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E. Ya. Davydov^a; V. P. Pustoshnyi^a; G. B. Pariyskii^a; G. E. Zaikov^a

^a Institute of Biochemical Physics, Russian Academy of Sciences, Moscow, Russia

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Molecular and Free Radical Products of Reactions of Nitrogen Dioxide with Polyvinylpyrrolidone

E. YA. DAVYDOV, V. P. PUSTOSHNYI, G. B. PARIYSKII
and G. E. ZAIKOV *

*Institute of Biochemical Physics, Russian Academy of Sciences,
Kosygin street 4, Moscow, 117977 Russia*

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The mechanism of reactions of nitrogen dioxide with polyvinylpyrrolidone at 295–363 K has been considered. The nature of the molecular and free radical products of reactions has been studied by UV and ESR spectroscopy. The main molecular products are nitrites and nitrozoamides. The formation of stable acylalkylnitroxyl and iminoxyl radicals was registered. The influence of the structural-physical modification of the polymer at filling by aerosil has been established on kinetics of the formation of radicals.

Keywords: Polyvinylpyrrolidone; nitrogen dioxide; reaction mechanism; free radicals

INTRODUCTION

Nitrogen oxides are toxic and aggressive compounds of atmosphere. For development of stabilization methods for polymeric materials the knowledge of the mechanism of reactions with the assistance of these gases is needed. Nevertheless, the data on the mechanism of interaction of nitrogen oxides with solid polymers are few [1] as compared with abundant literature dedicated to researches of such reactions in liquid phase [2]. In order to recognize the features of the reaction mechanism in polymers the nature of molecular and free radical

*Corresponding author.

products must be identified together with the type of active bonds of monomer links which are responsible for the initiation of the polymer degradation in the presence of nitrogen oxides. Also to solve the stabilization problem it is essential to clear up the role of the structural-physical organization of polymers in the kinetics and the mechanism of these reactions. It is interesting to consider, therefore, the interconnection between the reactivity of macroradicals and changes of the physical structure of polymer media, for instance, as a result of the interface layer formation in filled composites. In the present work the study of the mechanism of the nitrogen dioxide interaction with polyvinylpyrrolidone (PVP) has been carried out along with investigations of the influence of the filler content on kinetics of the radical reactions.

EXPERIMENTAL

Nitrogen dioxide was obtained by the thermal decomposition of lead nitrate. Nitrogen oxide, used in some experiments, was produced by the reaction of 30% nitrogen acid with copper. Experiments were conducted on PVP powder with $M_v = 50000$ prepared by the radical polymerization in the presence of hydrogen peroxide. Aerosil with the specific surface of $300 \text{ m}^2/\text{g}$ and the particle diameter of 20 nm was used as filler. The filled samples were prepared from 2% solution of PVP in chloroform, containing aerosil pre-ignited at 400° . The filled solution, after keeping it for 24 hours at room temperature, was evaporated under stirring. Charges of 50–100 mg were placed in quartz tubes for ESR measurements, which are completed with vacuum stopcock. Tubes were connected with glass vessel of volume 1.1. The stopcock was closed after pumping to the pressure 10^{-3} mm Hg, and the vessel was filled by NO_2 to concentrations of 10^{-4} – 10^{-3} M. As soon as NO_2 was drawn into the tube with a sample, ESR spectra were registered immediately. The ESR measurements were conducted at room temperature, 323 K and 363 K. A precision of the temperature control is ± 20 . The molecular products of reactions were identified by UV spectra of solutions of PVP in chloroform. The concentration of NO_2 in the gas phase was measured by the optical density in the region of 410 nm [3].

RESULTS AND DISCUSSION

The bands at 413 nm and 435 nm were observed in UV spectra of the reaction products of the interaction of PVP with NO₂ (Fig. 1). The peculiar spectral region makes possible to assign these bands to nitrosoamide groups [4]. Based upon the nature of monomer links, the following structure of may be attributed to nitrosoamides: $\text{N}(\text{NO})\text{COCH}_2\text{CH}_2\text{CH}_2$. The formation of these compounds in PVP must be connected with the splitting of the side cyclic fragments from the main chain. In addition, the UV absorption in the region of 320–380 nm was observed with the set of bands spaced at 10 nm. This fact testifies that alkylnitrites [5] are formed in the course of the reaction.

ESR spectra observed, when NO₂ is admitted into the initial and filled PVP, are shown in Figures 2a, b. These spectra represent a superposition of signals of the two type radicals. A comparison of HFS parameters with those known from the literature [6, 7] exhibits that

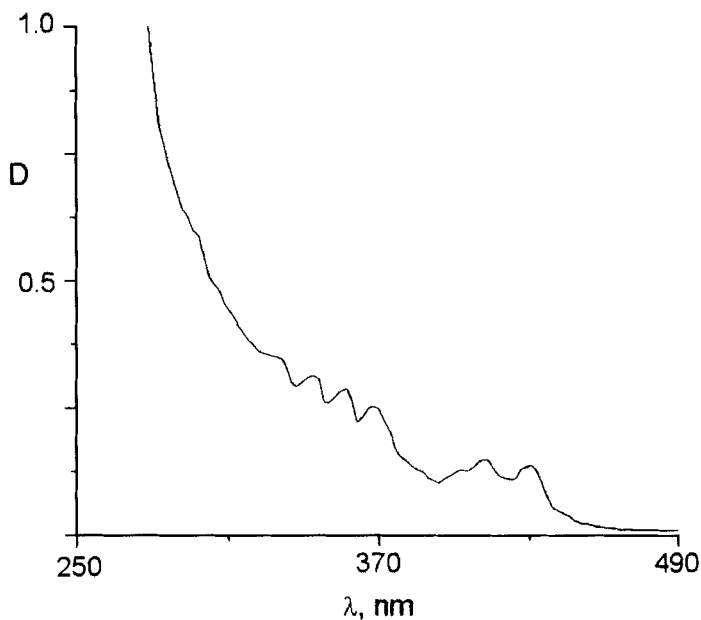


FIGURE 1 UV spectrum of PVP after exposure to NO₂.

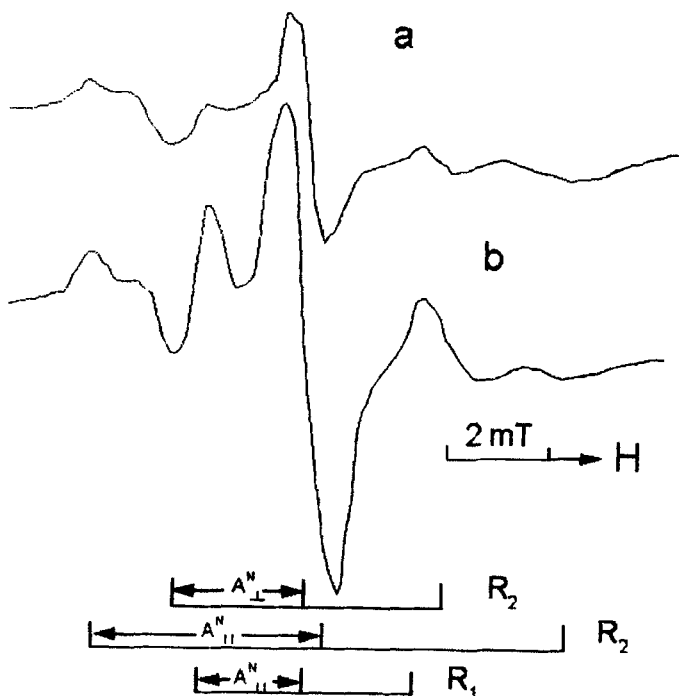
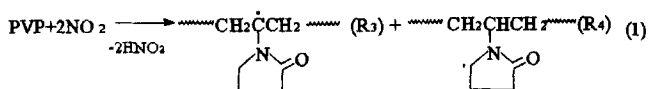


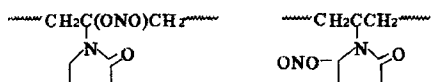
FIGURE 2 ESR spectra of PVP without (a) and with 50% aerosil (b) after exposure to NO_2 at 323 K.

nitrogen dioxide generates in PVP acylalkylnitroxyl radicals (R_1) and iminoxyl radicals (R_2). The anisotropic triplet signal with the constant of HFI of $A_{\parallel}^N \approx 1.94 \text{ mT}$ and g_{\parallel} corresponds to R_1 . The anisotropic signal with parameters $A_{\parallel}^N = 4.33 \text{ mT}$, $A_{\perp}^N = 2.44 \text{ mT}$, $g_{\parallel} = 2.0029$ and $g_{\perp} = 2.0053$ corresponds to R_2 [8].

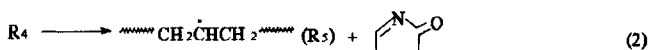
The results of analysis of the UV and ESR spectra permit us to propose the following mechanism of PVP conversion initiated by NO_2 . Most likely C—H bonds, which are in α -position with respect to amide groups, display the activity in the reaction of hydrogen atom abstraction. There are two kinds of such C—H bonds closely related in the scission energy, and, consequently, one can expect the formation in the primary reaction of two macroradicals with free valency localized in the main chain and side group:



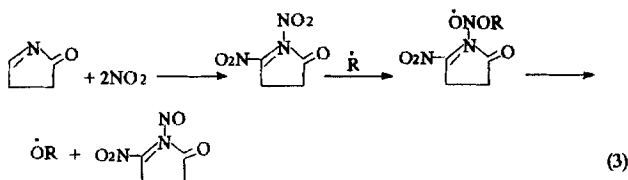
The recombination of R₁ and R₂ with NO₂ results in the formation of nitrites:



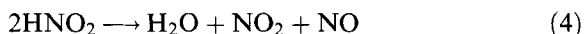
The formation of nitrosoamides is possible as a result of β-decomposition of R₄. As this takes place, the splitting out of the cycle occurs



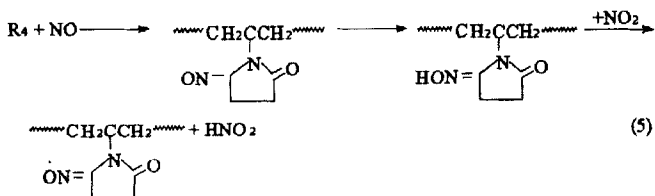
Thereafter the NO₂ reaction with double bonds of this fragment gives rise to the end product [9]:



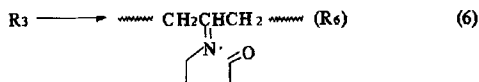
Nitric acid is thought to be the contributor of nitrogen oxide in the given system.



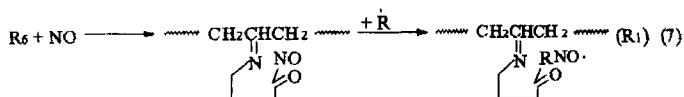
The recombination of NO and R₂ initiates the formation of iminoxyl radicals R₂. This process includes the following consecutive reactions: the formation of nitroso compounds, their isomerization into oxime [1], the abstraction of hydrogen atom by NO₂ from oxime.



The formation of NO by the reaction (4) can explain arising of acylalkylnitroxyl radicals R_1 . To do this would require an assumption of the R_3 decomposition with opening of the pyrrolidone cycle analogously their photodissociation [10]:



Furthermore, acylnitroso compounds and then R_1 are formed in the reaction of the twofold radical acceptance [11]:



Note that any unstable at ordinary temperature free radicals, for example, R_3 , R_4 , R_5 may be regarded as \dot{R} .

The suggested mechanism of the formation of nitroxyl radicals is supported by kinetic features of their accumulation. The concentration of NO_2 in the gas phase was varied, and also the mixture of NO_2 with NO was used in kinetic experiments. As is seen from Figures 3a, b, the kinetics of the R_1 and R_2 formation exhibits qualitative distinctions. As the concentration of R_1 approaches to the limit, that of R_2 passes through a maximum. The essential differences in kinetics are observed likewise at initial stages of the radical accumulation (Fig. 3b) when radicals R_1 are formed with the marked acceleration in contrast to R_2 .

These results are consistent with reactions (5–7). Actually, the formation rate of R_1 is bound to be higher as nitroso groups are accumulated to some steady-state concentration. The approach of nitroso groups and macroradicals R seems to be the limiting stage of the R_1 formation. This process can experience essential difficulties due to the low molecular mobility in solid polymers. The lack of any detectable induction period for the formation of R_2 may be explained by the pseudo-cage character of this process. Two molecules of nitric acid are formed at the close range in reaction of the hydrogen atom abstraction by dimerous NO_2 . As a result of the reaction (4), NO and NO_2 exist neighborhood of macroradicals R_4 . Therefore, one can concede that consecutive reaction (5) occur virtually in “cage” space and are not

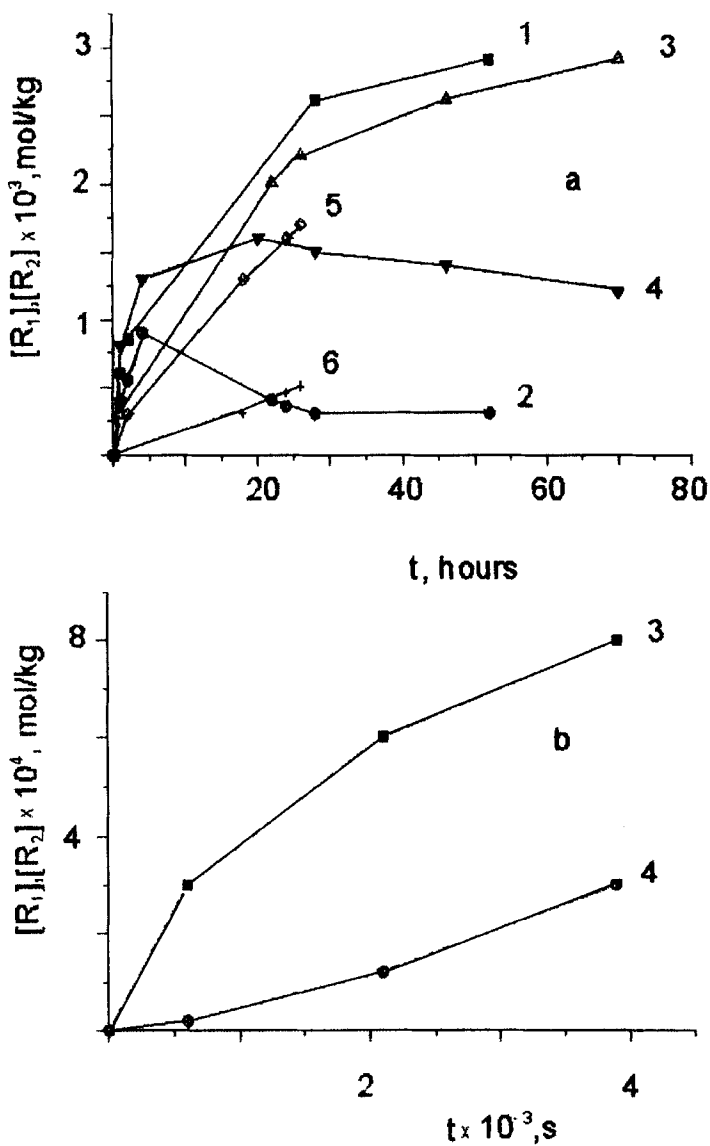
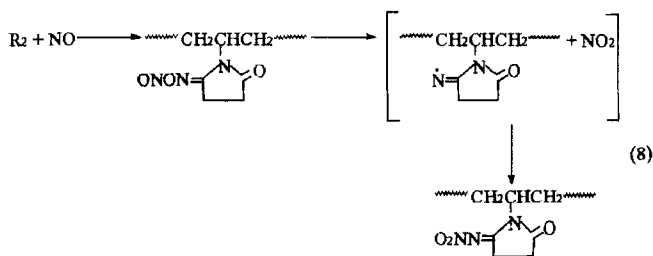


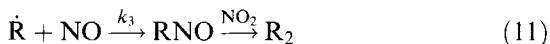
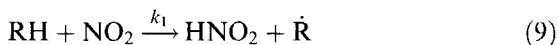
FIGURE 3 (a) Kinetics of the accumulation of R₁ (1,3,5) and R₂ (2,4,6) in PVP and (b) initial portion of curves 3 and 4. Concentrations of NO₂: (1,2) 8.55×10^{-4} and (3,4) 4.0×10^{-4} mol/l; (5,6) is the mixture of NO₂ (10^{-4} mol/l) + NO (3.0×10^{-4} mol/l).

controlled by the mutual diffusion of reactants. It is conceivable that the pass through a maximum of the concentration of R_2 is due to their decay in recombination with NO:



Related mechanism of the iminoxyl radical decay has been given consideration in the work [12]. The time of attainment and the value of the R_2 maximum concentration are the smaller, the higher the NO_2 initial concentration (Fig. 3a).

It is evident from Figure 3a, that the rate of the R_1 formation and their limiting concentrations are actually not changed at a twofold variation of the NO_2 initial concentration. On the basis of this fact, one can draw inferences about the rate-determining stage of their formation. It was found that the rate of the NO_2 absorbing the PVP is in direct proportion to the NO_2 concentration in the gas phase. The formally kinetic scheme of the PVP nitration process can be represented as follows:



Where \dot{R} are macroradicals generated in the primary reaction of PVP with NO₂ and R₆, R₅ are products of their decomposition. If it is granted that concentrations \dot{R} , R₆ and R₆NO are steady-state, one can obtain:

$$[R^*] = \frac{k_1[RH][NO_2]}{k_2[NO_2] + k_3[NO] + k_4 + k_7} \quad (16)$$

$$[R_6NO] = \frac{k_4}{k_6} \quad (17)$$

It is felt that $k_2[NO_2] \gg k_3[NO]$, because $[NO_2] \gg [NO]$ and $k_2 \sim k_3$. If $k_2[NO_2] \gg k_4 + k_7$ then $[R] \sim k_1[RH]/k_2$ and $d[R_1]/dt \sim (k_4k_1[RH])/k_2$. Thus, the independence of the rate of the acylalkylnitroxyl radical accumulation on the NO₂ concentration in the gas phase shows that the rate-determining stage of the R₁ formation is the transformation of primary radicals in reactions (12) and (15). This conclusion is also supported by kinetics of R₁ and R₂ under action of the NO₂ + NO mixture (Fig. 3a). The NO₂ concentration in this case is smaller than in experiments with NO₂ by a factor of ~ 8 , but the initial rate of the R₁ formation is decreased only twofold. The rate of the R₂ formation is strongly decreased under these conditions in accordance with the mechanism of their decay by the reaction (8) [12].

It should be noted that insignificant decreasing ($\sim 10\%$) of the NO₂ concentration in the gas phase was observed in all time of the accumulation of nitroxyl radicals. Therefore, the decrease observed of the R₁ formation rate under the PVP exposure reflects only the rate of the active pyrrolidone cycle consumption in reactions (11–14). The main amount of NO₂ absorbed is transformed into alkylnitrites and nitrosoamides.

The approach based on analysis of the nitroxyl radicals composition on the content of aerosil was put forward in the present work to elucidate the influence of structural-physical organization on the mechanism of radical reactions in PVP. A large body of research gives an indication of essential influence of fillers on free-radical processes of thermal degradation of polymers [13]. The strong dependence of kinetic parameters on the filler content has been revealed also by the example of low-temperature radical cage reactions initiated in polymers by triplet

carbons [14] and photolysis of iron chloride [15]. It is known that the structural-physical modification of polymers in interfaces is exhibited by the density change of the molecular packing and the molecular mobility intensity [16]. The structural effect of this kind can influence differently the rate of the R_1 and R_2 formation. More friable molecular packing in interfaces, as compared with that in a volume, results from the hindrance of relaxation processes in the course of a shaping of filled polymers from solutions [17]. The decrease of the molecular packing density can accelerate the relaxation, for example, through the increase of motions of side groups in macromolecules [18]. In doing so, the rate of reaction (6) involving the pyrrolidone cycle breaking increases. The packing density decrease provides also the rate enhancement of the reaction (7) which includes the approach of macroradicals \bar{R} and nitrosocompounds by diffusion. On the other hand, the iminoxyl radical formation by the reaction (5) is not associated with the considerable structural reorganization of a media to create the favorable mutual orientation of reactants and demands much smaller molecular mobility in comparison with reactions (6) and (7). From these considerations one can explain the fact that the quantitative relation between R_1 and R_2 is changed with the filling degree (Figs. 2a, b).

Fractions of R_1 as a function of the exposure time in NO_2 at different temperature are shown in Figures 4a, b, c for non-filled PVP, with 25 and 50% of aerosil. The estimation of this value was carried out by comparison of the area of the ESR spectrum of R_1 [19] with the area of the total ESR spectrum of R_1 and R_2 . The fraction of R_1 for non-filled PVP is only 6–7% at room temperature and does not change with time during three hours. Its growth up to 20% was observed during later time. The R_1 fraction at elevated temperatures increases at the beginning of PVP exposure, but further it goes to the plateau, with the limiting value of the R_1 fraction is the more, the higher temperature.

The alternative regularities were observed in filled samples. The fraction of R_1 at room temperature is somewhat increased up to 8–10% at the beginning and subsequently is not changed. Whereas the monotonic growth of the R_1 fraction with time was observed at 323 K and 363 K. In this case the R_1 fraction in initial stages of process the more, the higher temperature as in the non-filled PVP. The rate of its increase however at 323 K is higher than at 363 K. As a consequence, the

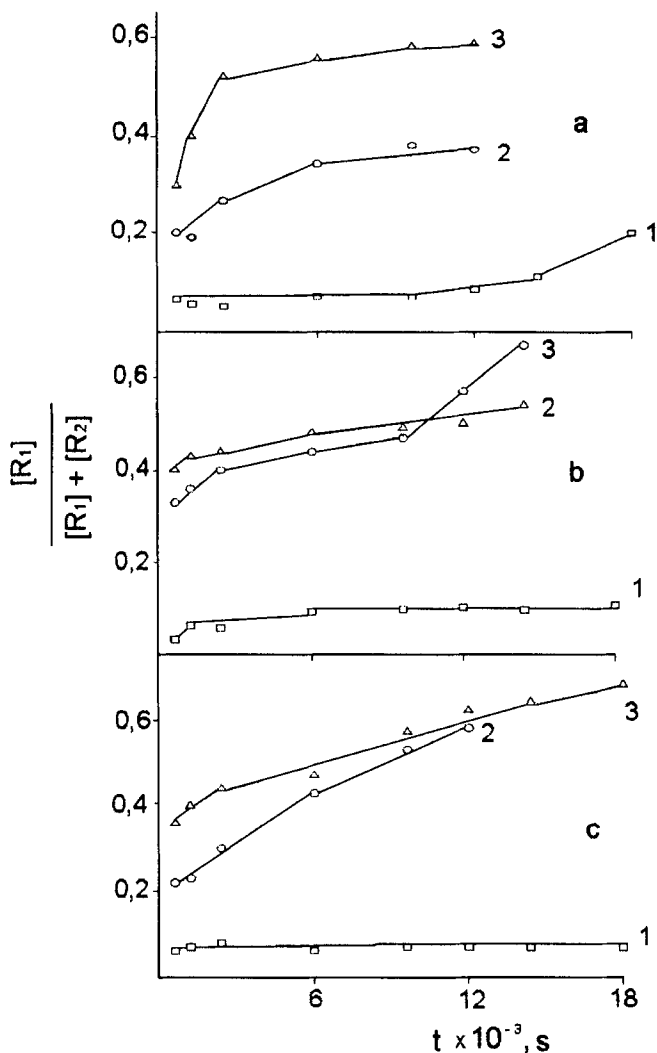


FIGURE 4 The dependence of composition of nitroxyl radicals on time in PVP without (a) with 25% (b) and 50% aerosil (c) at 295 K (1), 323 K (2) and 363 K (3).

R_1 fraction begins to exceed at 323 K after a time the corresponding value at 363 K in sample with 25% of aerosil.

The monotonic growth of the R_1 fraction at elevated temperatures in filled samples is connected with the R_2 concentration decrease at

prolonged exposure to NO_2 by reaction (7). Yet the R_2 concentration drop was not observed at the same time in PVP without filler. For comparison kinetic curves of the radical formation at 323 K and 363 K are represented in Figures 5a, b for samples with 25% and 50% aerosil. As is seen from this figure, the R_2 concentration passes through a maximum; in doing so the time of the attainment of the maximum concentration is the more, the higher the filling degree. So the maximum is reached respectively at 160 min and 80 min in samples with 25% and 50% aerosil. These results show that the structural reorganization of polymer phase in interfaces aids in the R_2 decay by the

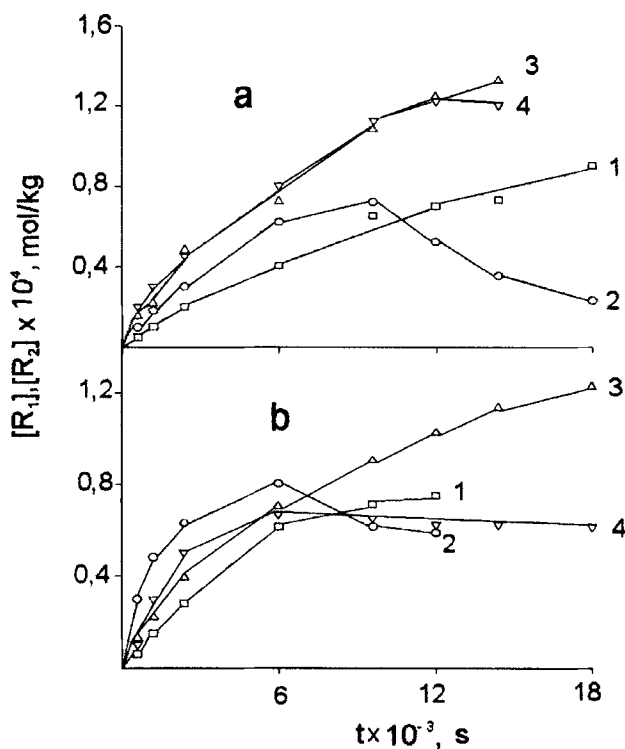


FIGURE 5 Kinetics of accumulation of radicals in PVP with 25% (a) and 50% aerosil (b): R_1 at 323 K(1), 363 K(3) and R_2 at 323 K(2), 364 K(4).

reaction (8). Conceivably the porosity of molecular packing, which is built up with the aerosil content, contributes to the conversion of intermediate products by the hidden-radical mechanism into the end products at 323 K.

In an analogous way the variable kind of the radical composition change with time at room temperature can be explained in filled samples and original PVP. The R₁ fraction increasing at the prolonged time of exposure (Fig. 4a) derives from the induction period of their formation by reactions (6), (7). On the contrary, the R₂ accumulation takes place in these conditions without noticeable induction period.

The decrease density of the macromolecular packing in interfaces of filled composites promotes the relaxation processes [18] and thus increases the R₁ yield in isothermal conditions. In so doing, the marked induction period for this process in filled PVP was not observed. The R₁ and R₂ formations in filled PVP take place with constant ratio of rates. As a result, the R₁ fraction is kept constant except some initial period of exposure in NO₂ (40–60 min) (Figs. 4b, c).

The attainment of a constant composition of nitroxyl radicals in samples without filler at elevated temperatures (Fig. 4a) is also indicative of a constancy of ratio of their formation rates after some time. The drastic increase of the R₁ yield by reactions (6) and (7) in this case is a consequence of ascending of molecular motions. Nevertheless, the R₂ decay proceeds not that efficiently as in filled PVP.

Thus, the dominant molecular products of the PVP nitration by NO₂ are nitrosoamides and nitrites. Along with them, the stable nitroxyl radicals are formed. Their structure and the formation mechanism testify that the primary reaction of the hydrogen atom abstraction from macromolecules is selective. The C—H bonds in α -position in respect to amide groups take part in this reaction. The structural-physical reorganization of PVP at filling effects essentially on the ratio of the conversion rates of nitroxyl macroradicals. The appreciable changes in the radical composition permit to consider the exposure in NO₂ as a sensitive method of detection of the structural-physical modification in filled polymer composites at the molecular level and to use this process for investigations of features of the mechanism of free-radical reactions in these systems.

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