Oxidative Radical Generation Via Nitrogen Dioxide Dimer Conversions Induced by Amide Groups of Macromolecules

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ABSTRACT: The features of initiation of free radical reactions in polymers by dimers of nitrogen dioxide are considered. The conversion of planar dimers into nitrosyl nitrate in the presence of amide groups of macromolecules has been revealed. Nitrosyl nitrate initiates radical reactions in oxidative primary process of electron transfer with formation of intermediate radical cations and nitric oxide. As a result of subsequent reactions, nitrogen-containing radicals are produced. The dimer conversion has been exhibited by estimation of the oxyaminoxyl radical yield in characteristic reaction of *p*-benzoquinone with nitrogen dioxide on addition of aromatic polyamide and polyvinylpyrrolidone to reacting system. The isomerization of planar dimers is efficient in their complexes with amide groups, as confirmed by *ab initio* calculations. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 108: 128–133, 2008

Key words: nitrogen dioxide; nitrosyl nitrate; polyamides; stable radicals; EPR spectra

INTRODUCTION

Nitrogen dioxide effectively reacts with various low- and high-molecular compounds.[1,2] Its reactions have a wide application in synthetic chemistry and can be used for chemical modification of polymers specifically for grafting stable nitrogen-containing radicals to macromolecules.[3] However, it should be remembered that NO_2 is a free radical of moderate reactivity: the ONO—H bond strength[4] is 320 kJ mol^{-1}. Because of this, NO_2 can initiate free radical reaction by abstracting hydrogen atoms only from the least strong, for example, allyl C—H bonds or by attaching to double C=C bonds.[5–8] Nevertheless, effective formation of stable radicals is observed also in polymers not containing labile hydrogen atoms or double bonds. For example, aromatic polyamidoimides, nylon, polyvinylpyrrolidone (PVP),[3] and aromatic polyamides (AP)[9] exhibit high activity in respect to nitrogen dioxide. These facts allow considering other probable mechanisms of radical initiation. The fact is that major radical products of the nitrogen dioxide interaction with AP and PVP are iminoxyl and acylalkylaminoxyl radicals that are produced from oximes and acylnitroso compounds.[3,9] The occurrence of these precursors of stable radicals in turn associates with presence of nitric oxide. In this connection, it is necessary to suppose a participation of NO_2 dimeric forms in radical initiation. The main dimers of NO_2 are planar nitrogen tetroxide O_2N—NO_2 (PD) and nitrosyl nitrate $ONONO_2$ (NN). *Ab initio* calculations[8] show that these dimers are formed with the most probability in NO_2 atmosphere; the form of nitrosyl peroxynitrite ONOONO is too unstable to be considered as efficient participant of reactions.

As NN has strong oxidative properties,[10] the generation of radicals can take place by an electron transfer from donor functional groups with the formation of intermediate radical cations:

$$RH + ONONO_2 \rightarrow \left[\overset{+}{R}\overset{\bullet}{H} + (NOONO_2)^- \right]$$
$$\rightarrow R^\bullet + NO + H^+ + ONO_2^- \qquad (1)$$
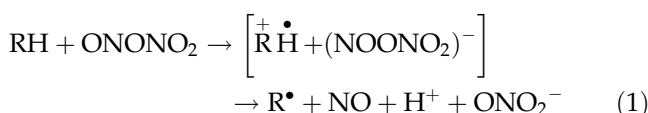
The recombination of radicals with nitric oxide gives nitroso compounds that undergo isomerization into oximes[11] to produce iminoxyl radicals in the reaction with NO_2:

$$\rangle C{=}NOH + NO_2 \rightarrow \rangle C{=}NO^\bullet + HNO_2 \qquad (2)$$
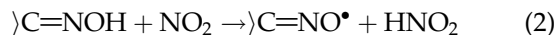
The nitroso compounds are effective spin traps and a source of stable aminoxyl radicals:

$$RN{=}O + R_1^\bullet \rightarrow R(R_1)N{-}O^\bullet \qquad (3)$$
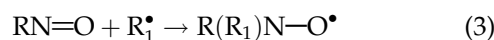
Thus, the mechanism involving reactions (1–3) formally could explain an appearance of stable radicals in the polymers not containing specific chemical bonds reacting with NO_2 mono radicals.[9] However, there are certain obstacles connected with energetic properties of NO_2 dimers for realizing such mechanism;

the energy of syn- and anti-forms of NN exceeds that of PD, respectively, 29.8 and 18.4 kJ mol^{-1} [8]; that is the equilibrium

$$O_2N-NO_2 \rightleftharpoons 2NO_2 \rightleftharpoons ONONO_2 \qquad (4)$$
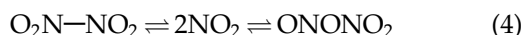
should be shifted to PD in gas phase. Nevertheless, the nitroso nitrite formation was observed during the interaction of olefins with nitrogen dioxide in liquid phase.[8,12] This fact is indicative of the participation of NN in these reactions. The shift of equilibrium (4) to NN can occur in liquid phase reactions, for instance, because of increasing the polarity of medium. In solid polymers with small macroscopic dielectric permeability (ε = 2–3), the formation of NN could be promoted by coordination of nitrogen dioxide with polar functional groups. However, stable nitrogen-containing radicals were not registered in such polymers with polar ester groups as poly(methyl methacrylate), polycarbonate, acetyl cellulose on exposure to nitrogen dioxide. On the basis of this fact, one can assume that the effective formation of NN and consequently realization of ion-radical process (1) are conditioned by specific donor–acceptor interactions of nitrogen dioxide dimers with certain functional groups facilitating the isomerization of PD into NN.

In the present investigation, the possibility of the PD conversion into NN under the influence of amide groups of PA and PVP with further generation of stable radicals by reactions (1–3) is considered. As the indicator of the dimer conversion, the dependence of yield of typical radicals in the reaction of PD with p-benzoquinone (BQ)[13] on the contents of PA and PVP in reacting system was used. The mechanism proposed of dimer conversions has been confirmed by ab $initio$ calculations.

EXPERIMENTAL

Nitrogen dioxide was obtained by the thermal decomposition of lead (II) nitrate.[14] Experiments were carried out on BQ ''Merck'', PVP with M_η = 3.0×10^5 and PA synthesized by polycondenzation of m-phenylenediamine and isophthalic acid. Powder-like composites of BQ with AP and PVP containing silica gel ''Chemapol'' with 100–160 μm diameter of particles were prepared. Samples of BQ + PVP + SiO$_2$ with constant quantity of BQ (100 mg), SiO$_2$ (100 mg), and variable quantities of PVP (10–30 mg) were prepared from 10% combined solutions of BQ and PVP in chloroform containing SiO$_2$ pre-heated at 400°C. After evaporation of the solvent by stirring at room temperature, samples were dried up carefully by pumping. Similarly composites of BQ (100 mg) + AP (20–100 mg) + SiO$_2$ (100 mg) were prepared. Samples were placed in quartz tubes for EPR measurements provided with a stopcock and connected to a flask of volume 0.5 L. After pumping to

a pressure of $\sim 10^{-3}$ mmHg, the stopcock was closed, and the flask was filled with NO$_2$ up to the concentration of 10^{-3} mol L^{-1}. As soon as NO$_2$ was drawn into the tube with the sample, EPR spectra were recorded on the spectrometer ''EPR-1306.'' The products of the nitrogen dioxide interaction with N-methylpyrrolidone (low-molecular analogue of PVP) ''Merck'' were analyzed in 1 : 1 mixture with pyridine ''Merck'' by IR spectroscopy. IR spectra were recorded using a Specord IR-75.

RESULTS AND DISCUSSION

Yields of nitrogen-containing radicals in composites of BQ with PVP and AP

On exposure of BQ to nitrogen dioxide, the formation of radicals I of oxyaminoxyl type[15] takes place by the following scheme[13]:
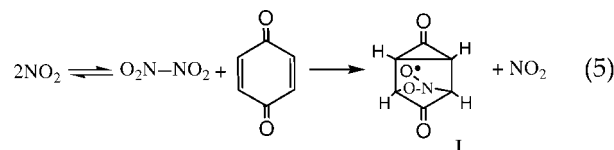
The scheme (5) is confirmed by kinetic data according to which the rate of the radical I accumulation is proportional to a square of NO$_2$ concentration in gas phase.[13] The stationary concentration of radicals I increases with decreasing temperature in the range from 285 to 300 K, as the equilibrium $2NO_2 \rightleftharpoons O_2N-NO_2$ is shifted to the right with decreasing temperature.[2] The EPR spectrum of radicals I obtained in BQ with SiO$_2$ at room temperature represents triplet with a^N = 2.82 mT and g = 2.0053 [Fig. 1(a)]. It should be noted that this spectrum does not show an anisotropy that is characteristic for EPR spectra of aminoxyl radicals in the solid phase.[16] This fact is caused by enough high molecular mobility as a result of a destruction of BQ crystal structure in layers between SiO$_2$ particles due to reactions of the radical I conversion.[13] In addition to I, iminoxyl radicals II occur in composites of BQ with AP on exposure to nitrogen dioxide. Under the same conditions, the sum of radicals II and acylalkyl-aminoxyl radicals III, along with I, was registered in composites of BQ with PVP. Signals of radicals II and III are masked by an intense signal of radicals I in the EPR spectrum. However, one can separate spectra of radicals II and III using the fact that radicals I exist only in an NO$_2$ atmosphere. In view of rather low thermal stability, radicals I quickly disappear at room temperature within several minutes after pumping out nitrogen dioxide from the samples. Remaining spectra of stable radicals II in AP and the sum of II + III in PVP are shown respectively in Figure 1(b,c). They represent anisotropic triplets with
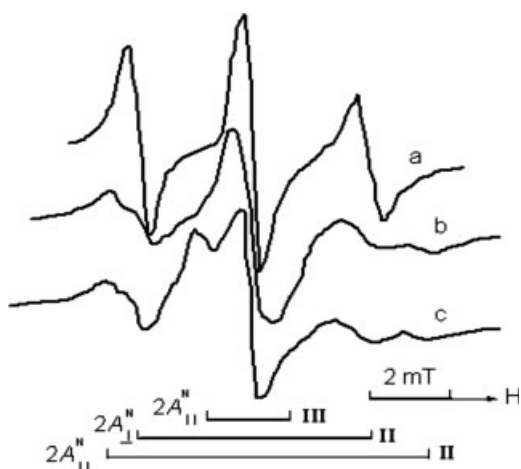
Figure 1 EPR spectra of $BQ + SiO_2$ after exposure to NO_2 (a); $BQ + AP + SiO_2$ (b) and $BQ + PVP + SiO_2$ (c) after preliminary exposure to NO_2 and subsequent pumping-out.

$A_\parallel^N = 4.1$ mT, $g_\parallel = 2.0024$ and $A_\perp^N = 2.6$ mT, $g_\perp = 2.005$ (radical II)[9] and with $A_\parallel^N = 1.94$ mT, $g_\parallel = 2.003$ (radical III).[3] Using this procedure, the maximum concentrations of radicals I, II, and III were separately determined in composites with the various contents of AP and PVP after exposure to NO_2 within 24 h. It should be noted that the parameters

of spectra of iminoxyl radicals II are identical in AP and PVP, therefore the same designation is accepted for these radicals. Because the formation of radicals of one or another type takes place in separate phases of BQ, AP, and PVP, concentrations of radicals in the heterophase composites were determined as a ratio of number of spins calculated by integration of EPR spectra to the weight of given phase.

The results obtained are shown in Figure 2(a,b). As is seen from the figures, the accumulated concentration of radicals I monotonously falls as the relative contents of AP and PVP is increased, while concentrations of radicals II and II + III vary within 10–20% of the average value that is within the accuracy of integration of EPR spectra. This fact is indicative of obvious dependence of the radical I yield on the contents of polymers with amide groups in composites, suggesting that PD is converted under the influence of amide groups into NN that generates stable radicals II and III in the polymeric phases. It is significant that an appreciable decrease of the yield of radicals I was not observed in control experiments when polymers of other chemical structure, for example, acetyl cellulose were used in composites. Therefore one can conclude that amide groups play special role in the process PD → NN.

Taking into account scheme (1, 2), the radical II formation in AP can be presented as follows:

$$(6)$$
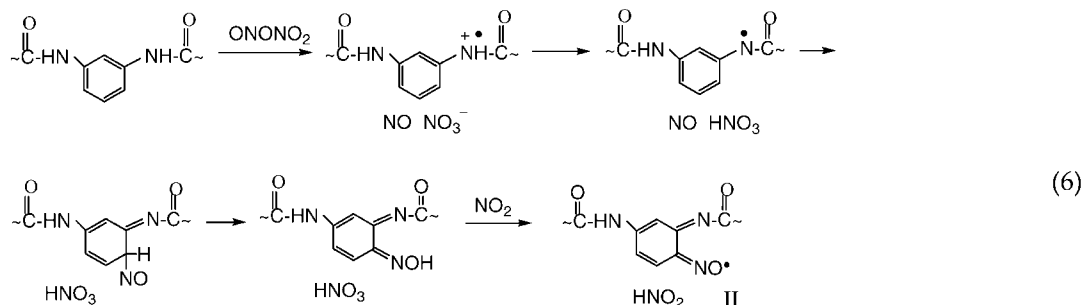
The structure of radicals II is confirmed by quantum-chemical calculations of hyperfine interaction constants.[9]

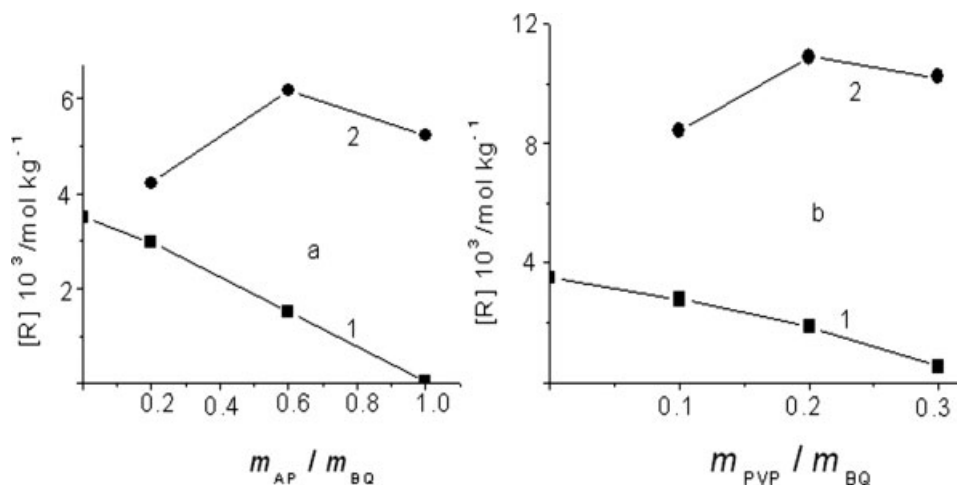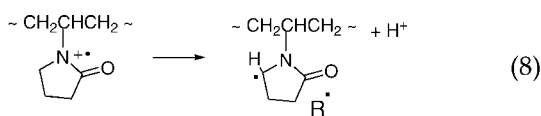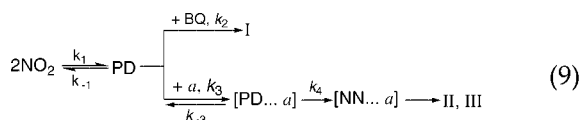The formation of radicals II and III in PVP can be described by the following reactions:

$$(7)$$
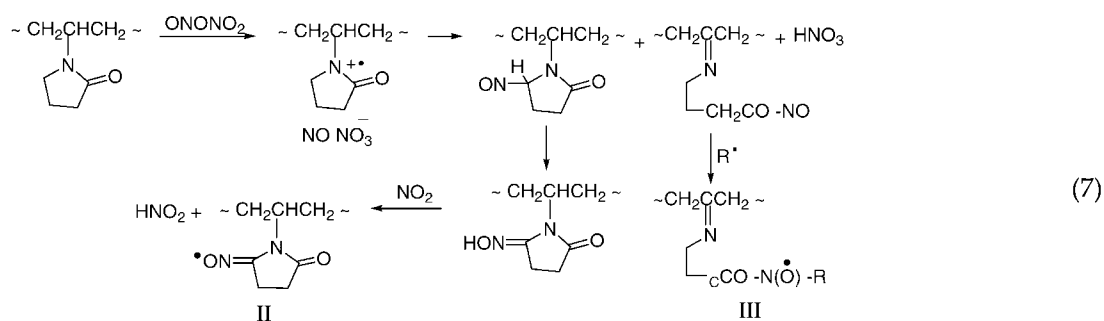
Figure 2 Dependencies of concentrations of radicals I (1), II (2) in BQ + AP + SiO$_2$ (a) and I (1), II + III (2) in BQ + PVP + SiO$_2$ (b) after exposure to NO$_2$ on weight ratio of BQ, AP, and PVP.

where R$^\bullet$ appears as a result of the radical cation decomposition:

$$(8)$$

The decrease of relative yield of radicals I on addition of polymers with amide groups to composites is apparent from the formal kinetic scheme:

$$(9)$$

where a is an amide group. Taking into consideration stationary state for concentrations of PD, NN, [PD$\cdots a$], [NN$\cdots a$], and invariance of BQ contents in composites, the following equations for rates of accumulation of radicals I, II, and III can be obtained:

$$\frac{d[\mathrm{I}]}{dt} = \frac{k_1 k_2 [\mathrm{BQ}](k_{-3}+k_4)[\mathrm{NO_2}]^2}{(k_{-3}+k_4)(k_{-1}+k_2[\mathrm{BQ}]+k_3[a]) - k_{-3}k_3[a]} \tag{10}$$

$$\frac{d[\mathrm{II, III}]}{dt} = \frac{k_1 k_3 k_4 [a][\mathrm{NO_2}]^2}{(k_{-3}+k_4)(k_{-1}+k_2[\mathrm{BQ}]+k_3[a]) - k_{-3}k_3[a]} \tag{11}$$

where [NO$_2$] is the concentration of nitrogen dioxide in gas phase, [a] is the surface concentration of amide groups. These equations can be simplified if concentrations of amide groups in composites are comparatively large, and the conversion of PD into NN

occurs enough effectively, that is $k_3[a] \gg k_{-1} + k_2[\mathrm{BQ}]$. Then

$$\frac{d[\mathrm{I}]}{dt} = \frac{k_1 k_2 [\mathrm{BQ}](k_{-3}+k_4)[\mathrm{NO_2}]^2}{k_3 k_4 [a]} \tag{12}$$

$$\frac{d[\mathrm{II, III}]}{dt} = k_1 [\mathrm{NO_2}]^2 \tag{13}$$

Thus the rate of accumulation of radicals II and III is determined by [NO$_2$], and concentrations of these radicals, accumulated on exposure to nitrogen dioxide, not depend appreciably on AP and PVP contents [Fig. 2(a,b (curve 2)]. In contrast, the yield of radicals I decreases as polyamides are added to composites and [a] is increased. These plots in character are representative of competitive pathways for PD interactions with BQ and amide groups. Note that the yield of radicals I is not changed in the NO$_2$ atmosphere in composites of BQ with other polymers, for instance, acetyl cellulose at any ratio of the components.

Ab initio calculations of energies for conversions of nitrogen dioxide dimers

For validating the mechanism proposed of the conversion of PD into NN, the calculations of energy changes in process of nitrogen dioxide interaction with simplest amide (formamide) have been carried out within the framework of density functional theory by the Gaussian 98 program.[17] The B3LYP restricted method for closed and open shell was used. The intention of the calculations is to correlate energy consumptions for PD → NN with those for other stages of the radical generation process. Ener-
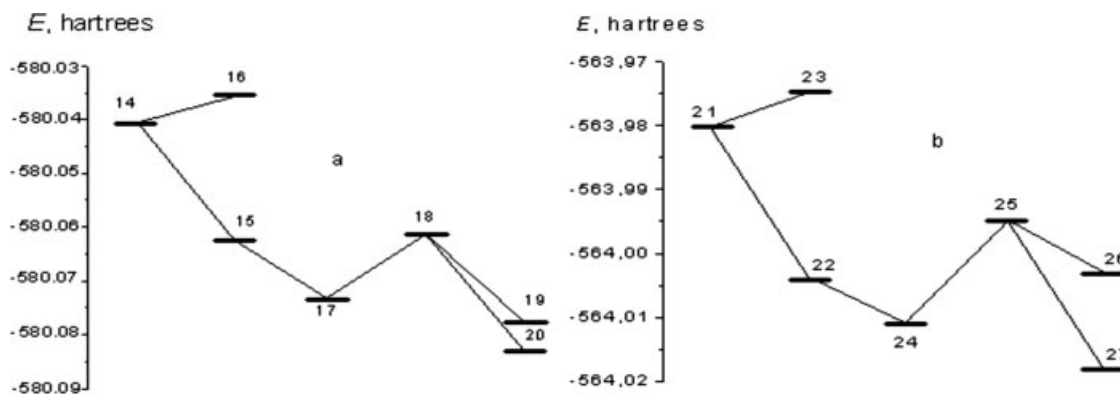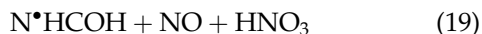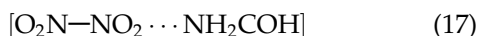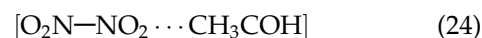
Figure 3 Changes of minimum energies calculated for reactions of NO_2 with formamide (a) and acetaldehyde (b).

gies of the following states according to scheme (9) were calculated:

$$2NO_2 + NH_2COH \qquad (14)$$

$$O_2N{-}NO_2 + NH_2COH \qquad (15)$$

$$ONONO_2 + NH_2COH \qquad (16)$$

$$[O_2N{-}NO_2 \cdots NH_2COH] \qquad (17)$$

$$[ONONO_2 \cdots NH_2COH] \qquad (18)$$

$$N^{\bullet}HCOH + NO + HNO_3 \qquad (19)$$

$$NH_2C^{\bullet}O + NO + HNO_3 \qquad (20)$$

The geometry optimization of all structures was performed applying the basis set 6-31G (d, p). The given process includes intermediate molecular complexes of PD and NN with formamide (17, 18). The changes of minimum energies are shown in Figure 3(a). One can see that the formation of PD from NO_2 is energetically advantageous process,[8] whereas NN is generated from NO_2 in an endothermic reaction. The complexation of PD with formamide is accompanied by release of energy: $\Delta E = 28$ kJ mol^{-1}. However, PD in complex (17) is not capable to react with formamide and can only leave the reacting cage. At the same time, PD in the complex can be converted approximately with the same energy consumption into NN (18), which further reacts by the electron transfer reactions (19, 20) giving radicals, nitric oxide, nitric acid, and significant release of energy (44–57 kJ mol^{-1}). Such sequence of transformations seems to be more efficient in comparison with a direct interaction of NN and formamide in state (15), as the energy of dimers in complexes (17) and (18) is lower than that of initial state (14). Thus, the results of calculations are not contrary to the mechanism proposed on the basis of experimental plots of Figure 2.

The specific role of amide groups of macromolecules in the process of PD into NN conversion is also apparent from similar calculations performed for interaction of the dimers with different functional groups, for instance, carbonyls. The results of calculations for the following reaction stages of the nitrogen dioxide interaction with acetaldehyde

$$2NO_2 + CH_3COH \qquad (21)$$

$$O_2N{-}NO_2 + CH_3COH \qquad (22)$$

$$ONONO_2 + CH_3COH \qquad (23)$$

$$[O_2N{-}NO_2 \cdots CH_3COH] \qquad (24)$$

$$[ONONO_2 \cdots CH_3COH] \qquad (25)$$

$$C^{\bullet}H_2COH + NO + HNO_3 \qquad (26)$$

$$CH_3C^{\bullet}O + NO + HNO_3 \qquad (27)$$

are represented in Figure 3(b). There are principal distinctions associated with capability for isomerization of PD into NN in complexes (17) and (24). As indicated by Figure 3(b), this process for complex (24)
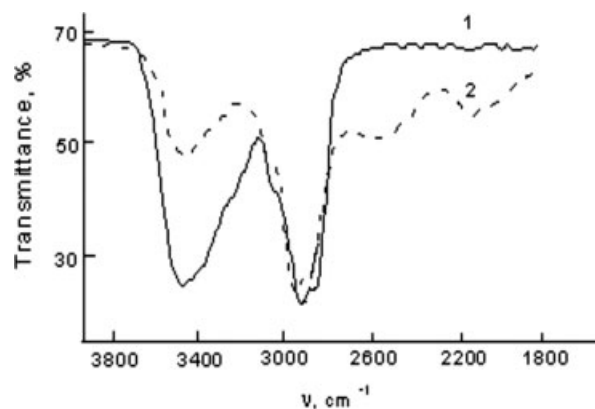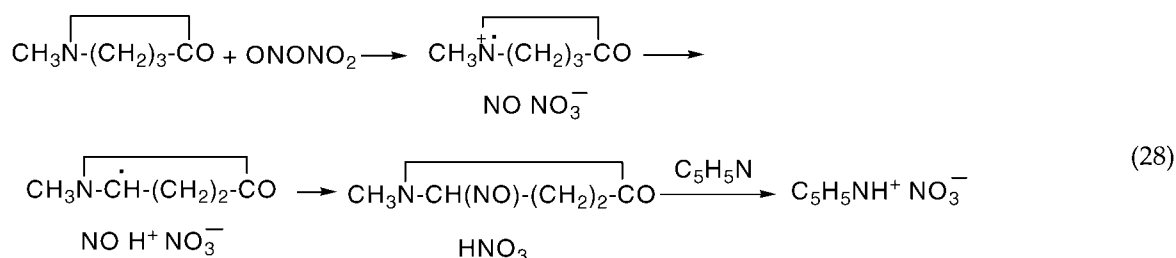

Figure 4 IR spectra of 1 : 1 *N*-methylpyrrolidone and pyridine mixture (1) and after exposure the mixture to NO_2 (2).

necessitates additional expenditure of ~ 24 kJ mol^{-1} as compared with the energy for transforming (24) into (22) with an exit of PD from reacting cages. Thus the coordination of PD with polar carbonyl groups can make difficulties for conversion of PD into NN.

Detection of intermediate radical cations in reactions of NN

The registration of radical cations by EPR could serve as a direct experimental evidence of the initiation of radical processes by scheme (1). However, in view of high reactivity and fast decomposition,[18] these intermediates are difficult to detect by this method. Nevertheless, the formation of radical cations can be discovered indirectly in their decomposition accom-panied by proton elimination. For detection of protons, we used pyridine, which is known to be capable of accepting protons to yield pyridinium cations. These products can be easily identified from their typical IR spectrum. Note that pyridine does not react directly with NO_2[19] and can serve only as a trap of protons formed in ion-radical reactions (1). Figure 4 shows IR spectra of mixtures 1 : 1 of pyridine and N-methylpyrrolidone (low-molecular analogue of PVP) before and after exposure to nitrogen dioxide. After 30 min exposure, two intense bands were observed in the spectrum (2) at 2400–2600 and 2200 cm^{-1} corresponding to the NH$^+$ stretching vibrations of pyridinium cations.[20] The scheme of reactions proceeding in this system includes the consecutive stages:

$$CH_3N\text{-}(CH_2)_3\text{-}CO + ONONO_2 \longrightarrow CH_3\overset{+\cdot}{N}\text{-}(CH_2)_3\text{-}CO \longrightarrow$$
$$NO \ NO_3^-$$

$$CH_3N\text{-}\overset{\cdot}{C}H\text{-}(CH_2)_2\text{-}CO \longrightarrow CH_3N\text{-}CH(NO)\text{-}(CH_2)_2\text{-}CO \xrightarrow{C_5H_5N} C_5H_5NH^+ \ NO_3^-$$
$$NO \ H^+ \ NO_3^- \qquad\qquad HNO_3$$

(28)

It appears that nitrogen dioxide can exhibit a noticeable activity for radical generation by an ion-radical mechanism discussed above selectively, namely, in the polymers containing functional groups which assist PD → NN conversions.

CONCLUSIONS

Amide groups are capable of inducing isomerization of planar dimers of NO_2 into nitrosyl nitrate having pronounced oxidative properties. Nitrosyl nitrate initiates a number of consecutive radical reactions with formation of nitrosation products and stable nitrogen-containing radicals. Most likely, the conversion is realized due to specific interactions of the dimers with amide groups of macromolecules. These interactions can provoke high activity of nitrogen dioxide in reactions even with such stable polymers as aromatic polyamides.

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