecule of any length and with any degree of branching does not absorb light at wavelengths above 200 nm, i.e. does not absorb sunlight reaching the surface of the earth. Fig. 1 presents the absorption spectrum of saturated hydrocarbons and the spectral composition of sunlight on the earth's surface† and at the limit of the atmosphere. It shows that the spectra hardly overlap, i.e. pure olefins should not be decomposed by sunlight and the reason for their chemical degradation must be some light-absorbing impurities.

Probably all the impurities present in polymers can be divided into two groups. Firstly, these are extraneous impurities which enter the polymer in some way: the residues from the catalyst, impurities sorbed by the polymer in the course of its manufacture and use, special additives to polyolefins, fillers, thermostabilisers, etc. Secondly, these are polymer reaction products: peroxides, carbonyl compounds, olefinic compounds, etc. Impurities of the first type can initiate the photochemical oxidation of the polymer, while those of the second type are responsible for degenerate chain branching during photochemical oxidation.

Fig. 2 presents the absorption spectra of the main impurities usually detected in polyolefins. They all absorb light at longer wavelengths much more effectively than polyolefins. Many of these impurities are photochemically active. For example, thermostabilisers

† The spectrum of sunlight in space in the earth's orbit was taken from Ref. 4 and the emission spectrum of the sun in the upper layers of the atmosphere and for different positions of the sun above the horizon was calculated from the absorption spectrum of ozone, which absorbs the ultraviolet component of the sun's spectrum.

usually contain phenols or aromatic amines. Compounds of both classes are known to be effective photosensitisers[3]. Attention has been drawn[3] to the fact that the photochemical degradation of polyolefins is much faster in the presence of aromatic hydrocarbons sorbed from air. Fig. 2 shows that the extinction coefficients of these substances are very large and their photosensitising activity is also well known.

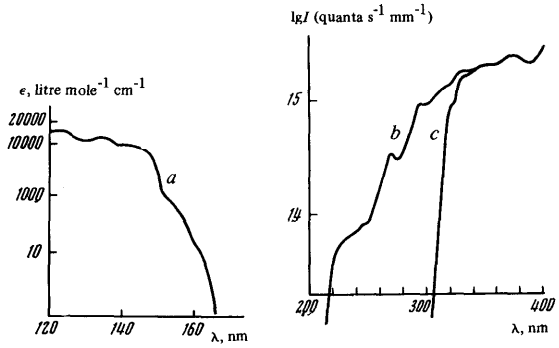


Figure 1. Absorption spectrum of n-butane (*a*) and the spectral composition of sunlight at the limit of the atmosphere (*b*) and on the surface of the earth (*c*).

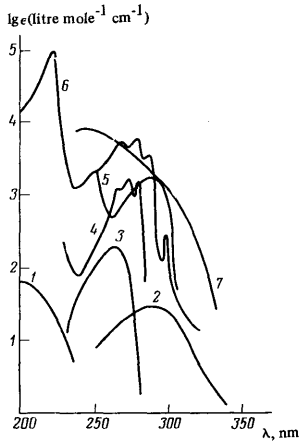
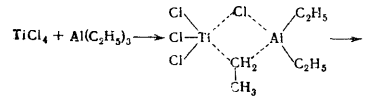


Figure 2. Absorption spectra of the main impurities in polyolefins: 1) acetic acid; 2) aliphatic ketones; 3) benzene; 4) phenol; 5) aniline; 6) naphthalene; 7) $Ti(OC_4H_9)_4$.

In a number of studies, it has been asserted that the main cause of the photochemical degradation of polymers is the presence of residues from the catalyst in the polymer. However, the photochemical activity of these compounds has not yet been investigated in detail. Moreover it is difficult to specify an individual substance responsible for their photochemical activity[4,5]. One can only point to studies where it has been shown that the presence of the catalyst at a low concentration accelerates the photochemical degradation of the polymer[5-8].

Ziegler—Natta catalysts, which are nowadays most widely employed, consist of a mixture of compounds of variable-valence metals (titanium, chromium, molybdenum, vanadium, etc.) and organometallic compounds, mainly aluminium derivatives. The principle of their action can be illustrated by the following scheme[9]:



$$\longrightarrow (C_2H_5)_2AlCl + Cl_3Ti{\cdots}C_2H_5 \longrightarrow TiCl_3 + C_2H_5^{\cdot}$$

Catalysts are removed from polymers by washing them with alcohols (isopropyl, butyl, etc. alcohols) but part of the catalyst nevertheless remains in the polymer. According to the data of Balabau and Preisler[10], less than 0.005% (0.001 M) of titanium and aluminium derivatives remains in polypropylene purified in this way. The residual catalyst has a fairly high extinction coefficient at about 300 nm (Fig. 2). The absorption of a light quantum may result in the formation of free radicals by the reaction[6]

$$M^{n+}X^{\cdot} + h\nu \rightarrow M^{+(n-1)} + X^{\cdot}$$

The occurrence of this reaction is postulated[6] by analogy with the corresponding reactions in a liquid, usually aqueous solution[11]. Neither the quantum yield of reactions of this kind nor details of the mechanism have been investigated.

The concentration of impurities in the polymer is of the order of 10^{-2}—10^{-3} M, i.e. it corresponds approximately to the concentration in the polymer of macromolecules with a molecular weight of 10^5—10^6. Thus if the impurities were decomposed in the photosensitisation step, the molecular weight of the polymer would decrease at most by a factor of several units and polymer degradation would then stop. The rate of the degradation process would then decrease with time. In fact, according to the literature, the accumulation of carbonyl groups, for example in the photochemical oxidation of polypropylene[12-14], is autocatalytic and the initial rate of these processes is very low. When the residual catalyst is introduced at a concentration up to 0.03 M (Ti), the photochemical reaction remains autocatalytic[10].

The data quoted show that impurities can have a significant influence only in the initial stage of the process, while at advanced stages of the latter impurities of the second kind, i.e. products formed in the course of the degradation of the polymer, play the main role.

III. DEGENERATE CHAIN BRANCHING IN THE PHOTOCHEMICAL OXIDATION REACTION (PHOTOLYSIS OF THE POLYOLEFIN OXIDATION PRODUCTS)

As mentioned above, degenerate chain branching in the photochemical oxidation of polyolefins can involve hydroperoxides and ketones. For a better understanding of this stage of the process, we shall consider the photolysis of these compounds.

1. Photochemistry of Aliphatic Ketones

The mechanism of the photolysis of low-molecular-weight aliphatic ketones has been investigated very intensively and is now believed to be largely understood.

Aliphatic ketones have an absorption maximum in the range 270—290 nm, their absorption bands extending up to 320—330 nm (for example the molar extinction coefficient of diethyl ketone is $\epsilon_{313} = 2.07$). This absorption is due to a forbidden singlet—singlet transition with electron transfer from the non-bonding n orbital located on the oxygen atom to the more delocalised π^* orbital of the carbonyl group. The same transition probably occurs in a polymer containing keto-groups. For example, the maximum in the absorption spectrum of the ethylene—carbon monoxide copolymer (1% CO), which has the same physical properties as low-pressure polyethylene, is very close to the absorption maximum of an aliphatic ketone[15] (Fig. 3).

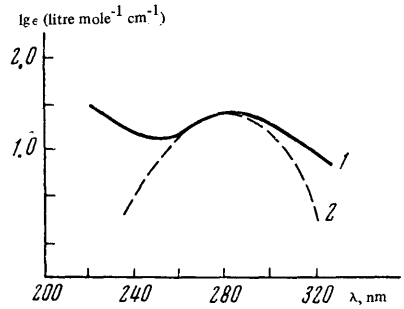


Figure 3. Absorption spectra of the ethylene—carbon monoxide (1%) copolymer (curve *1*) and of the ketone $CH_3(CH_2)_{10}CO(CH_2)_{10}CH_3$ (curve *2*) in heptane at 80°C.

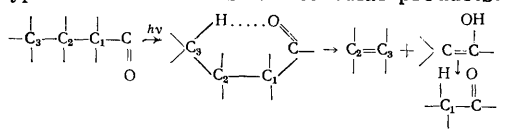
A very short time after the absorption of a light quantum, of the order of 10^{-11} s in the condensed phase, the excited electronic singlet state $^1(n, \pi^*)$ of carbonyl compounds is thermally equilibrated with the medium, whence the molecules can pass to the triplet state $^3(n, \pi^*)$ or can dissipate the excess energy in the form of heat.

Carbonyl compounds in the singlet and triplet excited states can also enter into chemical decomposition, addition, isomerisation, etc. reactions.

Numerous studies on the photolysis of ketones have shown that there are two main pathways to their decomposition, which are referred to in the literature as the Norrish type I and II reactions. The decomposition of ketones via the type I reaction results in the formation of free radicals:

$$R_1{-}\underset{\underset{O}{\|}}{C}{-}R_2 \xrightarrow{h\nu} R_1{-}\underset{\underset{O}{\|}}{C}\cdot + R_2^{\cdot} \quad \text{or} \quad R_1^{\cdot} + R_2^{\cdot} + CO$$

which can then react with the solvent. The decomposition via the type II reaction leads to molecular products:



Since decomposition via the type II reaction requires the formation of an intermediate six-membered complex, only ketones with at least one hydrogen atom in the γ-position relative to the carbonyl group can decompose via this pathway, i.e. in polyolefins with C=O groups in the main chain there is a possibility of an intramolecular hydrogen transfer in which an olefin and an enol are formed, the latter in its turn giving rise to a ketone with a shorter chain.

Hartley and Guillet[16] investigated the photolysis of model aliphatic ketones R—C(O)—R, with the chain length of the alkyl group ranging from C_7 to C_{43}, under the influence of light at a wavelength of 313 nm. It was shown that the decomposition quantum yields φ_I and φ_{II} depend on the chain length of the alkyl group in the ketone, viscosity, and temperature. Fig. 4 shows the variation of φ_I and φ_{II} with the chain length of the alkyl group. It is seen that an increase in the length of the carbon atom chain entails a decrease of φ_I and φ_{II}, φ_I reaching a limiting value at C_{40} and φ_{II} falling rapidly with increase of chain length and reaching 0.06 for the ketone containing 43 carbon atoms. After this, φ_{II} decreases much more slowly reaching a value of 0.025 in the polyethylene copolymer containing 1% CO.

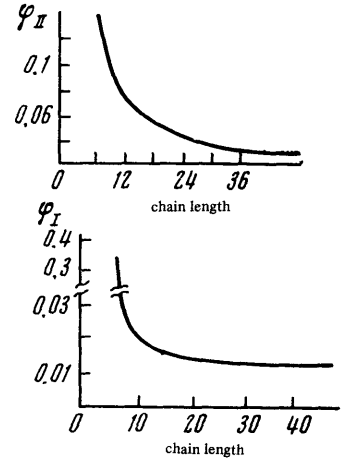


Figure 4. Variation of the quantum yields φ_I and φ_{II} of the decomposition of ketones with the length of the chain of the alkyl group (in liquid paraffin at 70°C).

The decrease of the quantum yield is probably caused by an increase in the probability of radiationless dissipation of energy with increase of the number of atoms in the ketone molecule. Table 1 presents the temperature variation of the quantum yields for the formation of the photochemical decomposition products of pentadecan-8-one, which decomposes according to the mechanism

$$CH_3(CH_2)_5CO(CH_2)_6CH_3 \xrightarrow[II]{h\nu} CH_2{=}CH(CH_2)_5CH_3 + CH_3CO(CH_2)_6CH_3,$$

$$CH_3(CH_2)_5CO(CH_2)_6CH_3 \xrightarrow[I]{h\nu} CH_3(CH_2)_6\cdot + \cdot CO(CH_2)_6CH_3$$

$$CH_3(CH_2)_6\cdot + CO \rightarrow CH_3(CH_2)_6CH_3 \cdot$$

The data in Table 1 show that the quantum yield of the type II reaction does not depend appreciably on temperature ($E_{act} \simeq 1$ kcal mole^{-1}). On the other hand, the quantum yield in the formation of heptane via the type I reaction increases fairly rapidly with temperature ($E_{act} = 4.8$ kcal mole^{-1}). The results can be explained bearing in mind that the type I reaction involves the dissociation of a bond in the molecule with formation of radicals. Consequently it should depend on temperature, albeit not as

markedly as the analogous thermal bond dissociation. An essential requirement for the type II reaction is the formation of a six-membered complex, which depends only on the extent to which the internal rotation of the groups in the molecule is free and this in turn is independent of temperature above the glass point of the polymer. φ_I and φ_{II} were found to be virtually independent of viscosity, which was varied from 0.28 to 9.2 cP.

Table 1.

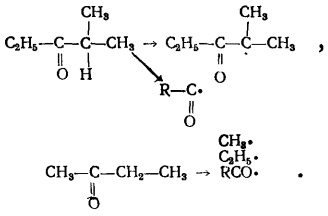
T, °C	$\varphi_I \times 10^2$	φ_{II}	φ_{II}
	heptane	hex-1-ene	nonan-2-one
30	0.22	0.066	0.067
60	0.42	0.068	0.067
90	0.87	0.091	0.086
120	1.4	0.087	0.091
145	1.9	0.092	0,102

Table 2.

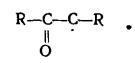
T, °C	Quantum yield of rupture reactions $\varphi_I + \varphi_{II}$	Quantum yield for accumulation of vinyl groups	
		φ_{II}	φ_I
120	0.05	0.025	0.025
90	0.04	0.025	0.015
25	0.028	0.025	0.003
—25	—	0.025	—
—50	—	0.020	—
—68	—	0.013	—
—95	—	0.005	—
—150	—	0.000	—

Both singlet and triplet states are involved in the photolysis of aliphatic ketones. Thus the photochemical decomposition of undecan-6-one is inhibited by cyclooctadiene (COD), a triplet acceptor, to an extent not greater than 55%;[17] similar results were obtained for certain other ketones and acceptors in studies[18-23] where it was shown that approximately 60—90% of the reactions in the photolysis of aliphatic ketones involve triplet levels. These results suggest that an appreciable proportion of the ketones decompose with participation of triplet states, but the mechanism of the decomposition, which is not inhibited by triplet acceptors, remains obscure.

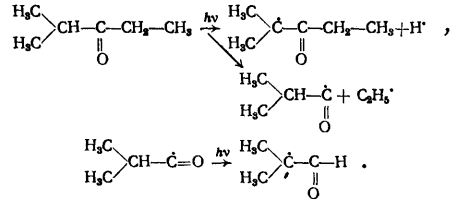
At low temperatures (77°K) the photochemical decomposition of aliphatic ketones (at wavelengths from 260 to 360 nm) leads to the formation of radicals at an appreciable concentration[24]. For example, the photolysis of ethyl isopropyl and ethyl methyl ketones results in the formation of radicals via the reactions



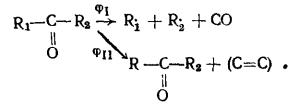
When specimens are irradiated with light at a wavelength higher than 400 nm and heated to −140°C, the singlet line of the R—Ċ=O radicals in the ESR spectrum disappears and only radicals in which the C=O group and the unpaired electron are separated remain:



On the basis of these data, the following mechanism has been proposed[24] for the photolysis of aliphatic ketones with dissociation of the C—C bonds adjoining the carbonyl group:



Thus analysis of data for the photolysis of low-molecular-weight aliphatic ketones made it possible to predict certain photochemical properties of polymeric ketones. The $R_1-\overset{\overset{O}{\|}}{C}-R_2$ polymeric ketone should probably decompose via type I and II Norrish reactions like aliphatic ketones:

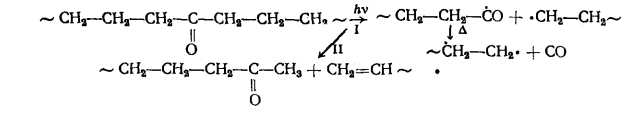


All polymeric ketones should decompose at room temperature via the type I reaction with a quantum yield of 0.05—0.1. Only ketones capable of forming the necessary six-membered complex, i.e. having a hydrogen atom joined to the carbon atom in the γ-position relative to the C=O group, decompose via the type II reaction.

On reducing the temperature, the quantum yield of the type I reaction changes slowly and the activation energy is 5 kcal mole^{-1}. The type II reaction depends significantly less on temperature but its contribution diminishes sharply with increase of the length of the R_1 and R_2 groups. Its importance can be appreciable only above the glass point of the polymer, since at lower temperatures the free rotation of the groups in the units of the macromolecule is inhibited, or in the decomposition of ketones with a C=O group close to the end of the polymer chain when at least one of the radicals formed is small.

The breaks in the polymer molecule lead to a significant change of the molecular weight of the polymer in both reactions only when the recombination of radicals formed in the type I reaction is ruled out. These conclusions have been confirmed quantitatively by the results of studies on the photolysis of pre-oxidised polypropylene and of the ethylene—carbon monoxide copolymer[15].

The physical properties of the ethylene—carbon monoxide copolymer containing 1—9% of carbon monoxide are the same as those of a low-pressure polyethylene. The polymer was irradiated with monochromatic light at a wavelength of 313 nm in decalin solution, and a decrease of its molecular weight, evolution of carbon monoxide, and the formation of vinyl groups were observed. These results were accounted for by the following reactions in the polymer:

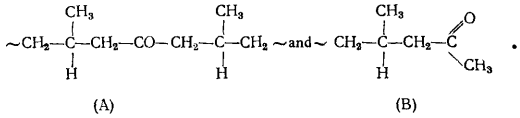


Carbon monoxide and polymeric radicals are formed by the type I reaction and the type II reaction gives rise to terminal ketones and vinyl groups. Polymer chains are ruptured in both reactions. In solution the polymeric radicals abstract a hydrogen atom from the solvent molecule and do not recombine with one another, so that the quantum yield of the rupture reactions is equal to the sum of the quantum yields of both reactions. The quantum yield of the type II reaction was determined from the change in the concentration of vinyl groups. Table 2 presents the relation between the quantum yields of both reactions and temperature.

Table 2 shows that the quantum yields of the type I reaction becomes significant above 25°C, where the quantum yield of the type II reaction is independent of temperature. This can be explained as follows. It has been established[25,26] that at −30°C free rotation about the C—C bond in polyethylene is hindered and hindered joint rotation of at least three units arises. At −120°C, the joint rotation is also inhibited. Since the properties of the copolymer are similar to those of low-pressure polyethylene, retardation of free rotation about the C—C bond can also be expected near −30°C, the probability of the formation of a six-membered complex and hence φ_{II} diminishing. At −120°C, φ_{II} becomes zero. Above −30°C, where rotation is not hindered, φ_{II} should be independent of temperature, which is in fact observed experimentally.

In the solid polymer the quantum yield of the formation of vinyl groups at 25° and 90°C does not differ from φ_{II} in solution[15]. This can be explained by the fact that the destruction of radicals formed in the type I reaction does not involve the formation of double bonds (the radicals do not disproportionate but recombine). Therefore in this case the quantum yield of the rupture reactions is probably determined by φ_{II}. Unfortunately Hartley and Guillet[15] did not make such measurements. The type I and II reactions probably also occur in the photolysis of poly(methyl vinyl ketone) containing the C=O group in the side chain[27]. The quantum yield of the type I reaction, determined from the evolution of carbon monoxide and methane, increases with temperature, as for the copolymer (25—80°C), and the occurrence of the type II reaction was established on the basis of the increase of the optical density in the range 220—230 nm, which was attributed to the accumulation of double bonds.

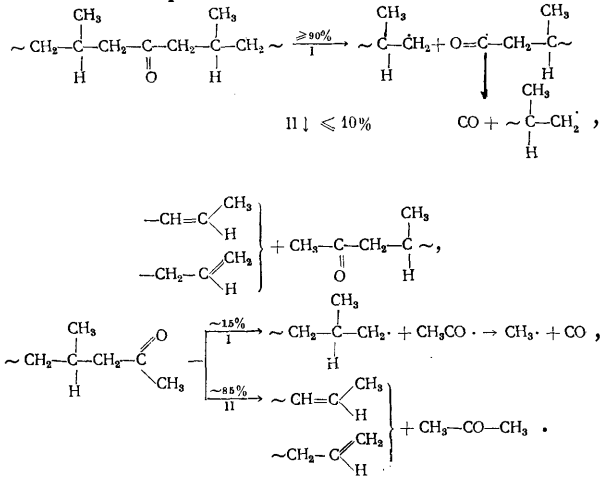
It has been shown[17] that at 80°C the triplet quenching agent COD retards the photochemical degradation of the ethylene—carbon monoxide copolymer in solution and the accumulation of vinyl groups in the solid phase by a factor not greater than two. In contrast to the ethylene—carbon monoxide copolymer, where the carbonyl groups were distributed only in the centre of the polymer chain, preoxidised (225°C) polypropylene contains two main types of keto-groups[28]:



(A) (B)

In the photolysis of oxidised polypropylene containing type (A) and (B) keto-groups, a decrease in the weight of the polymer was observed and the composition of the volatile products and the change of the optical density at the absorption maxima of the fragments (A) and (B) (1718 and 1726 cm^{-1} respectively) were analysed. The quantum yields for the decomposition of both ketones were approximately identical, amounting to 0.07 and 0.08 respectively.

Analysis of the volatile products (CH_4, CO, CO_2, C_2H_6, etc.) led to the conclusion that the ketones A and B decompose via the Norrish type I and II reactions, the ketone (A) decomposing mainly into radicals and the ketone (B) into molecular products:



This set of reactions provides a satisfactory description also of the kinetics of weight loss by the polymer.

Despite the fact that the photolysis of ketones involves the rupture of the chain, an appreciable decrease of viscosity on irradiation was not observed[28]:

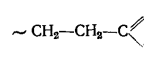
η before irradiation = 0.63; $M_v = 5.2 \times 10^4$,

η after irradiation = 0.60; $M_v = 4.8 \times 10^4$.

The present authors' calculation of the quantum yield of the rupture reactions on the basis of these data is 4×10^{-3}, which is consistent with the fact that the chain is ruptured only on decomposition of the central ketone (A) via the type II reaction. The macroradicals formed from the ketone (A) via the type I reaction and following the abstraction of a hydrogen atom from the macromolecule by the methyl radical [formed from the ketone (B) via the type I reaction] probably recombine, which does not lead to a decrease of the molecular weight of the polymer.

As was to be expected, the quantum yield for the decomposition of the terminal ketone via the type II reaction is higher by a power of ten, since the mass of one of the radicals adjoining the carbonyl group is small. The quantum yield of the type (I) reaction determined by Carlsson and Wiles[28] also exceeds the quantum yield of this reaction in the ethylene—carbon monoxide copolymer. We believe this to indicate that the rupture of the copolymer in the type II reaction takes place closer to the end of the molecule; owing to a change in the molecular weight distribution, the quantum yield of the rupture reactions found by Hartley and Guillet[15] from the change in viscosity is not equal to the sum of the quantum yields of the type I and II reactions and the values of $\varphi_I + \varphi_{II}$ and φ_I quoted in Table 2 are significantly too low.

We explain the change in molecular weight observed during the photolysis of the ethylene—carbon monoxide copolymer in decalin by the fact that the macroradicals formed abstract a hydrogen atom from the solvent, which results in the formation of a macromolecule with a lower molecular weight. We have been unable to find any studies on the photolysis of preoxidised polyethylene, but, if the latter contains terminal ketones,



their decomposition via the type I reaction should lead to the formation of low-molecular-weight CH_3 radicals. The recombination of these radicals with the polymer macroradicals gives rise to molecules with a lower molecular weight and the quantum yield of the rupture reactions should be relatively high, since the probability that the methyl radical abstracts a secondary hydrogen atom from polyethylene is lower than the probability that it abstracts a tertiary hydrogen atom from polypropylene.

2. Photolysis of Hydroperoxides and Peroxides

The decomposition of dialkyl peroxides (dimethyl peroxide[29], diethyl peroxide[30,31], ethyl t-pentyl peroxide[29], di-isopropyl peroxide[32,33], t-butyl isopropyl peroxide[29], and di-t-butyl peroxide[34-40]) in the gas phase has been investigated most thoroughly. It has been established that even in the gas phase the absorption spectra of these peroxides do not exhibit any structure (Fig. 5). This suggests that the O—O bond is dissociated immediately on absorption of a light quantum, without proceeding via an intermediate excited state, and two free radicals are formed.

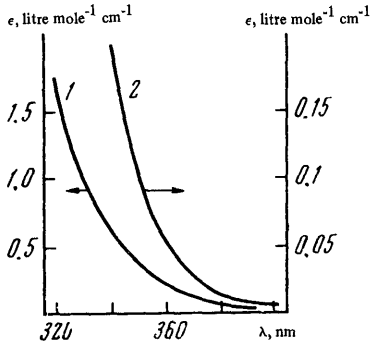


Figure 5. Absorption spectra of di-t-butyl peroxide (curve *1*) and t-butyl hydroperoxide (curve *2*).

The energy of the O—O bond in peroxides is less than 40 kcal mole^{-1}. Consequently, on irradiation with light at a wavelength of 254 nm, the excess energy of about 70 kcal mole^{-1} is distributed between two radicals. Therefore the absorption of each light quantum leads not only to the dissociation of the O—O bond but also to the formation of so called hot radicals carrying the excess energy.

The presence of a large energy excess in the radicals formed is confirmed by the analysis of the products of the photolytic decomposition of peroxides. Hot radicals readily decompose until they attain thermal equilibrium. For example, in the photolysis of di-t-butyl peroxide, acetone, methane, and ethane were detected in addition to other products; these can be accounted for by the following reactions:

$$(CH_3)_3CO^{\cdot *} \rightarrow CH_3^{\cdot} + CH_3COCH_3,$$

$$CH_3^{\cdot} + CH_3^{\cdot} \rightarrow C_2H_6 \text{ etc.}$$

McMillan[32], who investigated the photolysis of peroxides in the presence of nitric oxide (NO) as an inhibitor, reached the same conclusion. Apart from nitrites and nitrates, other products, mainly acetone, were detected in the peroxide decomposition products. On the hypothesis that only "non-hot" radicals react with the inhibitor and "hot" radicals decompose during this period, the fraction α of "hot" radicals formed in the photolysis of peroxides was determined. For example, $\alpha_{313} = 0.21$ and $\alpha_{254} = 0.6$ for di-isopropyl peroxide.

The characteristics of the photolysis of peroxides and hydroperoxides in solutions are largely the same as those of their decomposition in the gas phase. As in the gas phase, they decompose into radicals, probably without proceeding via an intermediate excited state. The absence of any long-lived excited state of the peroxide in the condensed phase is suggested to some extent by the finding that no investigation showed a retardation of their photochemical decomposition by any excited state quenching agents.

Nevertheless, the dependence of the composition of the photochemical decomposition products on the wavelength of the exciting light (Table 3) indicates the existence of hot species or complex pathways in the decomposition of peroxides by light of shorter wavelengths. The primary radical formed in the decomposition of dicumenyl peroxide (DCP) can decompose into acetone and a phenyl radical or into acetophenone and a methyl radical. This decomposition can occur in the primary photochemical step

$$[C_6H_5(CH_3)_2CO]_2 + h\nu \rightarrow \begin{cases} C_6H_5C(CH_3)_2O^{\cdot} + CH_3COCH_3 + C_6H_5^{\cdot} \\ 2C_6H_5(CH_3)_2CO^{\cdot} + 2CH_3^{\cdot} \text{ etc.} \end{cases}$$

Table 3. Yield of the main products of the decomposition of DCP at 20°C [42] as a percentage of the peroxide decomposed.

Decomposition product	Solvent			
	n-hexane		CCl_4	
	wavelength, nm			
	313	254	313	254
Dimethylbenzyl alcohol	95—100	90—95	—	—
Acetophenone	2	4	95—100	30
Acetone	—	—	5	70

The principal distinctive feature of the photochemical decomposition of peroxides in the condensed phase is a significant influence of the solvent on the composition of the decomposition products and the occurrence of induced decomposition of peroxides. For example, a study has been made[41,42] of the decomposition of t-butylhydroperoxide (TBHP) and DCP in n-hexane and carbon tetrachoride. Tables 3 and 4 present the compositions of the photolysis products of these peroxides.

The authors explain the observed composition of the products by the fact that, in solvents capable of hydrogenating the radicals (n-hexane), an alcohol may be formed by the reaction between the alkoxy-radical and the solvent. The occurrence of these reactions leads to an increase in the quantum yield of the photolysis of the peroxide owing to the induced radical decomposition. For example, the quantum yield of the decomposition of TBHP is 3.9 in n-heptane and 1.57 in DCP.

According to Martin and Norrish[41], in a solvent incapable of hydrogenating the radicals (carbon tetrachloride) the induced decomposition of the peroxide is due to the radicals formed from it.

Table 4. Main decomposition products of TBHP at 20°C [41] at 313 nm.

Decomposition products in CCl_4	Yield, % of decomposed peroxide	Decomposition products in n-hexane	Yield, % of decomposed peroxide
Oxygen	41.7	Oxygen	7.1
Carbon monoxide	0.72		
Carbon dioxide	—	Formic acid	1.2
t-Butyl alcohol	97	Alcohol	156
Acetone	3.1	Acetone	8.3
Water	5.4	Water	21

The validity of the above mechanisms for the decomposition of peroxy-compounds is confirmed by ESR data. Despite numerous attempts by various investigators, alkoxy-radicals were not detected in the photolysis of peroxides and hydroperoxides[43-46]. In solvents with a mobile hydrogen atom, an ESR signal was observed in the photolysis of hydroperoxides and their mixtures with peroxides and was attributed to peroxy-radicals from the solvent or the hydroperoxide. In solvents incapable of hydrogenation, a signal due to the peroxy-radicals formed from the hydroperoxide was observed. The absence of signals due to alkoxy-radicals can be explained by their high reactivity which results in their conversion into peroxy-radicals. This is illustrated by the data in Table 5, which lists, for clarity, the rate constants for the interaction of cumenyloxy- and cumenylperoxy-radicals with different substrates.

Table 5. Comparison of the rate constants for the interaction of hydroxy and peroxy-radicals.

Reaction	k, litre mole^{-1} s^{-1}	T°, C	References
RO· + cumene	$2.5 \cdot 10^8$	25	47
RO· + tetralinyl hydroperoxide	$2.0 \cdot 10^5$	25	48
RO· + cumene	0.64	57	49
RO· + tetralinyl hydroperoxide	12.0	67	49

In the photolysis of peroxides in aprotic solvents and sometimes at a low temperature in the absence of oxygen, radicals formed as a result of the decomposition of alkoxy-radicals are observed. For example, the signal due to methyl radicals formed by the reaction

$$(CH_3)_2C_6H_5CO\cdot \rightarrow CH_3\cdot + CH_3COC_6H_5$$

is observed in the photolysis of DCP at 77°K. Thus ESR data agree with the homolytic dissociation of the O—O bond as the primary step in the photolysis of the peroxide, with formation of alkoxy-radicals, which then enter into further reactions.

In certain cases, the ESR method makes possible a more detailed investigation of the step involving the decomposition of the peroxides into radicals[52]. Thus in the photolysis of acyl peroxides from peroxydisuccinic acid, peroxydiglutaric acid, and lauroyl, benzoyl, and acetylbenzoyl peroxides at 77°K (wavelength of irradiating light 300 nm), the ESR spectra consist of broad doublets which are attributed to radical pairs (RP). When a radical pair is exposed to a second light quantum, its constituent radicals emerge from the cage. A six-line spectrum due to the alkyl radicals R· is then observed. The formation of alkyl radicals from acyl peroxides under the influence of light proceeds via the following two-quantum mechanism:

$$R{-}\overset{\overset{O}{\|}}{C}{-}O{-}O{-}\overset{\overset{O}{\|}}{C}{-}R \xrightarrow{h\nu_1} RP \xrightarrow{h\nu_2} R\cdot + CO_2$$

$$[R{-}\overset{\overset{O}{\|}}{C}{-}O\cdot\cdot R]$$

Indeed, it has been established[50-52] that the yield of the radicals R· at 77°K in the photolysis of peroxides of aliphatic acids (butyric, lauric, caproic, and capric) is proportional to the square of the light intensity. Probably these results are related to the low mobility of the radicals in the solid matrix at liquid nitrogen temperature. At higher temperatures, the rate of photochemical decomposition of acyl peroxides is proportional to the light intensity and the fraction of acyl (70%) and alkyl (30%) radicals formed at 20—40°C is independent of temperature[53].

Table 6. Effect of sensitisers on the decomposition of peroxides.

Peroxide	Solvent	Sensitiser	Energy of sensitiser triplet level, kcal mole^{-1}	Effect
Benzoyl peroxide	benzene	acetophenone	73.6	+
ditto	"			
"	cyclohexane	benzophenone	68.5	+
"	benzene	"	68.5	+
"	"	*p*-chlorobenzophenone	68.5	+
"	"	2-acetonaphthone	59.3	+
"	"	penta-2,3-dione	54.7	—
"	"	benzil	53.6	—
"	"	fluorenone	53.3	—
"	"	anthracene	42	+
t-Butyl peracetate	cyclohexane	benzophenone	68.5	+
TBHP	CCl_4	acetophenone	73.6	+
"	CCl_4	benzophenone	68.5	+
"	benzene	"	68.5	+
"	chlorobenzene	"	68.5	+
CHP	cyclohexane	"	68.5	+
Di-t-butyl peroxide	"	"	68.5	—
ditto	benzene		68.5	—

3. Photosensitised Decomposition of Peroxides

Usually the dissociation of the O—O bond in the peroxide requires an energy of less than 40 kcal mole^{-1}. However, the absorption spectra of peroxides suggest that direct decomposition of peroxides requires a considerable amount of energy, of the order of 100—110 kcal mole^{-1} (300—250 nm). Therefore the decomposition of peroxides can occur in sensitised reactions when the sensitiser absorbs light at much longer wavelengths. Photosensitising reactions may be of two types. The absorption of light by the sensitiser can lead to the decomposition of the peroxide into radicals following energy transfer from the sensitiser to the peroxide[54-57] or the sensitiser can propagate the free radical-induced decomposition of the peroxide[58,59]. The sensitisers may be ketones[54,57], aromatic hydrocarbons[55], compounds with condensed nuclei[56], and variable-valence metals[60]. The commonest sensitisers of the

photochemical decomposition of peroxides are various ketones. Table 6 presents data for the effect of ketones on the decomposition of peroxides[56].

Probably sensitisation involves energy transfer from the triplet level of the sensitiser to the peroxide molecule, since the table shows that the sensitisers may be compounds with $n\pi^*$ and $\pi\pi^*$ excited states, where the energy of the triplet level is higher than 55 kcal mole^{-1}. Anthracene, which according to Tsvetkov et al.[68] sensitises the decomposition of peroxides via an excited singlet state with an energy of 76 kcal mole^{-1}, is an exception.

The mechanism of the sensitised decomposition of peroxides can probably be represented as follows[54]:

$$S \xrightarrow[\varphi']{h\nu} S^*$$

$$S^* \xrightarrow{k_d} S$$

$$P + S^* \xrightarrow{k_t} S + P^*$$

$$P^* \xrightarrow{k_d'} P$$

$$P^* \xrightarrow{k_r} \text{products},$$

where S is the sensitiser and P the peroxide. Hence

$$1/\varphi = \left(1 + \frac{k_d'}{k_r}\right)\left(1 + \frac{k_d}{k_t}[P]\right)$$

where φ is the quantum yield of the decomposition of the peroxide.

It has been found for the decomposition of benzoyl peroxide sensitised by benzophenone at room temperature that

$$\frac{k_d}{k_r} = 2.92 \text{ and } \frac{k_d}{k_t} = 0.03 \text{ mole litre}^{-1},$$

i.e. approximately 25% of the peroxide molecules decompose into radicals, while the remaining molecules return to the initial state as a result of the recombination of the radicals in the cage.

4. Photolysis of Polyolefin Hydroperoxides

The study of the photolysis of polymeric hydroperoxides is complicated by the fact that it is virtually impossible to obtain a polymer containing only hydroperoxy-groups[62]. In the low-temperature thermal and photochemical oxidation, hydroperoxy- and carbonyl groups accumulate simultaneously (Fig. 6). Therefore the photolysis of hydroperoxides is always accompanied by the photolysis of ketones.

The ratio of the molar extinction coefficients of hydroperoxides and ketones increases in the long-wavelength part of the spectrum (Fig. 7). Therefore the characteristics of the photolysis of hydroperoxides are clearly shown when they are irradiated with light at a wavelength longer than 365 nm. The decomposition of polypropylene hydroperoxide (PPHP) (at a concentration of 0.1—0.3 M) was observed[28] under these conditions, while the presence of ketones (0.01—0.1 M) in the polymer did not have a significant influence on this process.

As for low-molecular-weight hydroperoxides, the decomposition of polymeric hydroperoxides under the influence of light probably proceeds without an intermediate state. It involves the formation of two radicals, one of which (OH) can readily abstract a hydrogen atom from the polymer with formation of water. Indeed it has been shown[28], that, when PPHP is irradiated with light at a wavelength of 365 nm, each decomposed hydroperoxide molecule results in the formation of one water molecule.



Figure 6. Infrared absorption spectra of oxidised polypropylene films: *a*) oxidation in the melt at 225°C in air, thickness 37 μm: *b*) photochemical oxidation (λ = 370 nm) for 200 h, thickness 40 μm.

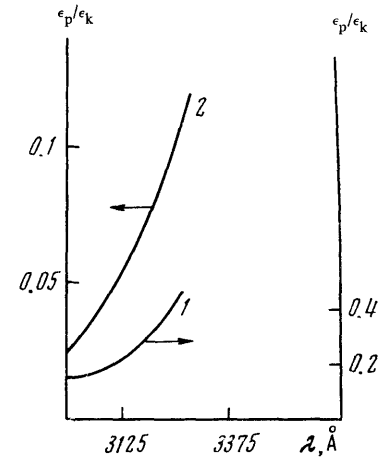
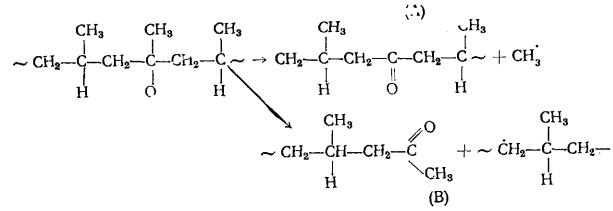


Figure 7. Dependence of the ratio of the molar extinction coefficients of the peroxides and 2,6-dimethylheptan-4-one on the wavelength of the light: 1) di-t-butyl peroxide; 2) t-butyl hydroperoxide.

The radical RO can abstract a hydrogen atom from the polymer with formation of an alcohol and can decompose via the following reactions:



Analysis of the photolysis products of PPHP leads to the conclusion that the ketones (A) and (B) are formed in approximately identical yields. The decomposition of

low-molecular-weight hydroperoxides in solution would result in the preferential formation of the ketone (B).[63,64] This is probably due to the reduced mobility of the high-molecular-weight skeleton of the molecules, which results in a decrease in the quantum yield of the main chain rupture reactions.

The amount of alcohol formed was determined by measuring the absorption in the region of 3400 cm^{-1} (corresponding to the hydrogen-bonded hydroxyls) before and after treating the film with SO_2 in order to remove hydroperoxides[65]. Since the concentration of the hydroperoxide greatly exceeds that of the alcohol, the error in the determination of the latter can be fairly large. However, the data of Carlsson and Wiles[28] indicate its presence in the photolysis products.

Data for the quantitative yield of water in the photolysis of PPHP and the weight loss by the specimen on decomposition of one mole of the peroxide (22 g $mole^{-1}$) show that the photolysis of each hydroperoxy-group gives rise to the formation of one OH· radical and that there is no induced decomposition of the hydroperoxide. This is also indicated by the low yield of the alcohol.

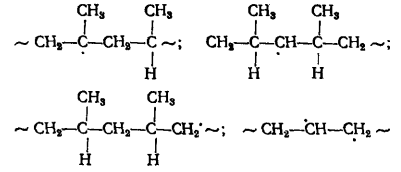
However, at a low temperature, the photolysis of this hydroperoxide is accompanied by the formation of the peroxy-radical $RO_2^{\cdot}$ [66] which can be formed in the absence of oxygen only as a result of the induced decomposition of the peroxide. However, details concerning the removal of oxygen dissolved in the polymer film are not given in Ershov's paper[66]. Possibly the $RO_2^{\cdot}$ radical is formed from the RO· or R· radical by reaction with oxygen. Thus the question of the induced decomposition of PPHP remains open. In the study of Carlsson and Wiles[28], the quantum yield of the decomposition of PPHP was found to be 4.0 ± 0.5, which the authors attribute to the difference between the molar extinction coefficients of PPHP and t-butyl hydroperoxide, the spectrum of which was used to determine the amount of absorbed light.

Sensitised decomposition by the ketones present in the polymer is not observed in the decomposition of PPHP under the influence of light at a wavelength of 365 nm. The quantum yield of the decomposition of the peroxide does not change when the concentration of ketones is altered almost by a power of ten. Thus the photolysis of PPHP occurs with a decomposition quantum yield close to unity with formation of alkyl radicals (polymeric or $CH_3^{\cdot}$), a ketone, and hydroxyl-radicals. The latter give a quantitative yield of water and alkyl radicals. The alkyl radicals probably do not recombine with one another, as shown by the small change in the molecular weight of the polymer during irradiation.

Very small amounts of methane and ethane, formed in different reactions of methyl radicals, were detected in the volatile photolysis products.

5. Radical Formation in Polyolefins

Degenerate branching of the photochemical oxidation chains occurs in those reactions of hydroperoxides and ketones where they give rise to free radicals. The formation of free radicals in the photolysis of polyolefins at low temperatures can be detected by the ESR method. However, sufficient data are not yet available for a quantitative comparison of the compositions of the photolysis products of oxidised polyolefins with the quantum yields for radical formation in these processes. The majority of studies on the amounts and structures of the radicals formed have been made with γ-irradiated specimens[68-70] and the effect of ultraviolet irradiation on polyolefins has been investigated very much less thoroughly[71-73]. When polyethylene is irradiated with ultraviolet light (77°K, total light of a mercury lamp) *in vacuo*, a signal, consisting of a mixture of a sextet (with a splitting of 21 G) and a quintet (with a splitting of 120 G) is observed. By analogy with data obtained for γ-irradiated specimens, the sextet is attributed to the radical $CH_2-\dot{C}H-CH_2$ and the quintet to the terminal radical $-CH_2-\dot{C}H_2$. The latter is detected only when polyethylene is irradiated by ultraviolet light; in particular it can be the radical formed by the photolysis of carbonyl compounds. When polypropylene is irradiated with ultraviolet light, a signal, consisting of two superimposed quartets with a splitting of 23 G is observed[24,67,71,73,74]. The narrower of the quartets refers to the methyl radical CH_3 and the second, broader, and more diffuse quartet refers to a mixture of radicals:



As with the γ-irradiated polymers, the fraction of each radical was not determined. When the irradiated polymer is heated to 178°K for 10 min, approximately 40% of the initial concentration of radicals remain, while on heating to room temperature all the radicals vanish[71]. On repeated irradiation of the specimen by light at wavelengths less than 270 nm, the broad signal of the polymeric radicals is partly converted into the narrower signal of methyl radicals[24].

When partly oxidised polypropylene is irradiated *in vacuo*[24,67,75], a complex asymmetric signal is observed, in which the singlet line of an oxygen-containing radical (RO· according to the authors) predominates. At the same time alkyl radicals are formed in the system. The fraction of each of these radicals and the quantum yields for their formation were not determined.

Unfortunately in all the studies quoted above the nature of the absorbing centres in the polyolefins and their role in the accumulation of radicals in the polymer were not investigated. Admittedly, the accumulation of radicals in oxidised polypropylene has been attributed[75] to the photolysis of hydroperoxides but the role of the keto-groups inevitably present in the polymer was not taken into account quantitatively.

Some investigators[3,24] believe that the absorbing centres in polyolefins responsible for radical formation are admixtures of aromatic hydrocarbons—naphthalene, anthracene, phenanthrene, etc., known to be photosensitisers of the ageing of polymers[4]. According to their data, the ESR spectrum obtained on irradiation of polypropylene with ultraviolet light in the presence of added phenanthrene agreed fully with the ESR spectrum of irradiated commercial polypropylene[24].

The differences between the ESR spectra of oxidised polypropylene and polypropylene containing photosensitising impurities are probably associated with the difference between the reactivities of the primary excited molecules or radicals obtained on low-temperature irradiation (77°K). The composition of the photolysis products of oxidised polypropylene shows that at higher temperatures methyl and alkyl radicals are also formed in the polymer[28].

In the photosensitised degradation of polypropylene, the initial rate of radical formation is proportional to the square of the light intensity[3,24]; this can be accounted for

by the transition of the impurity to a photochemically active state in a two-quantum process proceeding via a triplet state. The formation of radicals in polyolefins sensitised by aromatic compounds can probably be regarded as a result of transfer of excitation energy from the highest triplet levels of the sensitiser to the matrix or as a result of a two-quantum degradation of the sensitiser with subsequent reaction between the products and the polymer[76,77].

Naturally, similar two-quantum processes play a significant role at a low temperature and a high light intensity. The extrapolation of these data to natural conditions must be performed with much caution.

The free radicals formed in polyolefins under the influence of light can undergo various interconversions. Thus polymeric alkyl radicals can be converted into allyl radicals under the influence of the light of a xenonormercury lamp. The mechanism of this process has not so far been established. It is only known that the reaction is reversible and the reverse process was investigated in fair detail[78,79].

Photolysis of polymeric alkyl radicals by light at wavelengths less than 270 nm and low temperature leads to the formation of methyl radicals[24,89]. Photolysis of polymeric peroxy-radicals by light at wavelengths greater than 280 nm and also at low temperature yields an excited peroxy-radical which abstracts a hydrogen atom from the polymer and gives rise to a hydroperoxide and an alkyl radical via the reactions[89]

$$RO_2^{\cdot} + h\nu_{<280} \rightarrow RO_2^{*},$$
$$RO_2^{*} + RH \rightarrow [RO_2H + R^{\cdot}],$$

Under the influence of short-wavelength light (<280 nm), a peroxy-radical is probably formed in another excited state $RO_2^{*'}$ or the product is an exciplex decomposing into radicals:

$$RO_2^{\cdot} + h\nu_{<280} \xrightarrow{RH} [RO_2^{*'} + RH] \rightarrow \dot{R} + \dot{R}O + \dot{O}H \xrightarrow{+RH} 2\dot{R} + \dot{R}O + H_2O$$

i.e. in this case the photolysis of the peroxy-radical leads to branching of the oxidation chain.

Close to room temperature, appreciable concentrations of free radicals are not detected when polyolefins are irradiated by light under any conditions, i.e. the lifetimes of the radicals are then short. All the photochemical reactions of radicals are secondary photochemical processes and therefore their role can be appreciable only when the lifetime of the radical is long. Consequently the role of these processes in the photochemical oxidation of polyolefins is insignificant.

Thus one can regard it as established that free radicals are formed in the initiation steps and in the degenerate branching of the photochemical chain oxidation of polyolefins. There have not yet been any rigorous quantitative studies permitting the determination of the nature of the radicals and the quantum yields of the radical formation processes and enabling the role of the two-quantum processes and the photolysis of the polymeric radicals formed to be taken into account. However, the principal features of the reactions occurring in the degenerate branching step of the polyolefin photochemical oxidation chain are clear.

Hydroperoxides with an absorption spectrum of the type shown in Fig. 5 are decomposed with a quantum yield close to unity. The occurrence of sensitised decomposition of hydroperoxides has not been established exactly. The terminal and central aliphatic ketones have approximately identical absorption spectra (Fig. 3) and accumulate during the oxidation process in approximately equal concentrations. The average quantum yield of their photochemical decomposition is close to 0.1. Each ketone molecule decomposed yields on average of one alkyl radical and one molecule of another ketone with a single break in the chain of the polymer molecule.

In the presence of an excess of oxygen, all the alkyl radicals are converted into peroxy-radicals and, apart from the peroxy-radical, each alkoxy-radical gives rise to one ketone molecule and each hydroxy-radical yields a water molecule.

As a result, the degenerate chain branching stage in the photochemical oxidation can probably be represented as follows:

$$POOH + h\nu - PO + OH \xrightarrow{2O_2+2PH} H_2O + K + 2PO_2,$$
$$K + h\nu \xrightarrow{+O_2} PO_2 + K + S(=),$$

where POOH is the polymer hydroperoxide, PO and PO_2 are the alkoxy- and peroxy-radicals of the polymer, K is the ketone, and S(=) represents compounds with a double bond.

IV. PROPAGATION AND TERMINATION OF OXIDATION CHAINS

The chain propagation and termination stages in the photochemical oxidation of polyolefins probably do not differ from the analogous reactions in thermal oxidation and proceed without the involvement of light. Both these stages in the thermal oxidation of polyolefins have now been discussed in the literature[90-92], but we are not aware of analogous studies on photochemical oxidation. The oxidation chain propagation and termination stages can be best investigated separately in the course of sensitised oxidation. The kinetic mechanism of this process in the presence of an excess of oxygen can be represented by the following set of reactions:

$$\begin{aligned} &Y \xrightarrow{w_i} \dot{r} \xrightarrow{(O_2)} R \ (1) \text{ chain initiation},\\ &RO_2 + RH \xrightarrow{k_p} RO_2H + \dot{R} \ (2),\\ &R + O_2 \xrightarrow{k_p'} RO_2 \ (3) \text{ chain propagation},\\ &RO_2^{\cdot} + RO_2^{\cdot} \xrightarrow{k_t} (4) \text{ quadratic chain termination}, \end{aligned} \qquad (I)$$

where Y is a sensitiser decomposing into radicals at a rate w_i and k_p and k_t are the rate constants for chain propagation and termination.

The rate of oxidation w is determined by the rate of chain propagation. Therefore the rates of accumulation of hydroperoxides in reaction (2) and of absorption of oxygen in reaction (3) determine the value of w:

$$w = \frac{d(ROOH)}{dt} = \frac{d(O_2)}{dt} - nw_i = \frac{k_p}{\sqrt{k_t}}\sqrt{w_i}(RH)$$

where nw_i is a term taking into account the absorption of oxygen in the chain initiation step and its evolution in the chain termination.

However, it is hard to study the pure sensitised oxidation of polyolefins because it is difficult to introduce sensitisers capable of decomposing into free radicals at a sufficiently low temperature where the principal branching agents (hydroperoxides) do not decompose. There have been only two investigations where studies of this kind were made, namely the oxidation of atactic polypropylene and an ethylene—propene copolymer (with benzoyl peroxide as a sensitiser) in the temperature range 85—110°C [93] and the oxidation of low-pressure polyethylene (with DCP as an initiator) at 110—130°C.[94] The parameters $k_p/\sqrt{k_t}$ found are listed in Table 7.

Table 7. Rate constants for chain propagation and termination in the oxidation of polypropylene.

T, °C	k_p, litre mole^{-1} s^{-1} from Ref.95	k_t, 10^6 litre mole^{-1} s^{-1} from Ref.92	$k_p/\sqrt{k_t}$, 10^{-3} litre mole^{-1} s$^{-1/2}$			
			from Ref.92	from Ref.90	from Ref.93*	from Ref.94*
110	1.9	6.2	0.76	—	—	—
120	3.3	9.0	1.1	0.56	5.6	0.22**
130	4.2	9.0	1.4	0.86	—	—
140	4.6	6.6	1.8	1.4	—	—
E_a, kcal mole^{-1}	0	0	9	12.8	17	21.3

*These values of $k_p/\sqrt{k_t}$ were obtained in the sensitised oxidation of polymers.
**Low-pressure polyethylene.

The chain propagation and termination rate constants for polyolefins were obtained mainly in studies on degenerate branched-chain thermal oxidation. Degenerate branched-chain oxidation and unimolecular chain branching and quadratic termination reactions have been discussed[95]. The accumulation of the peroxide and the absorption of oxygen in such a system in the initial stages is described by a parabola in accordance with equations (5) and (6):

$$ROOH = ROOH_\infty (1 - e^{-\frac{k_0}{2}t})^2 \simeq ROOH_\infty \left(\frac{k_0}{2}t\right)^2, \quad (5)‡$$

$$\Delta O_2 = ROOH_\infty (2k_0 t - (5 - e^{-\frac{k_0}{2}t})(1 - e^{-\frac{k_0}{2}t}) \simeq ROOH_\infty \left(\frac{k_0}{2}t\right)^2, \quad (6)$$

where $ROOH_\infty$ is the limiting concentration of the peroxide and k_0 is the hydroperoxide decomposition rate constant.

It has been shown[90,91] that the thermal oxidation of polypropylene in the initial stage does indeed obey Eqns.(5) and (6) and at more advanced stages of the reaction, where the consumption of the polymer oxidised cannot be taken into account, the rate of oxidation decreases according to the law

$$\frac{1}{RH_0 - \Delta O_2} = 2\frac{k_p^2}{k_t}t + \text{const.} \quad (7)$$

Eqns. (5)—(7) make it possible to determine the same parameter $k_p/\sqrt{k_t}$ from the initial section of the kinetic curve and from the section where the concentration of the peroxide reaches a limiting level. The values of the parameter $k_p/\sqrt{k_t}$ found by these two procedures agree, which demonstrates the validity of the mechanism employed.

The absolute values of the constants k_p and k_t have been determined[84]. In the same study, the rate of steady-state autoxidation of polypropylene after the induction period was investigated. Under these steady-state conditions, measurements were made of the rate of absorption of oxygen $(dO_2/dt)_s$ and of the concentration of the hydroperoxide $(ROOH)_s$ and it was found that the decomposition of the peroxide in the formation of two radicals:

$$k_p = (-dO_2/dt)_s/(RO_2)(RH),$$
$$k_t = (-dO_2/dt)_s/2(RO_2)^2,$$

Table 7 list the values of k_p, k_t, and of the parameter $k_p/\sqrt{k_t}$ obtained. For comparison, the parameter $k_p/\sqrt{k_t}$ for polyethylene is also included. This value agrees well with the corresponding parameter for 1,3,5-trimethylpentane[96]:

$$\frac{k_p}{\sqrt{k_t}} = 8 \cdot 10^{-4} \text{ litre mole}^{-1}\text{ s}^{-1/2} (130°).$$

‡ Eqns. (1)—(4) are missing in the Russian original (Ed. of Translation).

The activation energy for the parameter $k_p/\sqrt{k_t}$, determined in the temperature range 110—140°C, is approximately 10 kcal mole^{-1}, which is also close to the corresponding value for low-molecular-weight compounds. Thus the chain propagation and termination stages in the oxidation of polyolefins above 100°C proceed in the same way as for low-molecular-weight compounds in the liquid phase.

At 200—250°K the kinetics of the destruction of radicals should not be determined by their chemical reactivity but by their mobility in the polymer matrix[88,89]. Therefore at a somewhat higher temperature, close to room temperature, the specific features of the solid phase can presumably also influence significantly the mechanisms of the chain propagation and termination reactions. However, we are unaware of any studies in which a detailed investigation was made of the influence of the specific features of the solid phase on the mechanism of the oxidation of polyolefins. One can only point to a study where a relation between the kinetics of the thermal oxidation of polypropylene and the supermolecular structure of the specimen was observed[97].

V. CHARACTERISTICS OF THE OXIDATION OF POLYMERS

The above discussion of the principal stages in the oxidation of polymers showed that, as in the oxidation of low-molecular-weight compounds, the principal products of the oxidation of polyolefins are peroxides, ketones, alcohols, and ethers. However, the great length of the polymer chain is responsible for certain specific features of the structure of these compounds. For example, polypropylene oxidised in a solution containing a sensitiser consists of "blocks" which incorporate between two and eight hydroperoxy-groups[98]. Data for the distribution of the hydroperoxy-groups in the blocks have been obtained by analysing the ultraviolet spectra of polyenes obtained from the hydroperoxide via the mechanism

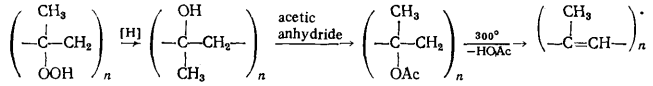
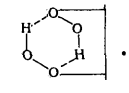


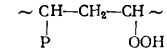
Fig. 8 presents data on the distribution of "adjacent" (located at neighbouring carbon atoms) hydroperoxy-groups in polypropylene hydroperoxide. The figure shows that the majority of the blocks contain two hydroperoxide groups. PPHP does not contain any isolated hydroperoxy-groups[98].

Analysis of the infrared absorption spectra of PPHP showed in addition that more than 90% of the hydroperoxy-groups are linked by hydrogen bonds. The PPHP structure can be represented as follows:



This structure shows that in each block with an odd number of groups one hydroperoxy-group is involved in hydrogen bonding.

By analogy with these data, it is believed[99] that isolated hydroperoxy-groups are also not encountered in polyethylene hydroperoxide (PEHP). The structure of PEHP can be represented by the formula



where P is a hydroxy- or carbonyl group. This structure of polyolefin hydroperoxides is consistent with ESR data. It has been noted[100] that the form of the ESR line associated with peroxy-radicals in polypropylene and polyethylene hardly changes with temperature in the range between −200° and 100°C. On the other hand, in Teflon, for example, the line form does depend significantly on temperature[101]. This result implies that the O—O group in polyolefins remains immobile in the temperature range investigated. The authors attribute this to the fact that fairly strong hydrogen bonds, capable of fixing the O—O group in a specified position, are formed in polypropylene and polyethylene.

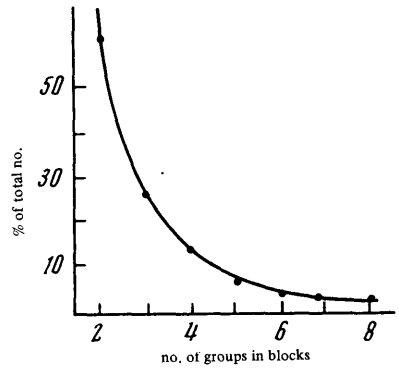


Figure 8. Distribution of hydroperoxy-groups in the blocks of oxidised polypropylene.

Table 8. Rate constants for reactions determining the kinetics of the decomposition of polyolefin hydroperoxides.

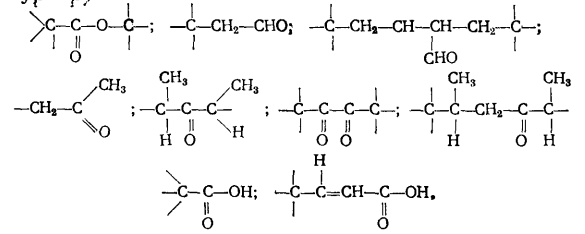
T, °C	k_{fast}, s^{-1}		k_{slow}, s^{-1}	E_{act}, for fast reactions, kcal $mole^{-1}$	
	from Ref.99	from Ref.103	from Ref.99	from Ref.99	from Ref.103
Polyethylene hydroperoxide					
110	$3.2\cdot10^{-5}$	$4.4\cdot10^{-4}$	—	—	—
110	—	$6.6\cdot10^{-4}$	—	20	25
120	$1.7\cdot10^{-4}$	$9.1\cdot10^{-4}$	$1.4\cdot10^{-5}$	—	—
	from Ref.102		from Ref.102		from Ref.102
Polypropylene hydroperoxide					
85	0.33		—		—
100	0.87		—		—
120	5.01		4.32		25
135	19.8		—		—

This structure of the polymer oxidation products is associated with the fact that the oxidation proceeds to a considerable degree via an intramolecular mechanism in the presence of a high local concentration of oxidation products. The presence of several functional groups in the immediate vicinity of one another within a single macromolecule alters their properties and reactivities. For example, thermal decomposition of PPHP and PEHP *in vacuo* proceeds according to a complex law and can be represented by two consecutive unimolecular reactions with rate constants differing by more than a power of ten[90,99,102,103]. Table 8 presents the rate constants for the slow and rapid stages of the decomposition of PPHP and PEHP.

The faster stage of the decomposition of the hydroperoxide is attributed to the decomposition of the hydroperoxy-groups linked by hydrogen bonds to similar OOH groups[99,102]. The slow stage is attributed to the decomposition of a β-hydroxyhydroperoxide. This interpretation is supported by the increase in the fraction of hydroperoxy-groups, undergoing a slower decomposition at more advanced stages of the hydroperoxide decomposition process and also in the presence of oxidation inhibitors, for example 2,6-di-t-butyl-*p*-cresol[102]§.

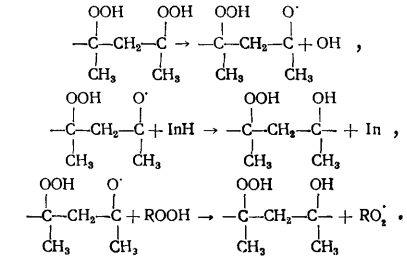
The rate constants for both stages of the decomposition of polyolefin hydroperoxides in solution and in crystalline and amorphous polymers are similar. This confirms that the decomposition of the hydroperoxide proceeds intramolecularly. The bulk of the polymer oxidation products are obtained as a result of further reactions of the hydroperoxides, the structures of the products being determined by the characteristics of the hydroperoxide structures. For example, the infrared spectra of oxidised polypropylene have a broad band in the region of absorption by the carbonyl group (1720 cm^{-1}), which, as already stated, is a result of a superposition of the absorption bands due to several ketones (Fig. 6).

By interpreting their spectra on a computer, Carlsson and Wiles[28] established that at least 9 ketones are formed in polypropylene at 220°C in air:



This result is probably not entirely unambiguous, since Adams[104] obtained a similar spectrum, which he interpreted as a result of the superposition of the absorption bands of ketones, aldehydes, acids, esters, and γ-lactones. At present it is apparently difficult to specify exactly the composition of the polyolefin oxidation products. Presumably they include two ketones corresponding to the location of the C=O groups at the end and in the middle of the chain and having absorption maxima at 1718 and 1726 cm^{-1} respectively.

§ In both these cases, the β-hydroxyhydroperoxide accumulates at a comparatively high concentration as a result of the reaction



Even the qualitative composition of the products accumulated in the polymer depends on its oxidation conditions. For example, under the conditions of the industrial processing of olefins (at about 200°C), polyolefin hydroperoxides decompose almost completely and from the entire range of oxidation products polymeric ketones are mainly obtained. At a lower temperature, considerable amounts of peroxides accumulate in the polymers[62,90,92]. However, it is almost impossible, as already stated, to obtain the pure polymeric peroxide by the oxidation reaction. It is always accompanied by decomposition products (ketones)[62].

VI. KINETICS OF THE PHOTOCHEMICAL OXIDATION OF POLYOLEFINS

The above discussion of the individual stages of the photochemical oxidation of polyolefins showed that the kinetic mechanism II of this process can be formulated as follows:

$$S_1 + h\nu \rightarrow PO_2 \quad (8)$$

$$POOH = h\nu \rightarrow PO^{\cdot} + OH^{\cdot} \xrightarrow{2O_2+2PH} 2PO_2 + H_2O + K \quad (9)$$

$$K + h\nu \xrightarrow{2O_2} (PO_2) \quad \text{for} \quad (K + S(=)) \quad (10)$$ (II)

$$PO_2 + PH \xrightarrow[k_p]{O_2} POOH + PO_2 \quad (11)$$

$$PO_2 + PO_2 \xrightarrow{k_t} K + POH + O_2 \quad (12)$$

where S_1 is the sensitising impurity in the polymer PH.

The photochemical oxidation of polymers which hardly absorb light thus differs from the thermal oxidation only by a greater complexity of the degenerate chain branching and chain termination steps. The kinetics of this process can be described by the following set of differential equations:

$$\frac{d(POOH)}{dt} = -\frac{\alpha I_0 (POOH)}{2} + \frac{k_p}{\sqrt{k_t}} \Pi H \sqrt{(\alpha POOH + \alpha_1 K + \alpha_0 S) I_0}, \quad (13)$$

$$\frac{d(O_2)}{dt} = (\alpha POOH + \alpha_0 S + \alpha_1 K)\frac{I_0}{2} + \frac{k_p}{\sqrt{k_t}} pH \sqrt{(\alpha POOH + \alpha_1 K + \alpha_0 S) I_0}, \quad (14)$$

$$\frac{dK}{dt} = \alpha I_0 POOH \quad (15)$$

where the coefficients α_0, α, and α_1 are products of the molar extinction coefficient and the quantum yield for the formation of free radicals in the photolysis of the impurity, the peroxide, and the ketone respectively.

Eqns. (13)—(15) become identical with Eqns. (5) and (6) describing the thermal oxidation of polyolefins when $\alpha_1 = 0$. The solution becomes particularly simple when $\alpha_0 = 0$; then, in the absence of photolysis of impurities, the mathematical description of the process becomes analogous to the description of the thermo-oxidative degradation given by Pudov[90]:

$$\frac{POOH}{POOH_\infty} = (1 - e^{-\frac{\alpha I_0}{4} t})^2,$$

$$\frac{K}{POOH_\infty} = \alpha I_0 t - 2(3 - e^{-\frac{\alpha I_0}{4} t})(1 - e^{-\frac{\alpha I_0}{4} t}), \quad (16)$$

$$\frac{\Delta O_2}{POOH_\infty} = \alpha I_0 t - (5 - e^{-\frac{\alpha I_0}{4} t})(1 - e^{-\frac{\alpha I_0}{4} t}),$$

where

$$POOH_\infty = \frac{4 k_p^2 PH^2}{\alpha k_t I_0}$$

is the limiting concentration of the peroxide which can accumulate in the system. The equations show that the concentration of the reactants initially increases autocatalytically according to a parabolic law:

$$\frac{\Delta O_2}{POOH_\infty} \simeq \frac{POOH}{POOH_\infty} \simeq \left(\frac{\alpha I_0}{4} t\right)^2, \quad \frac{K}{POOH_\infty} \simeq \frac{2}{3}\left(\frac{\alpha I_0}{4} t\right)^3; \quad (16')$$

After a time of the order of $0.2/\alpha I_0$, a significant concentration of the peroxide accumulates, whereupon after a time $t = 4 \ln 2/\alpha I_0$ the rate of accumulation of the hydroperoxide reaches its maximum value $\alpha I_0 (POOH)_\infty/8$ and after a time of the order of $10/\alpha I_0$ its concentration reaches a steady-state value.

The steady-state concentration of the peroxide is inversely proportional to the light intensity, but it is attained faster at higher light intensities. This is illustrated by the data in Fig. 9, which presents kinetic curves for the accumulation of the peroxide calculated from Eqn. (16) for light intensities differing by a factor of 100.

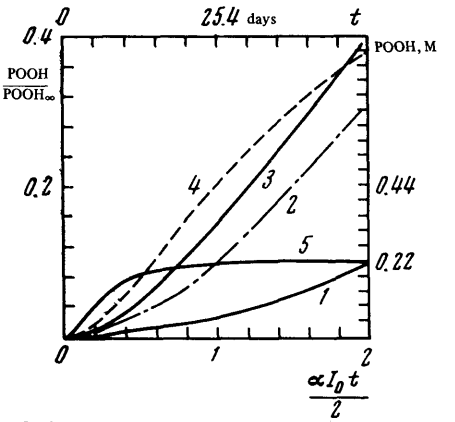


Figure 9. Calculated kinetic curves for the accumulation of peroxides at different incident light intensities: 1) $0.1\,I_0$; 2) $0.5\,I_0$; 3) I_0; 4) $2\,I_0$; 5) $10\,I_0$; $POOH_\infty$ corresponds to curve 3. The right-hand and upper scales correspond to $I_0 = 10^{16}$ quanta s^{-1} cm^{-2} (365 nm monochromatic light of PRK-7 lamp 6 cm from the centre). The extinction coefficient of the peroxide at 365 nm is 0.012 litre $mole^{-1}$ cm^{-1}.

The kinetic curves for the accumulation of peroxides and carbonyl groups and for the absorption of oxygen in the course of the photochemical oxidation are presented in Fig. 10. At the beginning of the process, the entire absorbed oxygen is used to form the peroxide; along this section, the kinetic curves *1* and *2* coincide. At more advanced stages of the oxidation process, the kinetic curves for the absorption of oxygen remain parabolic, while the accumulation of peroxides slows down, since their decomposition becomes significant. At roughly this time, relatively high concentrations of ketones accumulate.

The kinetic curve for the accumulation of ketones in the initial stages is close to a cubic parabola. After this,

as the concentration of the peroxide reaches its steady-state value, the rates of absorption of oxygen and of accumulation of carbonyl compounds also reach their steady-state values, which are equal. The kinetic curves in Figs. 9 and 10 were calculated for the condition where the polymer is free from impurities and does not absorb light in the first instants. Thus one can calculate the kinetic curves for the photochemical oxidation of "ideally" purified polyolefins, which is, so to speak, the curve for the slowest photochemical oxidation of polyolefins.

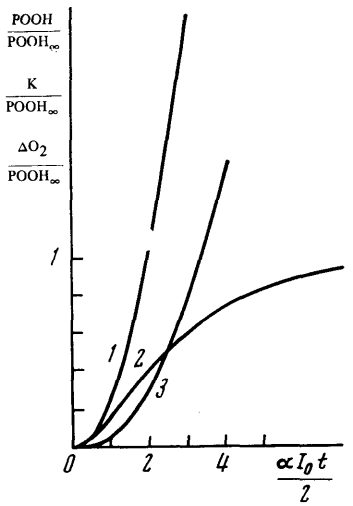


Figure 10. Calculated kinetic curves for the absorption of oxygen (curve *1*) and the accumulation of peroxides (curve *2*) and carbonyl groups (curve *3*) in photochemical oxidation.

We attempted to perform such a calculation for a real system. Fig. 9 presents the kinetic curve for the accumulation of peroxides in thoroughly purified isotactic polypropylene (curve *3*, the upper and right-hand side scales) on irradiation with light corresponding to the 365 nm line of the PRK-7 lamp at a distance of 7 cm from the source. The parameter $k_p/\sqrt{k_t}$ was calculated by extrapolating Chien and Ross's data[92] to a low temperature. Fig. 9 shows that under such conditions significant concentrations of the peroxide can accumulate in the purified polypropylene over a period of the order of one month.

The conditions $\alpha_1 = 0$ and $\alpha_0 = 0$ are fulfilled when polyolefins are irradiated with long-wavelength light whose spectral composition is close to that of sunlight [ketones do not absorb sunlight (Fig. 3) and, as shown above, impurities can have a significant influence only on the initial sensitisation].

If the sensitising impurity is not consumed in the course of the process, then its effect in the initial stage is characterised by the parameter

$$\varphi = \frac{\sqrt{\alpha_0 s I_0 k_t}}{k_p \mathrm{PH}} .$$

The initial stage of the accumulation of the peroxide is described in this case by the equation

$$\frac{\mathrm{POOH}}{\mathrm{POOH}_\infty} = \varphi \alpha I_0 t + \frac{1}{4}\left(\frac{1}{4} + \varphi\right)(\alpha I_0 t)^2 .$$

Fig. 11 presents rigorous solutions of Eqns. (13)—(15) for different values of the parameter $\varphi = \sqrt{\alpha_0 I_0 k_t s}/k_p \mathrm{PH}$. Evidently the quantity φ, characterising the role of extraneous impurities, has the greatest influence in the initial stages of the process and, when $\varphi \ll \alpha I_0 t/16$, it can be neglected. It is difficult to say anything about the value of φ owing to the wide variety of impurities in polyolefins, but, as stated above, the appreciable self-acceleration of the photochemical oxidation process suggests that it is small and decreases with time owing to the consumption of the impurity.

The absorption of light by ketones begins to be appreciable at advanced stages of the photochemical oxidation process and can be neglected when

$$I_0 \alpha t \ll \frac{(3 \div 4)\,\alpha}{\alpha_1} .$$

The ratio α_1/α is probably close to unity, since the extinction coefficient of ketones in the long-wavelength part of the spectrum is higher approximately by a power of ten than that of peroxides and the quantum yield of their decomposition into radicals is lower by a factor of 10—20 (data of Carlsson and Wiles[28,62] and Figs. 3 and 5). Thus the sections of the curves for the accumulation of peroxides up to the point of inflection should be described by Eqn. (7) for highly purified polymers.

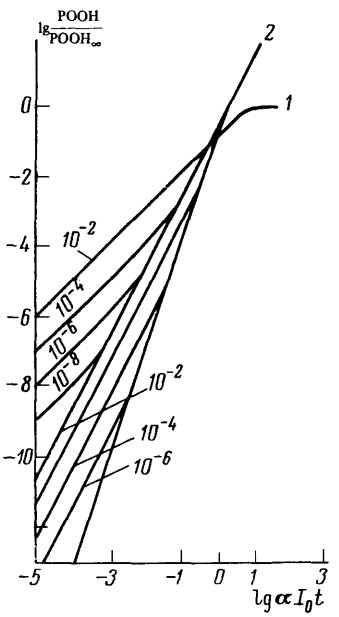


Figure 11. Logarithmic kinetic curves for the accumulation of peroxides (curve *1*) and ketones (curve *2*) in photochemical oxidation for different values of φ.

Unfortunately we were unable to find any studies in which a kinetic analysis of the photochemical oxidation of polyolefins has been carried out. Some investigators observed the accumulation of carbonyl groups in the course of photochemical oxidation and described it by an exponential relation[12] or by a curve with an induction period[13,14]. In all cases interpretation of the data quoted

permits their satisfactory description by a quadratic and cubic parabola within the framework of mechanism (II) quoted above, which corresponds to Eqns. (8)—(12). Fig. 12 presents experimental kinetic curves for the accumulation of carbonyl compounds in the photochemical oxidation of atactic polypropylene[13]. It also includes curves calculated from Eqns. (13)—(15).

For a quantitative description of the kinetics of the photochemical oxidation of polyolefins with the aid of Eqns. (13)—(15), it is necessary to know the spectral composition and absolute intensity of the light sources employed as well as the value of the parameter $k_p/\sqrt{k_t}$. It is then possible to make a quantitative calculation of the kinetic curves for the accumulation of peroxides and carbonyl compounds and for the absorption of oxygen. However, comparison of such calculation with experimental data involves certain difficulties. This is because the parameter $k_p/\sqrt{k_t}$ has not been measured at room temperature and its calculation by extrapolation of the data obtained at higher temperatures can lead to considerable errors. On the other hand, in many reports the necessary data concerning experimental conditions are lacking. Nevertheless we attempted to compare the kinetic curves for the accumulation of carbonyl compounds in the oxidation of polypropylene taken from Balaban et al.[12] with the calculated results; the parameter $k_p/\sqrt{k_t}$ was obtained by extrapolating Chien and Ross's data[92] to 30°C ($k_p/\sqrt{k_t} = 3.6 \times 10^{-5}$ litre mole^{-1} s^{-1}); the probability of the absorption of light quanta by a peroxide molecule ($\int \epsilon I d\lambda$) ^{105} was calculated from the absorption spectra of the light filters employed, the emission spectrum of the light source, and the absorption spectrum of the peroxide (Fig. 5), which are quoted by Melchore[13].

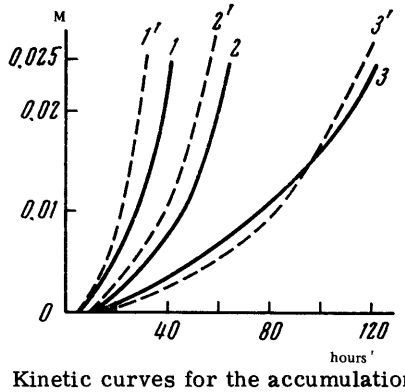


Figure 12. Kinetic curves for the accumulation of carbonyl compounds in the photochemical oxidation of atactic polypropylene[13]: 1)—3) from Melchore's data[13]; 1')—3') calculated data [1) without a filter; 2) and 3) with different light filters].

If the parameter $k_p/\sqrt{k_t}$ is calculated from the results of Pudov and coworkers[90,91], the accumulation of carbonyl compounds is found to be slower than in the experiments.

Thus Eqns. (13)—(15) apparently give a correct prediction of the scale of the phenomenon. However, in order to test rigorously the validity of mechanism (II), it is necessary to carry out special investigations.

It follows from Eqns. (13)—(15) that the dependence of the induction period, determined from the absorption of oxygen τ_{O_2}, the accumulation of the peroxides τ_{ROOH}, or the accumulation of ketones τ_K on light intensity and temperature is qualitatively different in each case. At the beginning of the process the induction period based on the accumulation of peroxides τ_{ROOH} is inversely proportional to the square root of the light intensity and corresponds to the same activation energy E_{ROOH} as the parameter $k_p/\sqrt{k_t}$. The induction period based on the accumulation of ketones is inversely proportional to $I^{2/3}$ and corresponds to the activation energy $(2/3)E_{ROOH}$. Indeed it has been shown[14] that the activation energy associated with τ_{ROOH} is 7 kcal mole^{-1}, which is close to the activation energy associated with the parameter $k_p/\sqrt{k_t}$, measured by Chien and Ross[92] (9 kcal mole^{-1}).

On the other hand, if the sensitivity of the method used to determine peroxides or ketones is relatively low, deviations from the above relations may be observed. It has been shown[12] that the induction period for the accumulation of ketones (τ_K) is inversely proportional to the square root of the light intensity. A small discrepancy may be due to the fact that degenerate chain branching owing to the photochemical decomposition of ketones, occurring because the irradiation was carried out with the unfiltered light of the mercury lamp, had an appreciable influence on this process.

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