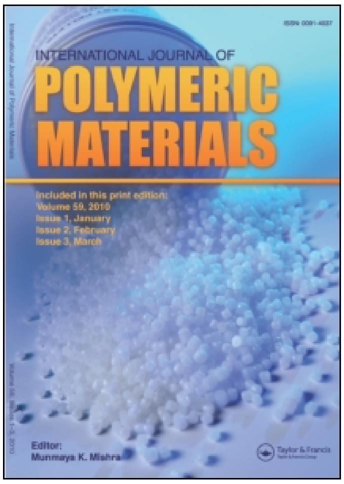

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Kinetic Features of Radical Dissociation in Filled Acetyl Cellulose

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The kinetic patterns of the diphthaloyl ethane dissociation in acetyl cellulose at 320–370 K with the formation of stable radicals have been considered as a function of the aerosil content. The profound filler effect was found to be upon the temperature dependence of the radical yield. Kinetic parameters of the radical dissociation are determined by the structural modifications of the polymer under shaping of interfaces.

Keywords: Acetyl cellulose; radical dissociation; kinetics diphthaloyl ethane; fillers

INTRODUCTION

Elementary reactions are of interest for the elucidation of the influence of the polymer composite molecular organization on the mechanism of chemical processes. The effect of inert filler (aerosil) on kinetics of the low-temperature cage reactions of carbenes and macroradicals have been shown in a number of polymers [1]. Kinetics was verified to have essential changes in response to a transformation of polymers in the structural state of interfaces. An assessment of the interface thickness has been carried out on the basis of kinetic data obtained. The further advancement of investigations along this line is connected with searching for other elementary reactions in which kinetics and mechanism are representative of structural-physical organization of

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*Corresponding author.

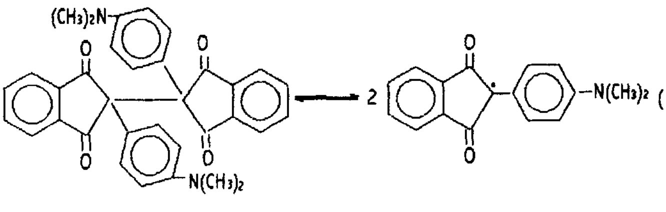
filled polymers at ordinary and elevated temperatures. In this work, the kinetic regularities of thermal dissociation of the arylindandionyl radical dimerous [2] has been studied in acetyl cellulose (AC) depending upon the aerosil content. The yield of radicals in the reaction is determined by the ratio of rates of the structural-sensitive steps: diffusive separation of primary radical pairs and decay of radicals as a result of their recombinations or transformations in a volume.

EXPERIMENTAL

Experiments were performed on 1,2-bis(4-dimethylaminophenyl)-diphthaloyl ethane (DPE) obtained by the procedure described in [3]. AC of $M_v = 330000$ was used as polymeric media. The AC films of 50 μ thick with DPE additives were prepared from the combined solution in chloroform. The DPE concentrations were $2-4 \cdot 10^{-2}$ M. Aerosil with the specific surface of 150 m^2/g and the particle diameter of 20 nm was used to prepare filled samples. Filled samples were obtained from 5% solutions of AC in chloroform containing DPE and the quantity required of aerosil heat-treated at 300°C. Filled solutions were then evaporated under stirring. DPE concentration in filled AC (up to 60% aerosil) was $2 \cdot 10^{-4}$ M relative to the polymer. Samples containing the spin probe (nitroxyl radical) in concentration of $\sim 10^{-4}$ M were prepared in much the same way. Kinetics of the DPE thermal decomposition was studied at 320–370 K in vacuum by the radical yield measured by ESR technique. An accuracy of the temperature control of samples was ± 1°.

DISCUSSION

The researches carried out in the liquid phase [2] shown that the system DPE – free radicals is equilibrium:



(1)

The somewhat different events are observed during the thermal decomposition of DPE in AC. The attainment of a steady state for radicals takes place in this case for an appreciable length of time (10–20 min) everywhere over the temperature range. The steady-state concentrations therewith are "frozen", that is, they are not changed reversibly with temperature.

The kinetic curves of the radical accumulation in AC films and the filled composite are shown in Figure 1. Notice that samples contain before thermal processing some quantity of radicals that are formed at the DPE dissociation in solution and survived after the solvent evaporation. As is evident from the figure, kinetic dependencies in filled and unfilled samples have qualitative distinctions. The radical concentrations in unfilled AC at steady state increase monotonically with increasing in temperature. After initial elevation, the decrease of $[R]_s$ is observed in the filled composite with a further rise of temperature.

The character of dependencies of the radical steady-state concentration upon the initial DPE concentration is indicative of changing of the radical decay mechanism in relation to temperature. The data obtained are given in Table I. As is seen, the relationship between the stationary concentration of radicals and $[\mathrm{DPE}]_0$ is changed from root into linear one. Owing to this the following formal schemes of the DPE conversion in AC can be assumed.

At comparatively low temperatures of 320–334 K:

$$\begin{tikzcd}
\mathrm{DPE} \arrow[r, shift left, "k_1"] & \mathrm{R\cdots R} \arrow[l, shift left, "k_{-1}"] \arrow[r, "k_2"] & 2\mathrm{R} \arrow[ll, bend left, "k_3"]
\end{tikzcd} \qquad (2)$$

The radical pair is formed in primary step as a result of the DPE thermal decomposition. The rigid cage surroundings hinder separation of radicals. Because of this, the portion of radical pairs decays in consequence of recombination in cages. The radicals emerged into a volume are capable of recombining by their diffusion giving DPE.

The linear decay of radicals in volume prevails as the temperature increases up to 344–364 K, and the reaction scheme takes the following form:

$$\mathrm{DPE} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{R\cdots R} \xrightarrow{k_2} \mathrm{R} \xrightarrow{k_3'} \text{products} \qquad (3)$$

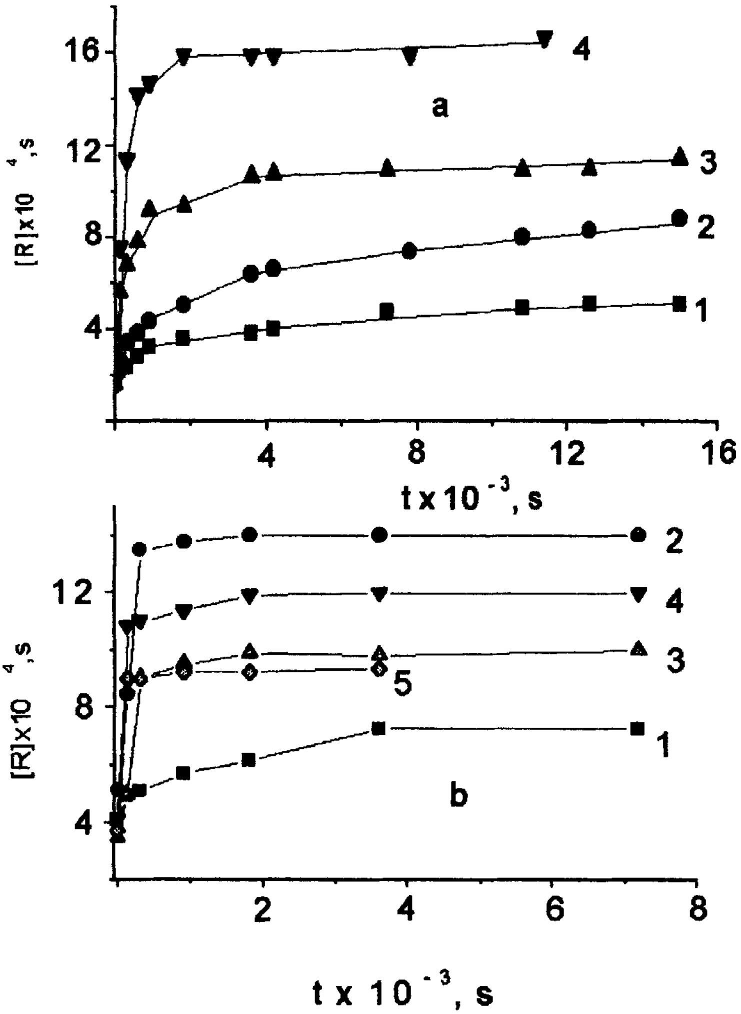
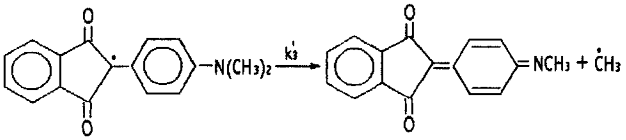


FIGURE 1 Kinetics of the radical accumulation in AC at (a) at 334 K – 1, 344 K – 2, 353 K – 3, 364 K – 4 and AC with 60% aerosil (b) at 321 K – 1, 344 K – 2, 354 K – 3, 359 K – 4, 364 K – 5.

The decomposition of radicals can be conceived as the possible reaction of the linear decay:



(4)

TABLE I The dependence of steady-state concentrations of radicals in AC on initial DPE concentration

T, K	$[DPE]_0 \cdot 10^2, M$	
	1,9	3,8
	$[R]_s \cdot 10^4$, M	
334	5,0	7,3
344	8,5	16,0
353	11,0	20,0

Considering that the concentration of radical pairs is stationary and $k_{-1} \gg k_2$ in the solid polymer, we obtain the following equations for $[R]_s$ at different temperatures:

$$[R]_s = \sqrt{\frac{k_1 k_2 [\mathrm{DPE}]_0}{k_{-1} k_3}} \tag{5}$$

$$[R]_s = \frac{k_1 k_2 [\mathrm{DPE}]}{k_{-1} k'_3} \tag{6}$$

Notice that Eqs. (5) and (6) are true on condition that $[\mathrm{DPE}]_0 \gg [R]_s$ which is in fact realized in AC.

The analysis of initial portions of kinetic curves exhibited in Figure 1a supports the change of the radical decay mechanism with a rise in temperature. The rate of the radical accumulation is determined from (2) and (3) in following manner:

$$\frac{d[R]}{dt} = \frac{k_1 k_2 [\mathrm{DPE}]_0}{k_{-1}} - k_3 [R]^2 \tag{7}$$

$$\frac{d[R]}{dt} = \frac{k_1 k_2 [\mathrm{DPE}]_0}{k_{-1}} - k'_3 [R] \tag{8}$$

Upon integrating (7) and (8) we obtain in view of (5) and (6) the equations:

$$\ln(\alpha/\beta) = 2k_3 [R]_s t \tag{9}$$

$$\ln \ln \gamma = k'_3 t, \tag{10}$$

where $\alpha = \frac{[R]_s + [R]}{[R]_s - [R]}$, $\beta = \frac{[R]_s + [R]_0}{[R]_s - [R]_0}$, $\gamma = \frac{[R]_s - [R]_0}{[R]_s - [R]}$, and $[R]_0$ is the initial concentration of radicals in AC before heat treatment. The kinetics of the radical formation to the attainment of steady state is represented in Figure 2 in coordinates of Eqs. (9) and (10).

The activation parameters of formation and decay of radicals were estimated from plots obtained. The temperature dependencies of the rate constant of the radical decay by the first order law reaction (4) are shown in Figure 3. The following equation was derived for the rate constant: $k_3' = 4.96 \cdot 10^8 \exp(-68/RT), \mathrm{s}^{-1}$. It should be marked that the activation energy of this process is close to that of the radical decomposition in solid polymers, for instance, in polymethylmethacrylate and polymethacrylic acid [4]. The value of the activation parameter for the radical formation is $E_1 + E_2 - E_{-1} \approx 108\,\mathrm{kJ/mol}$. Since the strength of bonds by which dissociation of DPE takes place is about 77 kJ/mol [2], it is believed that E_1 has mach the same value. Then the activation parameter determining the efficiency of the radical exit from cages is $E_2 - E_{-1} \approx 31\,\mathrm{kJ/mol}$.

The rate constant of recombination of radicals in volume was determined from the kinetics at 334 K (Fig. 2): $k_3 = 0.7\,\mathrm{M}^{-1}\mathrm{s}^{-1}$. The

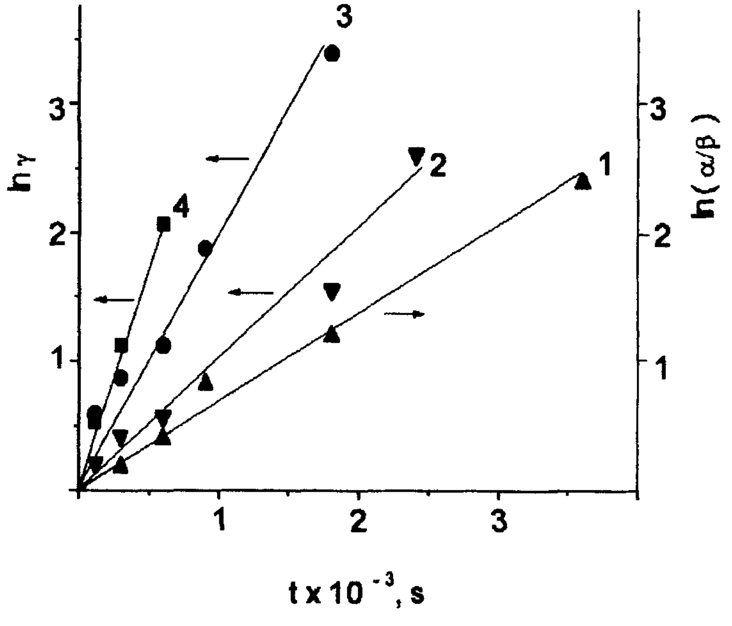


FIGURE 2 Approximations of kinetics of the radical accumulation in coordinates of Eqs. (9) and (10) at 334 K – 1, 344 K – 2, 353 K – 3, 364 K – 4.

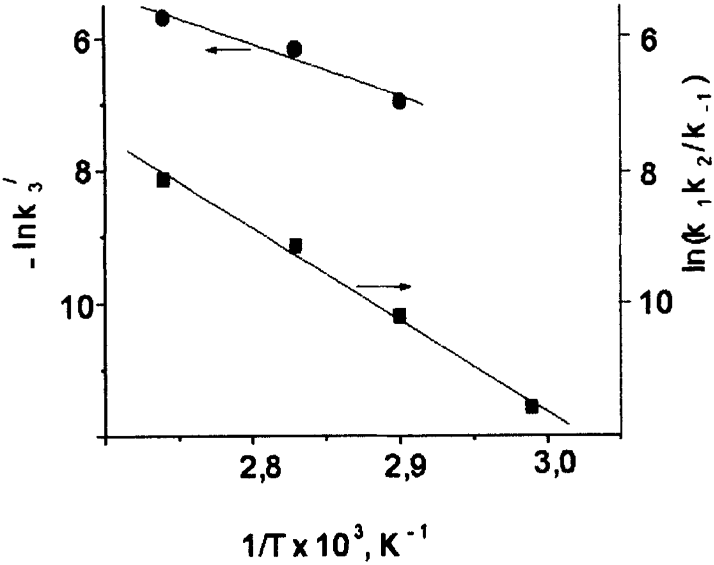


FIGURE 3 The temperature dependencies of the rate constant of the radical linear decay and effective kinetic parameter of radical formation.

assessment of k_3 according to the Smoluhovski expression

$$k_3 = 8\pi rD, \tag{11}$$

where r is the size of cages in which radicals are recombined, D is the diffusion coefficient, gives about the same value, if to believe that $r \approx 0.5\,\text{nm}$ and $D \approx 10^{-15}\,\text{cm}^3/\text{s}$. Such D magnitude is quite possible for radicals in the rigid polymer matrix at $T < T_g$.

The initial rates of the radical formation and limiting concentrations of radicals at lower temperatures in filled samples exceed those in unfilled AC. (Fig. 1b). But an opposite regularity is observed in range of high temperatures (Fig. 4). A peculiar kind of the temperature plots for stationary concentrations of radicals at 320–370 K in filled AC testifies that the structural modification of polymer influences upon reactivity of radicals. The estimation of the average distance between the aerosil particles by the Eq. (5)

$$l = d[(\varphi_m/\varphi)^{1/3} - 1], \tag{12}$$

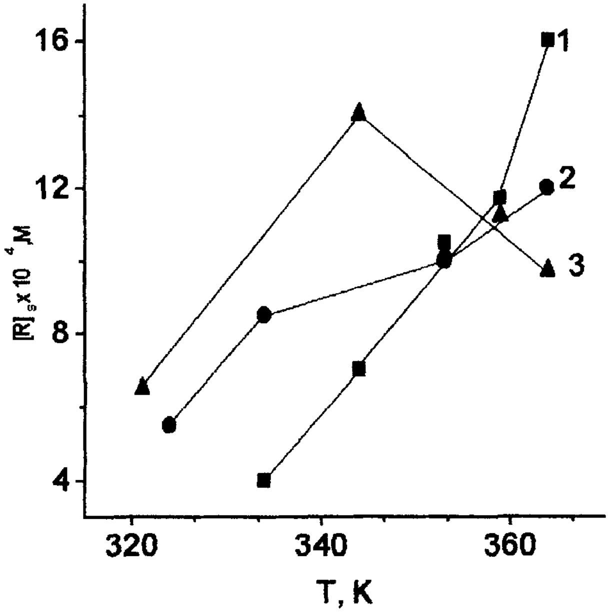


FIGURE 4 The temperature dependencies of steady-state concentrations of radicals in AC with 0% – 1, 30% – 2 and 60% – 3 aerosil.

where d is the particle diameter, φ is the volume fraction of a filler, φ_m is the most of possible filler fraction (~ 0.8), gives the value of 10 nm.

Previously [1] we demonstrated that distances of this order correspond to the limit value of l whereby interfaces begin to be overlapped, causing the polymer transition into different structural state. The influence of aerosil on the kinetics of radical reactions is most conspicuous in this structural state. The increase of initial rates and stationary concentrations of radicals in filled AC at 321 – 344 K is evidence for essential decreasing of the radical decay efficiency, that is, the parameters $k_{-1}k_3$ or $k_{-1}k'_3$ are reduced with respect to k_1k_2 in Eqs. (5) and (6).

A comparison of the temperature dependencies of the spin probe correlation time in AC and filled samples (Fig. 5) is indirect evidence for structural changes in interfaces. Although the spin probe technique defines only the highly-frequency range of all spectrum of molecular motions at $T < T_g$ [6], nonetheless, from Figure 5 we notice that filling has a tangible influence on the molecular dynamics and, consequently,

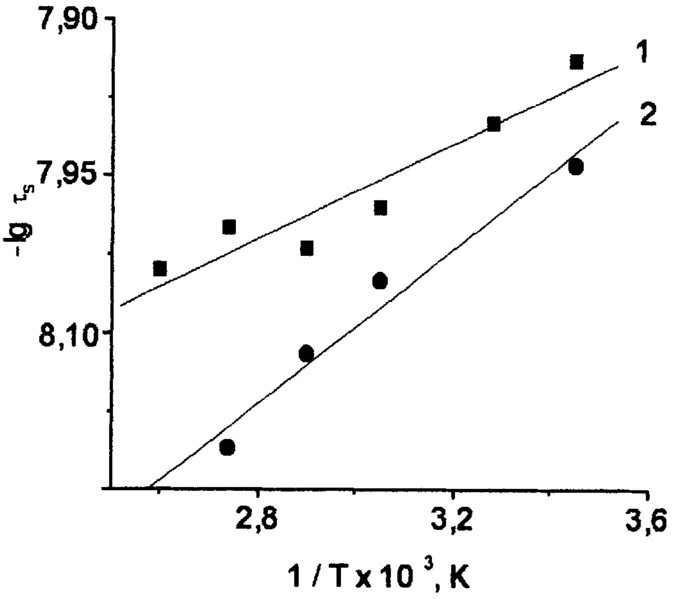


FIGURE 5 The temperature dependencies of the correlation time of the spin probe rotation in AC with 0% – 1 and 60% – 2 aerosil.

on the relation between kinetic parameters of the radical dissociation. There is good reason to believe [6] that the rotation frequency of probes, determined below the glass temperature, corresponds to their movements in micropores. Thus the effective activation energy of this mobility increases from 4.6 kJ/mol in AC to 7.6 kJ/mol in AC with 60% of aerosil. When taken into account that the radical recombination in cages is limited by their rotational mobility, it is thought that k_{-1} has about the same activation energy. Under these conditions we obtained that effective activation energy of the radical yield from cages E_2 is 35.6 kJ/mol.

Referring to Figure 4, variations in stationary concentrations of radicals in filled samples depends on the filler content. The temperature coefficient of changed of $[R]_s$ becomes negative at $T > 344$ K. The intermediate variant of the temperature dependence is likely to be realize in samples containing 30% of aerosil. In this case only decreasing of the efficiency of radical formation was observed with an increase in temperature. In contrast, the radical yield grows essentially in filled samples at moderately low temperatures when the quadratic mechanism of the radical decay is dominated. These facts permit to conclude that the structural modification at filling exerts the most effect on the radical decay step. Because of this, the temperature dependence inversion of Figure 4 is observed in the region of transformation of the bimolecular radical decay into linear one. The increase of the activation energy of rotational mobility in filled AC (Fig. 5) allows to assume that the activation energy of the bimolecular decay rate constant (k_3), connected with the translation mobility of radicals, increases as well owing to the interrelationship of dynamics of these motions [7]. The increase of E_3 from 44 kJ/mol to 47 kJ/mol must lead to a rise observed in stationary radical concentrations at 320–340 K in filled AC as compared with unfilled samples.

The radical concentration drop at high temperatures is possible in AC with 60% of aerosil, if to assume increasing of the linear decay activation energy from $E_3 \approx 68$ kJ/mol to 124 kJ/mol under introducing of filler. That sharp increasing of the activation energy of the radical decay by the reaction (4) may be due to a retardation of the molecular relaxation in interfaces [8] which must stimulate the change of valency angles and chemical bond lengths at the radical decomposition. The delay of this process of the chemical bond rehybridization in reference to the radical decomposition act has, in doing so, the same effect as the activation energy increase in the reaction (4).

CONCLUSION

Thus, the yield of stable radicals during the DPE thermal dissociation is highly sensitive to a molecular organization of filled polymer composites. In this connection, the temperature dependence of the stationary concentration of these radicals may be considered as characteristic of the structural change degree under filling. The peculiarity of given process is its versatility from the point of view of possibility to conduct it in a wide diversity of polymeric materials. The development of given approach to investigate the physical microstructure of polymers provides the determination of relationship between kinetic parameters of the radical dissociation process and specific characteristics of the polymer morphology.

References

[1] Davydov, E. Ya., Vorotnikov, A. P., Pustoshnyi, V. P., Pariyskii, G. B. and Zaikov, G. E. (1997). *Vysokomolek Soed.*, **B39**(12), 2059.
[2] Davydov, E. Ya. and Zaikov, G. E. (1998). *J. Russian Chem.*, **42**(3), 66.
[3] Pisarenko, L. M., Nikulin, V. I. and Gagarina, A. B. (1998). *Izvestiya AN SSSR, ser. khimich.*, **6**, 1237.
[4] Khudyakov, I. V., Pisarenko, L. M., Gagarina, A. B., Kuzmin, V. A. and Emanuel, N. M. (1975). *Doklady AN SSSR*, **222**(6), 1390.
[5] Nikulin, V. I. and Pisarenko, L. M. (1985). *Izvestiya AN SSSR, ser. khimich.*, **1**, 151.
[6] Davydov, E. Ya., Pariyskii, G. B. and Toptygin, D. Ya. (1977). *Vysokomolek. Soed.*, **A19**, 977.
[7] Lipatov, Yu. S., Privalko, V. P. and Sharov, A. N. (1982). *Doklady AN SSSR*, **263**(6), 1403.
[8] Kovarskii, A. L., Wasserman, A. M. and Buchachenko, A. L. (1979). Molecular motion in polymers by ESR. Eds., Boyer, R. and Keinath, S., Michigan: MMI press. p. 54.
[9] Wasserman, A. M., Barashkova, I. I., Yasina, L. L. and Pudov, V. S. (1977). *Vysokomolek. Soed.*, **A19**, 2083.
[10] Malinskii, Yu. M. (1970). *Uspekhi khimii*, **39**(8), 1511.