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Yu. A. Mikheyev^a

^a Institute of Chemical Physics, the USSR Academy of Sciences, Moscow, USSR

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Heterophasic Mechanism of Arylation of Cellulose Triacetate and Polycarbonate by Benzoyl Peroxide

YU. A. MIKHEYEV

Institute of Chemical Physics, the USSR Academy of Sciences, 117977 Moscow, USSR

The peculiarities of kinetics and the material balances of interactions of glassy cellulose triacetate and polycarbonate with benzoyl peroxide are analyzed. A new theoretic description of the thermal and photochemical arylation of the polymers as a heterophasic radical chain reaction is given.

KEY WORDS Arylation, cellulose triacetate, polycarbonate

INTRODUCTION

In the previous work,¹ a carcass-cellular model of supermolecular structure of amorphous polymer was formulated. In this model, the microporous carcass cell, capable of absorbing the low molecular additives, is of great importance. It was proposed that the microheterogeneous structure of the carcass cell must predetermine the nonhomogeneous character of the radical chain reaction in the polymers because the intracellular micropores are not equivalent by their structure and their role in the chemical process. In particular, the inside surface of the cell capsule (*S*-zone) is covered with the enlarged micropores being extended under the mechanical tension which is generated by the intracellular microporous core ball (*V*-zone). Both a relatively high capacity of *S*-micropores and the operation of surface forces of the paracrystalline carcass promotes the dissociation of initiator molecules in the *S*-zone. Being under the elastic strain simultaneously, the polymer chain *S*-links must be promoted for the chain scission as the macroradicals are formed here in any way.

In *V*-zones, the microporous balls of polymer chains are compressed by the forces which are generated by the curved surface of the conglomerate of *V*-micropores. Here, the microporosity is tighter than in the *S*-zone, and it must suppress the dissociation of initiator molecules and the fragmentation of macroradicals.

The chemically selective role of *S*- and *V*-zones is demonstrated in the present work by the model chain reaction of glassy polymers (cellulose triacetate (CTA) and polycarbonate (PC)) being exposed to the attack of benzoyl peroxide (BP).

A theoretic explanation of insufficiently discussed results of the early works²⁻⁶ is presented, and the heterophasic mechanism of thermal and photochemical interaction of the polymers with BP is discussed in detail.

This reaction has been selected as a model due to the rich literature on BP conversion in homogeneous liquid media. The changes both in the kinetic law of the reaction and in the composition of reaction products, under the replacement of homogeneous liquid solvent by polymer, is methodologically of great importance in our case.

The occurrence of BP chain reactions in polymers was first established for polystyrene, polyethylene and polypropylene with the help of nonkinetic sear technique using the dependence of the decomposed BP dose on the initial BP contents and that for the accumulated reaction product (phCOOH, CO₂).⁷⁻¹⁰ The peculiarities found allowed the authors⁷⁻¹⁰ to postulate the chain BP reaction in second order by BP, that is induced by the attack of benzoyloxyl on BP to produce phenylbenzoate.

The conclusion drawn is refuted, however, by the kinetic measurements.¹¹⁻¹³ Actually, the chain reaction is not second order by BP and is induced by the attack of macroradicals. The yield of phenyl benzoate is very small in these cases. Thus, the real phenomenology of the model reaction can be established only by a detailed study of both the reaction kinetics and the BP conversion products. The present communication sums up the analysis of the results obtained earlier for CTA and PC.

It should be noted that the experiments were carried out using films (of thickness 20–50 μm) which were prepared from the solutions in the dry methylene chloride. Under the concentrations of BP used, the films keep the high optical transparency of the original polymers due to the fact that the admixed BP does not form its own crystalline phase. The specimens are heated in sealed evacuated glass tubes and in tubes with air. The BP contents that appear are determined using a spectrophotometric manner of the iodimetric method. The decomposition products are analyzed using thin-layer chromatography. The number of polymer chain scissions is calculated by the data of viscosimetry of polymer solutions in methylene chloride.

1. Phenomenology of the thermal model reaction

Heating of the CTA and PC specimens in sealed evacuated glass tubes induces the BP decomposition in accordance with the exponential law

$$C = C_0 \exp(-kt) \quad (1.1)$$

where C_0 , C are the initial and current BP concentrations, respectively, and k is the effective rate constant of BP decomposition. The straight anamorphosises of BP disappearance curves, being plotted in the coordinates of the equation

$$\lg(C/C_0) = 1 - 0.434kt,$$

are presented in Figure 1 (CTA) and Figure 2 (PC), the temperature being 371 K.

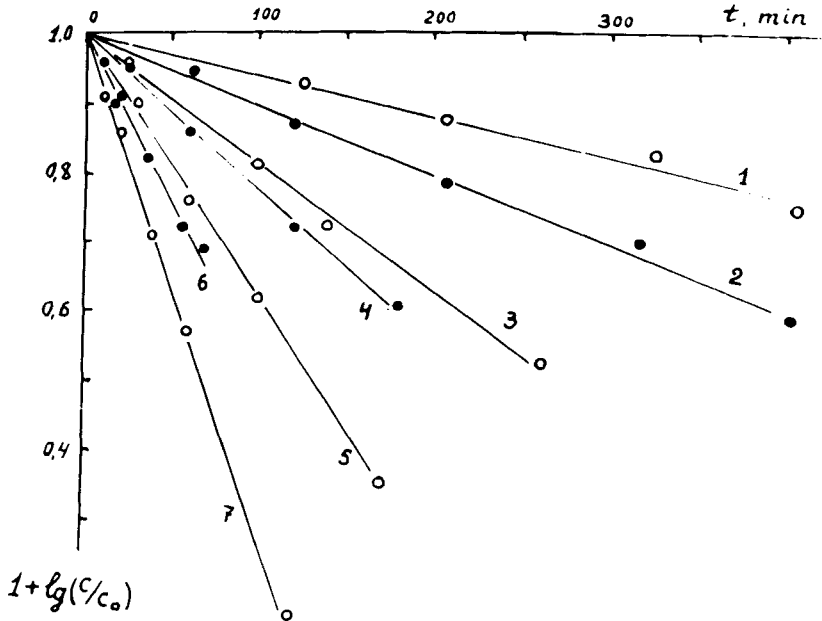


FIGURE 1 Anamorphoses of BP decomposition curves for evacuated CTA films, obtained at the following temperatures (in °K): (1) 353, (2) 359, (3) 365, (4)–(7) 371. (4) C_0 –0.06, (5) 0.196, (1)–(3), (6) 0.38, (7) 0.69 mol/kg.

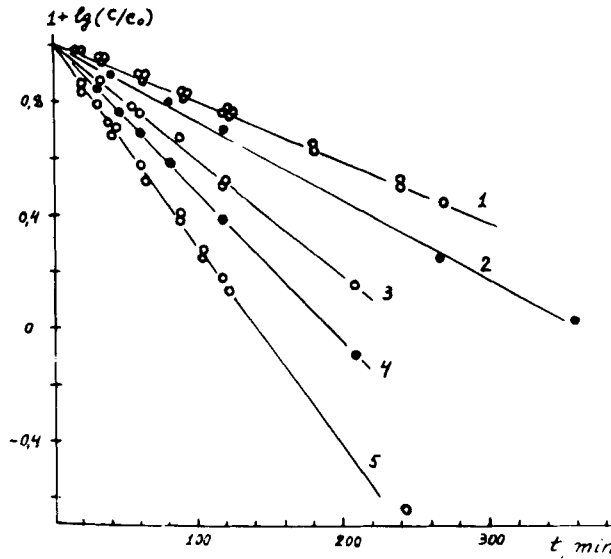


FIGURE 2 Anamorphoses of BP decomposition curves for (1) aerated and (2)–(5) evacuated PC films, obtained at 371 K. (1) C_0 – 0.12, 0.21, 0.41, 0.70, 0.83; (2) 0.1; (3) 0.33; (4) 0.5; (5) 0.83 mol/kg.

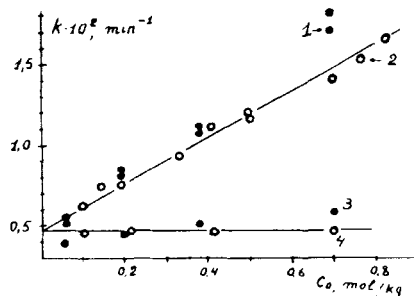


FIGURE 3 Dependence of k constant on C_0 at 371 K in (1), (2) evacuated and (3), (4) aerated (1), (3) CTA films and (2), (4) PC films.

For both polymers, the constant k is linearly dependent on the C_0 value (Figure 3, plots 1, 2)

$$k = k_0 + k_c = k_0 + k_i C_0 \quad (1.2)$$

where k_0 is the rate constant of nonchain BP decomposition, that is calculated by the cutoff on the ordinate axis on Figure 3. The same k_0 value characterizes the exponential curves of BP decomposition in the aerated films (Figure 3, plots 3, 4). Comparison of the straight lines 1, 2 and 3, 4 (Figure 3) shows that oxygen inhibits the chain reaction of BP in eliminating the constant k_c and producing no polymer peroxides being titrated.

In the absence of O_2 , the BP decomposition rate in nonaromatic CTA and aromatic PC can be considered equal. In both cases at 371 K, the constants of equation (1.2) are: $k_0 = (4.8 \pm 0.5) \cdot 10^{-3} \text{ min}^{-1}$, $k_i = (1.5 \pm 0.2) \cdot 10^{-2} \text{ kg} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$. At 353 K in PC,³ $k_0 = (7 \pm 1) \cdot 10^{-4} \text{ min}^{-1}$ and $k_i = (10 \pm 1) \cdot 10^{-4} \text{ kg} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$. The effective activation energy of nonchain BP decomposition $E_0 = 117 \text{ kJ/mol}$ is equal for CTA⁴ and PC, that is, somewhat lower as regards the liquid phase. The effective activation energy of the chain reaction $E_i = 160 \text{ kJ/mol}$ is higher than E_0 (whereas in liquids quite the reverse is true: $E_i < E_0$; see the next section).

The BP decomposition induces the degradation of both polymers according to the kinetic law of the first order as regards BP. Thus, the rate of chain scission for CTA is

$$dN/dt = k_N C = k_N C_0 \exp(-kt), \quad (1.3)$$

and the increase in the number of chain scissions is described by the formula

$$N = (k_N C_0 / k) [1 - \exp(-kt)] = N_x [1 - \exp(-kt)] \quad (1.4)$$

Figure 4 represents the plots of equation (1.4) reconstructed for the straightforward form

$$\lg[N_x / (N_x - N)] = kt.$$

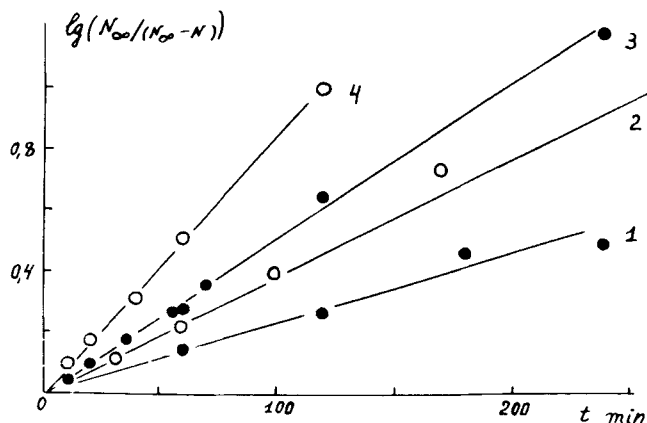


FIGURE 4 Anamorphoses of the kinetic curves of scission of polymer chains for evacuated CTA films at 371 K. (1) $C_0 = 0.06$; (2) 0.196; (3) 0.38; (4) 0.69 mol/kg.

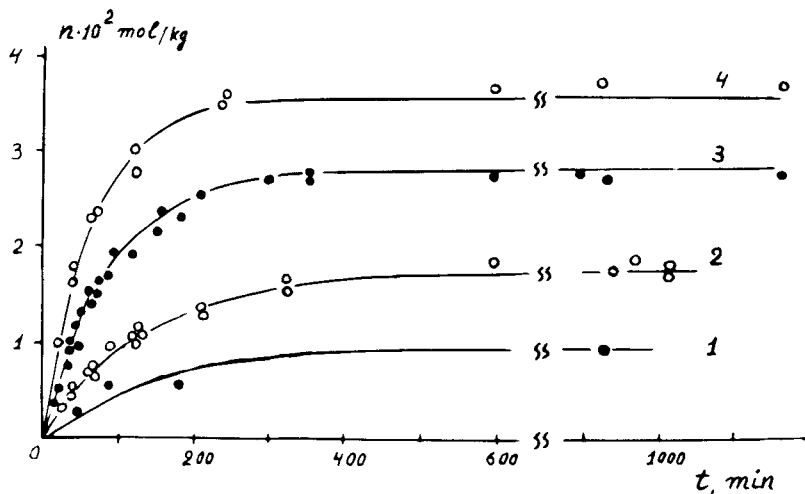


FIGURE 5 Kinetic curves of PC degradation in a vacuum at 371 K. (1) $C_0 = 0.083$; (2) 0.19; (3) 0.45; (4) 0.83 mol/kg.

The rate constant k values, calculated by these plots, correspond to those found by BP decomposition kinetics. It should be noted that here N is the number of disrupted chemical bonds per initial CTA macromolecule with $M_n = 330,000$.

The k_N constant, calculated from the limit number of scissions $N_\infty = k_N C_0 / k$ for 371 K, is equal to $0.1 \text{ kg} \cdot \text{mol}^{-1} \cdot \text{min}^{-1} \cdot \text{macromolecule}^{-1}$, which gives $k_n = 3.0 \cdot 10^{-4} \text{ min}^{-1}$ after recalculation for the concentration of chain scissions (n , mol/kg).

Obtained for PC, the kinetic curves of polymer chain scission are presented in Figure 5 (371 K). They can be well described by the first-order equation by BP³

$$n = n_\infty [1 - \exp(-kt)], \quad (1.5)$$

where $n_\infty = k_N C_0 / k$ and $k_n = 6.9 \cdot 10^{-4} \text{ min}^{-1}$. The constants k and k_n do not depend

on the molecular mass of PC (the values of M_{vo} in experiments³ were 128,000, 113,000, 100,000, 64,000, 35,500).

In aerated films the polymer chain scission rate and the kinetic curves are described by the following expressions:

$$\begin{aligned} d(n^a)/dt &= k_n^a C = k_n^a C_0 \exp(-k_0 t), \\ n^a &= n_z^a [1 - \exp(-k_0 t)] \end{aligned} \quad (1.6)$$

where $n_z^a = k_n^a C_0 / k_0$.

Figure 6 represents the plot of the straight line corresponding to equation (1.6). Using this plot, it is not difficult to calculate the effective constant $k_n^a = (3 \pm 1) \cdot 10^{-4} \text{ min}^{-1}$.

The k_n^a constant for aerated CTA films, calculated by the data published elsewhere,⁴ is $(1.3 + 0.3) \cdot 10^{-4} \text{ min}^{-1}$. For both polymers there is a correlation: $k_n^a = 0.5 kn$.

During BP decomposition, benzoic acid (rH) is accumulated in the evacuated polymer films as well as arylated macromolecules and a small amount of phenyl benzoate (rph).⁶ Assuming a general case, let us consider that a final product X is formed both in nonchain and chain reactions with probability of α_x and β_x , respectively. In such a case, the rate of accumulation of X is

$$d[X]/dt = \alpha_x k_0 C + \beta_x k_i C_0 C \quad (1.7)$$

By integrating (1.7), taking into consideration (1.1), we find the expression for current concentration:

$$[X] = [(\alpha_x k_0 + \beta_x k_i C_0) / k] C_0 [1 - \exp(-kt)]$$

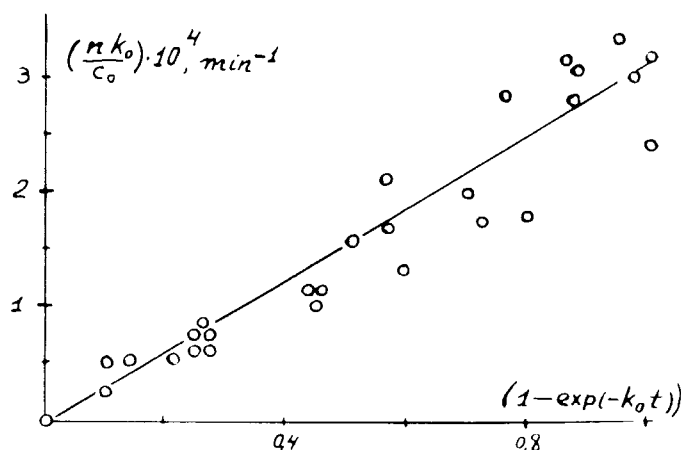


FIGURE 6 Anamorphosis of the curves of initiated degradation of aerated PC at 371 K. $C_0 = 0.13 \div 0.65 \text{ mol/kg}$, M_v 25,000–128,000.

and for the limit concentration of product (at $t \rightarrow \infty$):

$$[X]_{\infty} = (\alpha_x k_0 + \beta_x k_i C_0) C_0 / k \quad (1.8)$$

Expression (1.8) is to be converted for

$$k[X]_{\infty} / C_0 = \alpha_x k_0 + \beta_x k_i C_0 \quad (1.9)$$

in determining the α_x and β_x coefficients by the straightforward plots. The plots of equation (1.9) are presented in Figure 7. Using these plots, it is not difficult to establish the reaction providing the X product. It is seen, in particular, that the degradation of CTA and PC is associated only with the nonchain decay of BP: $\beta_n = 0$; $k_n = \alpha_n k_0 = 3 \cdot 10^{-4} \text{ min}^{-1}$ (CTA), $6.9 \cdot 10^{-4} \text{ min}^{-1}$ (PC).

The rH product is formed by both the nonchain ($\alpha_{rH} k_0 = 1 \cdot 10^{-3} \text{ min}^{-1}$) and the chain reactions ($\beta_{rH} k_i = 2 \cdot 10^{-2} \text{ kg} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$) nearly equally in CTA and PC. The rH yield of the nonchain reaction is small ($\alpha_{rH} = 0.2$), and in the chain reaction it is maximum ($\beta_{rH} = 1$). The same relation is obtained for the yields of arylated CTA: $\alpha_{CTAA} = 0$, $\beta_{CTAA} = 1$.

A high transparency of CTA in the uv region with $\lambda > 260 \text{ nm}$ allows us to record the uv absorption of CTAA (Figure 8a). Figure 8b represents the diagram of equation (1.9) in which the $[X]_{\infty}$ value is replaced by the optical density D_{∞} of CTAA solution in methylene chloride (the CTAA solutions are prepared following the complete BP decomposition under vacuum at 371 K and after the film extraction with ethanol, the concentration being 3.85 g/l and the optic cell thickness – 1 cm; $\lambda 284 \text{ nm}$). As Figure 8b shows, the CTAA product is formed in the chain reaction

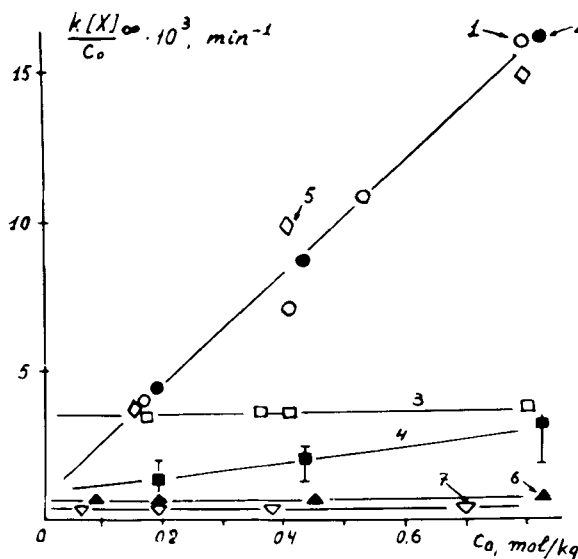


FIGURE 7 Dependence of normalized maximum yield of BP reaction product in (1), (3), (5), (7) CTA and in (2), (4), (6) PC on C_0 : (1) benzoic acid, (3), (4) phenylbenzoate, (5) CTAA, (6) scissions of PC, and (7) CTA macromolecules.

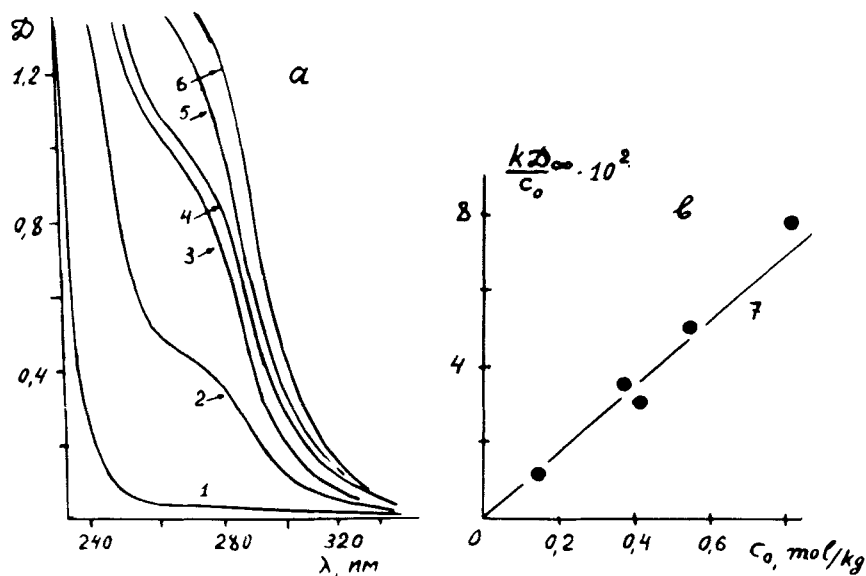


FIGURE 8 Change in uv absorption of methylene chloride containing (1)–(6) CTAA and in optical density of the solution at the uv wavelength of (7) 284 nm in dependence on C_0 , after the CTA arylation. Polymer concentration in solutions: (1), (2), (7) 3.85, (3), (4) 2.56, (5) 1.92, (6) 1.28 g/l. (1) $C_0 = 0.00$, (2) 0.17, (3) 0.36, (4) 0.41, (5) 0.54, (6) 0.80 mol/kg.

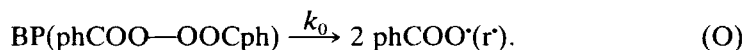
of BP only. The molar extinction coefficient, calculated for CTAA by the data presented in Figures 7 and 8, is $1.100 \pm 200 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ and corresponds to alkylbenzenes and alkylbenzoic acids.

Phenyl benzoate is formed mainly in a nonchain way, in CTA $\alpha_{\text{rph}} = 0.8$ and $\beta_{\text{rph}} = 0$, in PC $\alpha_{\text{rph}} = 0.2 \div 0.6$ and $\beta_{\text{rph}} < 0.2$.

The portion of low molecular weight products of the nonchain BP decomposition corresponds $(\alpha_{\text{rH}} + \alpha_{\text{rph}}) = 1$ in CTA and $0.4 \div 0.8$ in PC. Probably, the benzene rings of PC capture parts of the free radicals occurring due to nonchain BP decomposition.

2. Homogeneous mechanism of BP decomposition

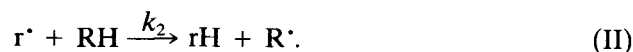
Now, we give a brief description of the homogeneous BP reaction. Its elementary stages play a key role in any heterophasic process. The BP conversion is known to begin with the dissociation act



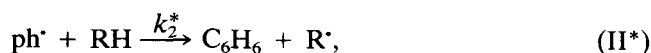
Thereafter the formed benzoyloxyls are decarboxylated



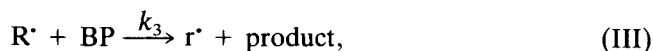
or detach hydrogen atoms from the solvent



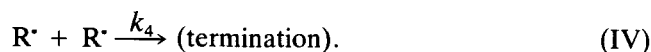
The solvent radical $R\cdot$, which is also formed by the reaction



does attack the peroxide



or it is combined with the other radical



The scheme above leads to the following expression of the total BP decomposition rate:

$$-dC/dt = k_0C + k_3(k_0/k_4)^{0.5}C^{1.5}. \quad (2.1)$$

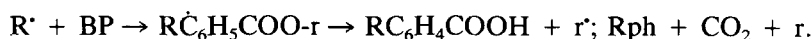
For liquids, the most frequent order of chain reaction equals 1.5 as in (2.1),¹⁴ an order 1 is rare, while values 0.5 and 2 are probably unknown. This may be caused by high rates of (I), (II), (II*) reactions providing the inevitability of stages (III) and (IV).

Actually, the k_1 constant is high $-1 \cdot 10^8 \text{ s}^{-1}$ at 403 K ($6 \cdot 10^5 \text{ s}^{-1}$ at 313 K, the activation energy $E_1 = 58.6 \text{ kJ/mol}$).¹⁵ Reaction (II) with a secondary CH group of hydrocarbons has activation energy $E_2 = 36.4 \text{ kJ/mol}$ and can occur parallel to (1).¹⁶ The phenyl radical easily splits off the hydrogen atom from aliphatic compounds, the constant $k_2^* = (0.2 \div 6.2) \cdot 10^6 \text{ M}^{-1} \text{ s}^{-1}$ is significantly higher than for the similar reaction of alkyl radicals ($10 \div 10^3 \text{ M}^{-1} \text{ s}^{-1}$).¹⁷

The mechanism of reaction (III) is dependent on the chemical nature of the $R\cdot$ radical. For example, the free radicals of ethers predominantly attack the oxygen^{18,19} of the peroxidic bond



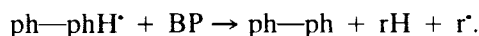
If free valency in $R\cdot$ is not adjacent to the O atom, then the BP phenyl ring is predominantly attacked.²⁰⁻²²



In benzene solution, the $r\cdot$ and $ph\cdot$ radicals interact with C_6H_6 molecules. The appearing σ -complex of benzoyloxyyl with benzene can reversibly dissociate.^{23,24}

There is a significant shift of the equilibrium toward dissociation. However, the side reactions of the σ -complex are possible, for example, its oxidation with dissolved oxygen (or with peroxide itself) into phenyl benzoate. The detected small amount of disalicylic ester²⁵ could occur from the σ -complex of benzoyloxyl with BP through the intermediates as the benzoyloxylated BP and its intramolecular σ -complex.

The phenyl radical irreversibly attaches to aromatic molecules^{17,22,26} with a high rate constant $(5 \div 10) \cdot 10^6 \text{ M}^{-1} \cdot \text{s}^{-1}$. Due to this the reaction between ph^\cdot and BP is to be considered in a number of cases, for example, in explaining the isotopic distribution of the reaction products of labeled reagents.²⁷ Nevertheless, the main way of the induced BP decomposition in benzene is the attack of phenylic σ -complex of benzene²⁶



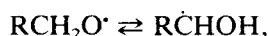
In alkylbenzenes, the attack on BP is provided by σ -complexes $\text{phC}_6\text{H}_5\text{Alk}$ or by aryl-alkyls $\text{C}_6\text{H}_5\text{Alk}^\cdot$. In these media, the order of chain reaction by BP is equal to 1.5, which indicates the bimolecular termination with the radicals which do attack BP.²⁸

The rare case of the efficient chain reaction of first order by BP was observed for the BP solutions in chlorobenzene and bromobenzene,²⁹ which can be connected with the termination of the reaction chains by combining the r^\cdot radicals with σ -complexes of halidobenzenes.

The rate constant values of the BP dissociation $k_0 = A \exp(-E_0/RT)$ are somewhat different according to different authors, for example, $A = 1.18 \cdot 10^{14} \text{ s}^{-1}$, $E_0 = 125 \text{ kJ/mol}$ ³⁰ and $A = 3 \cdot 10^{13} \text{ s}^{-1}$, $E_0 = 124 \text{ kJ/mol}$.³¹ There are also values of $E_0 = 138 \div 139 \text{ kJ/mol}$.^{14,32} A stoichiometric coefficient of initiation with BP is the maximum value of 2 for the benzene solution at 351 K²⁶ and 318 K.³³ The activation energy of chain reaction E_i is less than E_0 (in benzene $E_i = 105.5$ and in acetic anhydride 104.5 kJ/mol),¹⁴ in accordance with (2.1) (the E_i value includes one half of the E_0 value).

The rate of chain decomposition of BP is the lowest in benzene, toluene and ethylbenzene and it increases in nonaromatic solvents. For example, the ratio of the initial rate of chain BP reaction to the initial rate of BP dissociation $W_i^0/W_0^0 = k_i C_0^{0.5}/k_0$ (at $C_0 = 0.2 \text{ M}$, $T = 353 \text{ K}$) is equal¹⁴ for: benzene, toluene—0.58; cyclohexene—1.07; *tert*-butylbenzene—2.09; cyclohexane—2.29; ethylacetate—1.82; acetic acid—2.81; acetic anhydride—1.82.

In nonaromatic liquids, the accumulated products of BP decomposition inhibit BP decay. For example, in acetic anhydride, the current W_i/W ratio can achieve the value of 0.59¹⁴ from the initial one of 1.82. Among the usual solvents, ethers and alcohols react with BP most rapidly. In alcohols, the induced BP decomposition is associated with the transfer of the hydrogen atom from the alcoholic radical to the peroxide group^{30,34}



The attachment of the alkoxy radical to the phenyl ring of BP is also possible. This is evidenced by the fact that BP interaction with isobutanol yields both aldehyde and a large amount of isobutoxybenzoic acids.³⁵

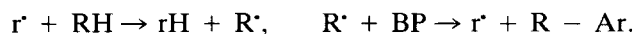
In liquids, dissolved oxygen inhibits the chain BP reaction due to oxidation of active radicals into peroxy ones which do not react with BP.^{14,36}

3. Heterophasic reaction of the polymers with BP

In evacuated glassy CTA and PC films, the chain reaction of BP has the same efficiency of $W_i/W_0 = k_i C_0/k_0 = 2 \div 2.5$, as in carboxyl containing liquids. As is seen, a very great superiority of polymers against liquids as regards macroscopic viscosity (over 10^{14} times) does not lay obstacles to the bimolecular acts of induced decomposition of BP. In this respect, the polymers do not differ from liquids, providing high mobility for the low molecular weight particles such as BP and benzoyloxy.

The additives, however, do not diffuse from the evacuated films. They disappear exclusively in the chemical process, which is evidenced by the material balance $\beta_{rH} = \beta_{CTAA} = 1$. The above stated can be associated with the fact that light particles move relatively freely within the core sponge of enclosed carcass cells.¹

In polymers, the chain BP reaction is inhibited by oxygen as well as the liquid-phase reaction. Its order by BP is 1.0 and the material balance gives evidence of the simple stoichiometry $BP + RH = rH + R-Ar$, because the chain-carrying benzoyloxy radicals react without decarboxylation



By this characteristic, the CTA and PC films significantly differ from liquids.

The other difference is that a simple stoichiometry of the chain reaction is combined with a complex rate constant $k_c = k_i C_c$ which includes the initial BP concentration. Besides, the efficiency of the chain reaction is practically independent of the chemical difference between CTA and PC. These facts cannot be explained by the homogeneous reaction mechanism.

The latter also cannot explain why the reactions of benzoyloxy radicals and macroradicals do not induce polymer chain scissions in the reactional chains of arylation, while the scissions are associated with the primary conversion of both benzoyloxy radicals and macroradicals only ($\alpha_n = 6.7 \cdot 10^{-2}$ for CTA and $14.3 \cdot 10^{-2}$ for PC).

As regards polymer degradation, the kinetic first order by BP (equations 1.3)–(1.5)) means that the primary macroradicals undergo only the scission of polymer chains and do not interact with either BP or r' . At the same time, the secondary macroradicals appearing for chain arylation make no scissions and react, due to some reason, only with BP molecules. The situation is that the two separated reactional chains must coexist, and that the intermediates of the primary reactional chain do not affect those of the secondary reactional chain.

We shall explain the noted peculiarities, taking into consideration the specificity of zonal structure of the carcass-cellular microreactor absorbing the BP additive. Taking into account that the force field of tight, and narrow, micropores prevents the dissociation of both BP and r' ,¹ let us assume that these acts are practically

inhibited in the intracellular core sponge (*V*-zone). At the same time, the dissociation is possible near the carcass domains in the capacious micropores of the *S*-zone, that is, promoted by the carcass surface forces. The primary radicals being formed are converted predominantly within the *S*-zone. This is associated with rather low molecular-segmental mobility of polymer chains, and again the light radicals, being exposed to the force field of the carcass domains, react in the adsorbed state.

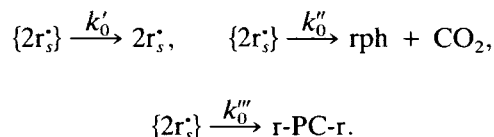
Nevertheless, a rare number of the interzonal transfer of free valency does occur under the influence of light particles when crossing the *S,V*-boundary. The particles of such *S,V*-cross-service, in our case, are those possessing benzene rings (original BP and rH); we indicate them by ϕH .

If one takes into account that the ϕH compounds form σ -complexes with *S*-radicals inducing BP decomposition (see 2) and that $[\phi\text{H}]$ -concentration undergoes little change during the reaction, then the specific form of the chain constant $k_c = k_i C_0$ can be associated with the participation of ϕH compounds in the interzonal *S,V*-transfer of free valency.

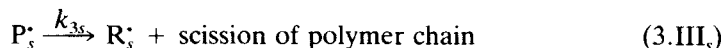
Addressing the reaction scheme, let us write the stages of formation of the primary radical pair:



The radical pair either escapes from the cage or forms phenyl benzoate and, in another way, adjoins to macromolecules (in PC):



The escaped benzoyloxy r_s^* does produce benzoic acid and macroradicals

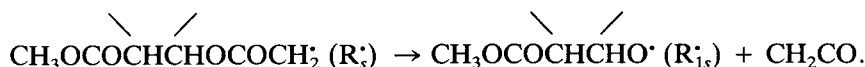


where P_s^* is related to the radical having a free valency on the backbone of a macromolecule (in CTA this is the main group $\text{O}-\dot{\text{C}}-\text{O}$, in PC it is the σ -complex of r^* with a benzene ring)³⁷ to be disrupted. R_s^* is related to the radical with a free valency on the side or terminal group of the macromolecule. Due to the low yield

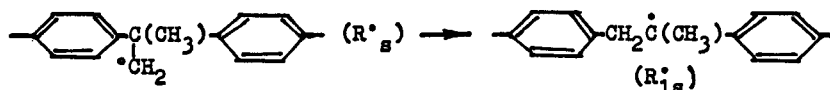
of the induced polymer chain scission, it should be considered that the yield of the P_s radicals is small, so a majority of the R_s radicals possess free valency on the side groups.

According to experiment, the P_s , R_s indicated polymer radicals do not take part in the arylation process, i.e., they do not react with BP and benzoyloxy. The cross-linking of polymer chains by combination of the R_s radicals is also not observed. Probably, a decomposition of R_s occurs by appearance of the intermediate R_{1s} radicals.

In particular, for CTA the following stage is known:³⁸

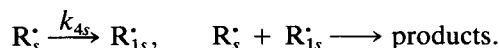


For PC the isomerization can be assumed:

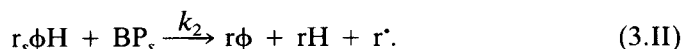
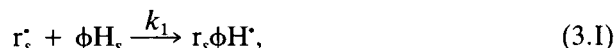


by the analogy with the known stage of radical catalytic isomerization of isopropylbenzene into *n*-propylbenzene.³⁹

In such a case the *S*-radicals must terminate by disproportionating of R_s and R_{1s} . The R_s decomposition by the formation of light radical CH_3 also cannot be excluded. In both cases, the termination scheme of *S*-radicals follows:



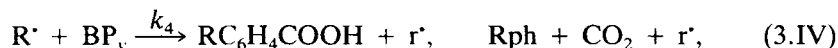
As is noted, the initiation of arylation chains involves the *S,V*-transfer of free valency with the ϕH compounds



It should be stressed that the rate of this transfer must be rather low with no change in the concentration of *S*-radicals.

Benzoyloxy r^{\cdot} , when getting into a narrow *V*-micropore, must localize into the micropore volume being exposed to the force field of the surface with a high negative curvature. As a result, the dissociation $r^{\cdot} \rightarrow \text{ph}^{\cdot} + \text{CO}_2$ is prevented for the r^{\cdot} interaction with CH bond to promote. Within the narrow *V*-micropore, the conditions may be more favorable for the r^{\cdot} reaction with the macromolecular side groups which can attain a more convenient reactional disposition within the micropore.

The above stated allows us to write a similar scheme of the chain reaction for CTA and PC:



where R^{\cdot} corresponds to the side radical $-\dot{C}H_2$. In both polymers, the termination of arylation chains probably occurs according to linear law, through the adsorption of r^{\cdot} on the surface of the carcass cell



The recorded scheme of the chain reaction does not correspond to the homogeneous version, as it levels the chemical difference between CTA and PC. Just this is required by the observed kinetic equivalence of both polymers in the reaction with BP.

One can assume that the studied CTA and PC pattern possess nearly identical structural-physical characteristics of micropores and intracellular zones. The close similarity of those details is probably the reason for the equivalency of the rate constants of main stages in heterogeneous BP conversion.

In this connection it should be noted that the globular elements of the spatial lattice have dimensions from 150 to 300 Å for both CTA⁴⁰ and PC.⁴¹ In their micropores, the effective viscosity for low molecular weight particles, similar to the BP molecule is $\eta \approx 10$ poise and it depends weakly on temperature.^{1,42} The frequency of jumps of such particles, for a distance of $\lambda = 10$ Å (average micropore dimension), $\nu = k_b T / \lambda^3 \eta \approx 5 \cdot 10^6 \text{ s}^{-1}$ (where k_b is Boltzmann's constant) is 9–10 orders higher than the frequency of BP decomposition ($k < 10^{-3} \text{ s}^{-1}$). Therefore, it can be considered that the rate of reaction does not affect the interzonal BP equilibrium which determines the steady concentration C_s in both CTA and PC

$$dC_s/dt = k_v C_v - k_s C_s - k_{os} C_s \approx k_v C_v - k_s C_s = 0,$$

whereof

$$C_s = k_v C_v / k_s = K_e C_v, \quad (3.1)$$

where K_e is the equilibrium constant.

Relation (3.1) allows us to express the local concentrations C_s and C_v through the calculated $C = N/m$ (N is the number of BP moles, m is the specimen mass in kg). Let the mass of cells with BP be equal to $\alpha_j m$ (α_j is the portion of cells in the specimen); then the BP concentration in cells $C_j = N / \alpha_j m = (\alpha_j^{-1}) C$. This very value C_j we express by averaging the BP contents in the zones of cells (total

mass of zones is $m_s + m_v = m_j$): $C_j = (m_s C_s + m_v C_v)/m_j$. Combining both expressions with (3.1), we obtain

$$C_s = Cm_j[\alpha_j(m_s + m_v/K_e)]^{-1}, \quad C_v = Cm_j[\alpha_j(m_s K_e + m_v)]^{-1}.$$

Taking into account that V -micropores capture the additive like a sponge (i.e., $K_e < 1$) and that $m_s < m_v$, we obtain

$$C_s = (m_j/\alpha_j m_v) K_e C \approx (\alpha_j)^{-1} K_e C, \quad (3.2)$$

$$C_v = (m_j/\alpha_j m_v) C \approx (\alpha_j)^{-1} C. \quad (3.3)$$

It should be noted that the direct proportionality between C_s , C_v and C will be fulfilled only in the absence of structural changes in reactional micropores and under the stability of zonal masses in carcass cells.

The reactional scheme given by us allows us to express the steady state for the primary benzoyloxyls

$$d[r_s^*]/dt = 2k'_0 k_{0s} C_s / \Sigma k'_0 - (k_{1s} + k_{2s}) [r_s^*] - k_1 [r_s^*] [\phi H_s] = 0,$$

where the values $[\text{PH}_s]$ and $[\text{RH}_s]$ are included in the constants. Hereof, neglecting the last member (due to low probability of the interzonal transfer of free valency), we shall find the concentration

$$[r_s^*] = 2k'_0 k_{0s} C_s / (k_{1s} + k_{2s}) \Sigma k'_0. \quad (3.4)$$

The steady concentration of the secondary benzoyloxyls can be obtained when using the rate equality for the initiation (3.I) and the termination (3.V) of arylation chains

$$d[r^*]/dt = k_1 [r_s^*] [\phi H_s] - k_5 [r^*] = 0$$

taking into account the found expression of $[r_s^*]$,

$$[r^*] = 2\gamma k'_0 k_{0s} k_1 C_0 C_s / k_5 (k_{1s} + k_{2s}) \Sigma k'_0,$$

where $[\phi H_s] = \gamma C_0$.

By substitution of $[r^*]$ and $[r_s^*]$ into the expression of total rate of the BP decomposition in the carcass cells

$$W_j = -(dC_s/dt + dC_v/dt) = k_{0s} C_s + k_4 [R^*] C_v = k_{0s} C_s + k_3 [r^*] [\text{RH}],$$

we shall obtain

$$W_j = k_{0s} C_s + 2\gamma k'_0 k_{0s} k_1 k_3 [\text{RH}] C_0 C_s / k_5 (k_{1s} + k_{2s}) \Sigma k'_0,$$

and taking into consideration equations (3.2) and (3.3), we obtain the experimentally observed rate for the polymer films

$$W = \alpha_j W_j = -dC/dt = k_0 C + k_i C_0 C = kC, \quad (3.5)$$

where $k_0 = k_{0s} K_e$.

Equation (3.5) is adequate to the empiric (1.1). It should be noted that the ratio $[\phi H_s] = \gamma C_0$ corresponds to the constant number of low molecular weight particles within the cells, that is to be fulfilled under the condition

$$[rH_s]/[rH_v] = 2K_e, \quad \gamma = 2K_e/\alpha_j.$$

The theoretic rates for the formation of rH

$$\begin{aligned} W_{rH} &= \alpha_j (d[rH_s]/dt + d[rH_v]/dt) = \alpha_j (k_{1s} + k_{2s}) [r_s^*] + \alpha_j k_3 [r^*] [RH] \\ &= (\alpha_{rH} k_0 + k_i C_0) C, \end{aligned}$$

for the polymer arylation

$$\alpha_j (d[RAr_v]/dt) = \alpha_j k_3 [r^*] [RH] = k_i C_0 C,$$

for the polymer degradation

$$\begin{aligned} \alpha_j (dn_s/dt) &= \alpha_j k_{3s} [P_s^*] = \alpha_j k_{1s} [r_s^*] \\ &= \alpha_j 2k'_0 k_{1s} k_{0s} C_s / (k_{1s} + k_{2s}) \Sigma k'_0 = \alpha_n k_0 C = k_n C, \end{aligned} \quad (3.6)$$

also correspond to the experimental expressions (1.3)–(1.5), (1.9), and the ratio $\beta_{rH} = \beta_{RAr} = 1$ is also fulfilled.

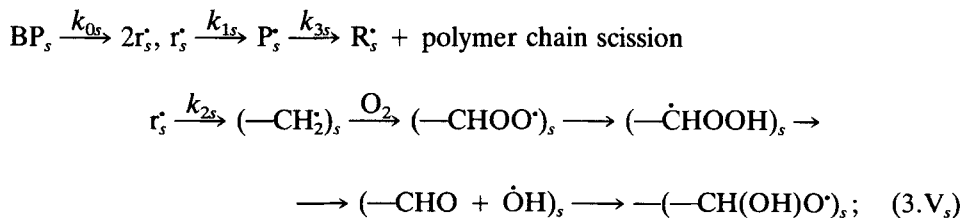
It should be stressed that in inferring the expressions above, the following inequalities were used:

$$k_1 [r_s^*] [\phi H_s] \ll (k_{1s} + k_{2s}) [r_s^*], \quad k_1 [r_s^*], \quad k_1 [r_s^*] [\phi H_s] \ll k_3 [r^*] [RH],$$

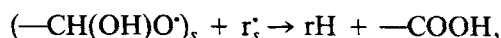
which correspond to rare and long reactional changes of the arylation.

Oxygen effect in the model reaction. As has been noted, oxygen inhibits the chain stage in CTA and PC nearly to an equal extent (Figure 3, plot 2). Under air, hydroperoxide polymers are not accumulated in the films, and a twofold decrease in the degradation constant is observed: $k_n^a = 0.5 k_n$. Pure oxygen does not change this situation.

The facts that are obtained are explained by the following *S*-scheme:



then the hydroxyalcoyl that appears interacts with the primary benzoyloxy



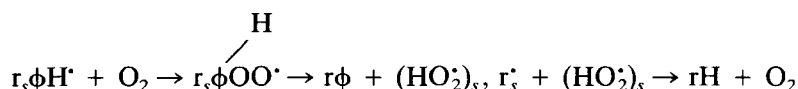
thereby decreasing the r_s^* concentration and modifying the expression for the polymer degradation rate

$$\begin{aligned} \alpha_j (dn^a/dt) &= \alpha_j k_{3s} [P_s^*] = \alpha_j k_{1s} [r_s^*] \\ &= \alpha_j k'_0 k_{0s} k_{1s} C_s / (k_{1s} + k_{2s}) \Sigma k'_0 = 0.5 k_n C = k_n^a C \end{aligned}$$

in accordance with the experiment (see equations (1.6), (3.6)).

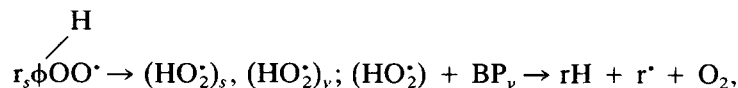
Here, it is important that the oxidation process should not involve the P_s^* radical which is to be disrupted. Such an assumption seems reasonable, as the intracellular *V*-sponge absorbs O_2 molecules, decreasing the frequency of O_2 interaction with the P_s^* radicals situated on the walls of *S*-micropores. By steric conditions, the side R_s^* radicals should more readily undergo oxidation, as they appear in the volume of *S*-micropores during their oscillation-rotational motions.

The inhibition of BP chain decomposition can be explained by the rapid oxidation of radical σ -complexes in the *S*-zone^{43,44}



when eliminating the interzonal *S, V*-transfer of free radicals.

At sufficiently high temperatures (378–388 K) a noticeable first-order chain reaction of BP appears in CTA.⁴ Probably, in this case a part of HO_2^* radicals get into *V*-zone of carcass cells where they react with BP



inducing the chain oxidation of RH groups by scheme similar to (3.V_s) with a difference, as regards *V*-zone, that is the alcohol *V*-radical is to react in the propagation $-\text{CH}(\text{OH})\text{O}^* + \text{BP}_v \rightarrow -\text{COOH} + r\text{H} + r^*$ rather than in the termination.

Taking into account the reaction of termination (3.5), one can obtain the theoretic equation of BP decomposition rate for the aerated films

$$-(dC/dt)^a = (k_0 + k_i^a C_0)C,$$

which is in agreement with the experiment, and $k_i^a < k_i$.

Now, we complete the discussion of the model reaction in its thermal version, but we should like to note the following. The structural-kinetic model of the reaction was constructed taking into consideration the supermolecular formations which are absent in the homogeneous system and are characterized with colloid-microheterogeneous scale (micropores and zones of carcass cells). As is known for heterogeneous systems, the rate of chemical reactions is in many respects dependent upon the factor of structural rearrangement. Our schematic description is related to the polymeric specimens with stable carcass-cellular structure. Meanwhile, the structure of the microheterogeneous elements in the carcass cells are capable of changing under thermomechanical effects, then changing the kinetics of a complex reaction.

Actually, experiments show the significant changes in the characteristic function $k = f(C_0)$ of BP decomposition for CTA films prepared using water-saturated solvent methylene chloride, and for CTA cotton-wool obtained by polymer precipitation from the solution.⁴⁵ The BP-reaction kinetics change considerably when the PC films are drawn for a structural evolution,⁴⁶ namely, the decomposition rate increases considerably, probably due to enhanced mobility of the elements of structural zones and increased frequency of the interzonal transfer of free radicals.

Thus, under the state of supermolecular structure, the different polymers (such as CTA and PC) must simulate each other in a reaction and, to the contrary, a polymer possessing an original molecular structure must simulate the different chemical compounds. In short, the chemistry of polymers is inalienably connected with both prehistory of specimens and their structural change in the reaction course.¹

We devote the next section to the photochemical reaction of CTA with BP in a temperature range of from 293 K to 341 K. In this reaction, the structure of the films, obtained using dry methylene chloride, should be stable at not less than 371 K.

4. Kinetic model of the BP photodecomposition

The interaction of BP with CTA at from 293 K to 341 K was induced by uv radiation with frequency $\bar{\nu} < 32,000 \text{ cm}^{-1}$ (that is outside the region of own CTA absorption).⁵ At the studied values of C_0 , optical density ($D < 0.05$) of the films provided the uv absorption nearly uniformly upon the thickness (15–25 mcm) of specimen. The kinetics of the photochemical process is described by the exponential equation (1.1), as well as the thermal one. In the evacuated films, the effective rate constant of BP photodecomposition

$$k_p = k_{0,p} + k_{i,p}C_0 \quad (4.1)$$

is a higher value (Figure 9, plot 1) than in the aerated films (Figure 9, plot 2)

$$k_p^a = k_{0,p}^a + k_{i,p}^a C_0;$$

here $k_{0,p} = k_{0,p}^a$ is a photodissociation rate constant, a quantum yield of photodissociation $\varphi_{0,p} < 0.1$, an activation energy $E_{0,p} \approx 13$ kJ/mol.

The kinetic phenomenology of the photoprocess does not differ qualitatively from the thermal one. Accordingly, it can be assumed that the heterophasic mechanism discussed above is suitable for the BP photodecomposition as well. An important condition of the photochemical mechanism is that for the BP molecules, being exposed to uv irradiation, to dissociate in the *S*-zone of carcass cell only. At the same time, the BP photodissociation should be inhibited by force field in the narrow *V*-micropores,¹ thus in the *V*-zone, the energy of BP photoexcitation should be converted into heat only.

The above means that the photoprocess should include the interzonal transfer of free valency. Just the *S,V*-phototransfer can be associated with the specific phenomenon⁵ when exposing the film to the uv-band $\bar{\nu}_1 = 30,500$ cm⁻¹: the BP decomposition rate increases under the simultaneous exposure to the inactive for BP UV component with $\bar{\nu}_2 < 27,600$ cm⁻¹. In experiments,⁵ the k_p value changed from $6.5 \cdot 10^{-4}$ to $8.5 \cdot 10^{-4}$ s⁻¹, and the k_p^a value changed from $3.7 \cdot 10^{-4}$ to $4.7 \cdot 10^{-4}$ s⁻¹.

This effect gives evidence for the intermediate photosensitive particles whose steady concentration is achieved from the beginning of the conversion. By their spectral region of photosensitivity, these particles correspond to benzene σ -complexes (those undergo photolysis with ejection of H atom)⁴⁷ and to peroxy radicals of such σ -complexes.⁴³

Taking into account the above, one can assume that the thermal *S,V*-transfer of radicals (reaction (3.II)) becomes practically "frozen" at $T < 340$ K (it occurs with low frequency at 371 K). Meanwhile, the possibility of phototransfer remains due

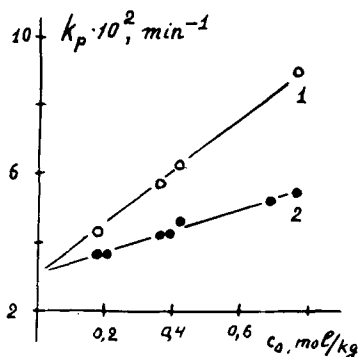
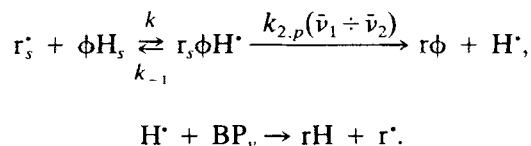


FIGURE 9 Dependence of effective constant of the BP photolysis rate on the value of C_0 in (1) evacuated and (2) aerated CTA films at 293 K. The uv light intensity in the spectrum region $\bar{\nu} < 32,200$ cm⁻¹ is $7.6 \cdot 10^{-3}$ e m⁻² s⁻¹.

to photolysis of the σ -complexes and their peroxy radicals. The S, V -transfer scheme for the evaluated films will attain the following form:



Under the invariability of the other elementary stages of the heterophasic mechanism (3), this scheme allows the kinetic equation of BP photodecomposition.

Taking into account the equality of the initiation rate and the termination rate for the reactional chains in the V -zone $k_{2,p}[r_s \phi H^*] = k_5[r^*]$ and expressing the term $[r_s \phi H^*]$ in accordance with the scheme of S, V -phototransfer, we find

$$[r^*] = k_{2,p} k_1 [r_s^*] [\phi H_s] / k_5 (k_{-1} + k_{2,p}).$$

Then by substituting the obtained expression $[r^*]$ into the expression of total BP photodecomposition rate $W_{pj} = k_{0s,p} C_s + k_3 [r^*] [RH]$ and taking into consideration equations (3.4), (3.2) and (3.3), we obtain as a result the following equation:

$$\begin{aligned} dC/dt &= [k_{0,p} + \text{const} \cdot k_{2,p} k_{0,p} C_0 / (k_{-1} + k_{2,p})] C \\ &= (k_{0,p} + k_{i,p} C_0) C = k_p C, \end{aligned} \quad (4.2)$$

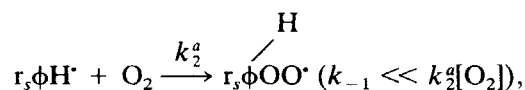
where k_p constant is adequate to the experimentally observed one (4.1).

According to the theoretic equation (4.2), the value of $k_{i,p}$ can depend superlinearly on the intensity (τ) of the acting uv radiation, as the numerator in $k_{i,p}$ includes the product of $k_{0,p}$ and $k_{2,p}$ constants which depend on τ . This is to be observed if the value of $k_{2,p}$ will be small as compared with that of k_{-1} in the reverse dissociation of $r_s \phi H^*$ radicals. The superlinear dependence is actually observed.⁵

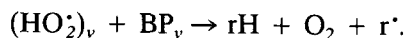
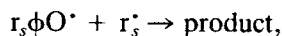
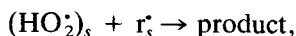
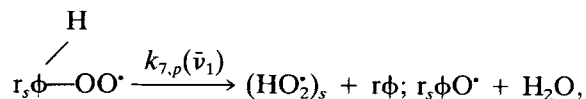
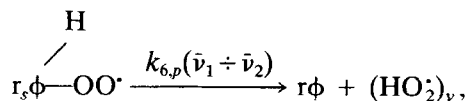
From the structure of equation (4.2), one can understand the reason for the acceleration of BP decomposition with a supplementary source of long-wave irradiation with $\bar{\nu}_2 < 27,600 \text{ cm}^{-1}$. This irradiation does increase the $k_{2,p}$ rate constant of decomposition of $r_s \phi H^*$ radicals toward the initiation of the chain stage in the V -zone of carcass cells.

The efficiency of chain decomposition ($k_{i,p}/k_{0,p}$), calculated by the data presented in Figure 9 is close to the value of k_i/k_0 , calculated by the data presented in Figure 3 for T-371 K. Probably, at room temperature the S, V -phototransfer of free radicals is combined with a high translational mobility of BP and r^* particles within the carcass cell.

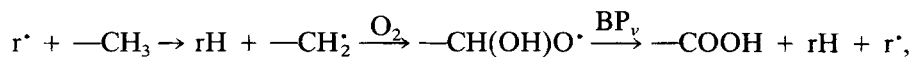
In the aerated films, the S, V -serving radical $r_s \phi H^*$ is quickly oxidized



and an adequate scheme of interzone transfer will attain the following form⁵:



Assuming that the reactional chains in the *V*-zone are the same, as in the thermal process (3)



and their termination occur by the former reaction (3.5), we will find

$$[r^*] = 2k_{6,p}k_2^a C_0 [r_s^*] / k_5(k_{6,p} + k_{7,p}).$$

Then, taking into consideration the expressions (3.4), (3.2), (3.3), we obtain the following expression of the BP photodecomposition rate for the aerated films:

$$\begin{aligned} -dC/dt &= [k_{0s,p}^a + \text{const} \cdot k_{6,p} k_{0s,p} C_0 / (k_{6,p} + k_{7,p})] C \\ &= (k_{0,p}^a + k_{i,p}^a C_0) C = k_p^a C, \end{aligned} \quad (4.3)$$

which is in agreement with the experiment.

According to (4.3), the long-wave uv radiation (nonabsorbable by BP $\bar{\nu}_2 < \bar{\nu}_1$) can increase the reaction rate at the condition $k_{6,p} \leq k_{7,p}$, and the dependence of k_p^a on τ value being directly proportional, that was actually observed.⁵

Completing the section, we note that the mechanism of BP photoconversion was not formulated in the previous work⁵ because the discussion logic in the work did not go beyond the frame of a homogeneous scheme. A successful result, as is shown in the present section, is achieved due to taking into consideration the functions of microheterogeneous elements of the supermolecular structure during the chemical process.

As regards the heterophasic mechanism as a whole, one can state that some minor details remain unclear so far. For example, a concrete nature of R_{1s}^* radicals is to discuss more details. Again, the certain difficulties may arise in bringing to

light the nature of both the S, V -serving radicals ($r, \phi H^{\bullet}$ or $R, \phi H^{\bullet}$ in the scheme) and the S, V -messenger radicals (H^{\bullet} , HO_2^{\bullet} or r^{\bullet}). But at the same time, one or another schematic choice does not change the key position of the mechanism, namely, the heterophasic distribution of the reaction chains within the S - and V -zones of carcass cells.

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