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Generation of nitroxyl radicals in reactions of nitrogen dioxide with *p*-benzoquinones

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The formation of oxynitroxyl radicals has been observed by EPR in the course of exposure of *p*-benzoquinones to nitrogen dioxide. This process involves addition of nitrogen dioxide to the double bond system of quinones. Thermal conversion of oxynitroxyl radicals lead to the formation of acyl(alkyl)nitroxyl and iminoxyl radicals along with molecular nitration products. Kinetics of the oxynitroxyl radical formation depending on the nitrogen dioxide pressure has been defined. The temperature dependence of stationary concentrations of oxynitroxyl radicals at 230–310 K is determined by the equilibrium between the monomer and dimer forms of nitrogen dioxide. Nitrogen tetraoxide was found to initiate radical formation in *p*-benzoquinones.

Kinetic studies of radical reactions of organic compounds with conjugated double bonds, initiated by nitrogen dioxide, are important for understanding the mechanism of interaction of aggressive nitrogen oxides with various natural substances of a vegetative and animal origin. In view of the fact that quinones are found in the structures of a number of biologically active substances, such as ferments, vitamins and pigments, the work presented here describes an investigation into the interaction of nitrogen dioxide with *p*-benzoquinone and 2,6-di-*tert*-butyl-*p*-benzoquinone (TBQ). It should be mentioned that at present there is a lack of data on the mechanism of reactions of nitrogen oxides with quinones.

It is known that the reactions of radicals such as NO_2 with conjugated double bonds can involve their consecutive addition[1] with the formation of the appropriate molecular products similar to reactions of NO_2 with alkenes.[2,3] Oxynitroxyl† radical formation in a one-step mechanism also becomes possible when the conjugated double bonds act as spin traps for NO_2.[4] At moderate temperatures nitrogen dioxide has a rather low reactivity in hydrogen atom abstraction from alkyl C–C bonds. Therefore, there is reason to believe that NO_2 does not initiate radical formation by interaction with *tert*-butyl groups, and that the radical processes in TBQ as well as in *p*-benzoquinone are caused by reactions with double bonds. The investigation into the reaction mechanism focussed mainly on the structures of nitrogen-containing radicals and the kinetic features of their accumulation. With this aim IR spectroscopy was also used to analyse some of the molecular products of the radical reactions.

Experimental

Nitrogen dioxide was obtained by the thermal decomposition of lead nitrate. Experiments were carried out on TBQ, which was obtained using a technique described in previous work,[5] and on commercial *p*-benzoquinone. To increase the surface of interaction with NO_2, fine grained samples representing 1 : 1 mixtures by weight of quinones and aerosol with a specific surface area of 300 $m^2\ g^{-1}$ were used in most of the experiments. The samples were prepared from 5% solutions of quinones in methylene chloride, containing aerosol pre-heated at 400 °C, by evaporation of the solvent whilst stirring at room temperature. Composites of quinones, aerosol and acetyl cellulose (AC), similarly prepared, were used in some experiments. Samples of 0.1 g were placed in tubes provided with a stopcock for EPR measurements; the tubes were connected to a flask of volume 0.5 l. After pumping to a pressure of $\sim 10^{-3}$ mm Hg, the stopcock was closed, and the flask was filled with NO_2 up to a certain pressure. As soon as NO_2 was drawn into the tube with the sample, EPR spectra were immediately recorded on the X-band spectrometer "1306 (USSR)" with 100 kHz modulation. The EPR spectra were recorded at room temperature and above. The temperature was controlled to within ±1°. The hyperfine coupling constants and *g*-factors of radicals were measured with the help of the standard spectrum of Mn^{2+} ions. Exact measurements of the magnetic field at the centre of the spectrum of the standard and its *g*-factor were carried out relative to the resonant frequency of protons of water using the NMR sensing unit. *g*-factors of radicals were measured to an accuracy of ±0.0004 by comparison with the *g*-factor of Mn^{2+}. The accuracy of the hyperfine coupling constant values were determined to within ±0.03 mT using the splitting between the third and fourth components of the Mn^{2+} signal as standard. The concentrations of radicals were estimated to an accuracy of 20% by integration of their EPR spectra and by comparison with a standard signal (ultramarine) containing a known quantity of spins. Nitration of the pure form of *p*-benzoquinones and benzene solutions ($C \sim 0.1$ mol l^{-1}) has also been performed. The IR spectra of the nitration products were recorded using a Specord IR-75 spectrometer with samples supported on fluorite plates.

Results and discussion

EPR spectra and structures of nitrogen-containing radicals

After exposure of the samples to NO_2, the slow growth of the EPR spectra was observed over several days up to the maximum level dependent on the gas pressure. The EPR spectra registered at room temperature and during subsequent heating of TBQ are shown in Figs. 1(a), (c) and (d). Essentially the same spectrum was observed for *p*-benzoquinone (Fig. 1(b)). This fact shows that the quinone free radicals have the same structure and any influence by the *tert*-butyl groups of TBQ on the

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† The IUPAC name for nitroxyl is aminoxyl.

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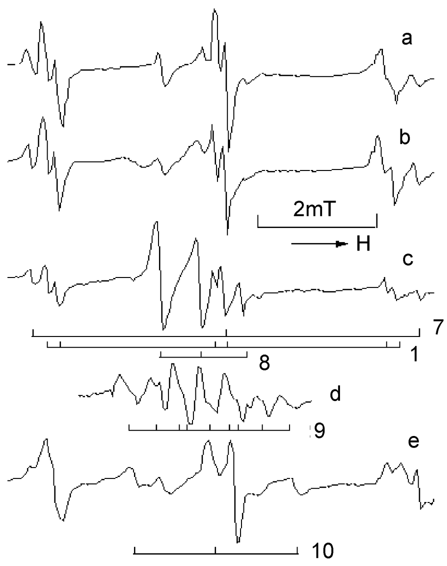
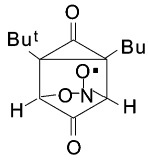


Fig. 1 EPR spectra of TBQ (a, c and d) and *p*-benzoquinone (b) with aerosol and TBQ in benzene (e) after exposure to NO_2 at 293 K (a, b and e), 307 K (c) and 339 K (d).

radical formation mechanism can be neglected. In the spectra shown in Fig. 1(a and b), it is possible to distinguish the signals of three types of radical. The triplet signal, characterised by the nitrogen coupling constant a_N = 2.82 mT and g = 2.0053, corresponds to oxynitroxyl radicals[4,6] arising from the addition of nitrogen dioxide to the double bonds of the quinones. A doublet splitting of this signal with a_H = 0.17 mT is also observed because of the hydrogen atom adjacent to the nitrogen. Based on the given values for a_N and the g-factor as well as the doublet splitting of the triplet components,[7] two possible structures of oxynitroxyl radicals for TBQ can be considered to form in the first step.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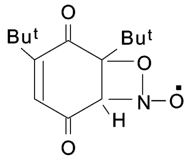
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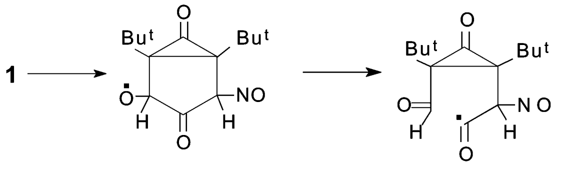
Similar structures can be suggested for the radicals in the *p*-benzoquinone reactions. From the available data, oxynitroxyl radicals have not been detected in reactions of nitrogen dioxide with compounds containing isolated double bonds, in which it might be expected for nitrogen dioxide to add to such bonds to form structure **2**; however, radicals of type **2** have not been detected either in low-molecular weight alkenes or in polymers, for example, polyisoprene[8] On the other hand, oxynitroxyl radicals with similar EPR parameters have been detected in reactions of nitrogen dioxide with phorone,‡[4] in which it is believed that these radicals are produced by NO_2 addition to two double bonds of the ketone. In this connection, structure **1** of oxynitroxyl radicals in *p*-benzoquinones seems more preferable.

It should be noted that the absence of anisotropy in the spectrum of **1**, which is characteristic of EPR spectra of nitroxyl radicals in the solid phase at room temperature. This fact is indicative of the high mobility of the radicals, which formally corresponds to a correlation time of rotational diffusion $\tau_c < 10^{-9}$ s. The high mobility of radicals in samples filled by aerosol can be caused by the destruction of the quinone crystal structure in the layers between the filler particles. The gradual "melting" of TBQ without aerosol and its transformation into a viscous liquid were visually observed on exposure to nitrogen dioxide. The generation of the major portion of radicals **1** in filled samples, apparently, occurs in the "liquid" sites. The effective diffusion of nitrogen dioxide takes place just in such sites from the gas phase.

In addition to **1**, two other radicals can be identified from the EPR spectrum shown in Fig. 1(a and b). The triplet signal with parameters a_N = 3.21 mT and g = 2.0045 belongs to the iminoxyl radicals with averaged anisotropy of interaction of unpaired electrons with nitrogen nuclei.[9] Another type of radical is characterised by a triplet signal with a_N = 0.71 mT and g = 2.0072. Such EPR parameters are typical of acyl(alkyl)-nitroxyl radicals.[10] The fraction of iminoxyl and acyl(alkyl)-nitroxyl radicals at room temperature is fairly small (Fig. 1 (a and b)); the estimation shows that their signals do not exceed 20% of the total EPR spectrum.

Obviously the emergence of iminoxyl and acyl(alkyl)nitroxyl radicals cannot be explained by the direct interaction of nitrogen dioxide with the double bonds of the quinone system. It is natural to believe that these radicals are formed as a result of thermal conversions of primary radicals **1** even at ordinary temperatures, most likely because of the strong angular strain arising from their bicyclic structure. A hypothetical suggestion for the mechanism of the iminoxyl radical formation, based on some indirect literature data,[8] is that the radicals **1** are able to decompose giving alkoxyl radicals, which subsequently breakdown leading to the destruction of the quinone structure and the formation of acyl radicals containing nitroso groups [eqn. (1)].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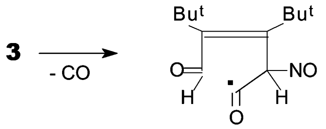
(1)

The cyclopropanone fragments of radical **3** appear to be unstable at ordinary temperatures compared with cyclopropanone,[11] and the radical reacts with elimination of CO in the following manner [eqn. (2)].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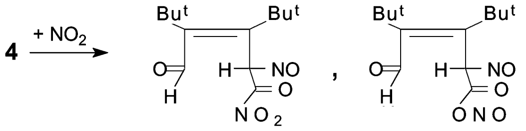
(2)

Further transformations of radical **4** produce both molecular products and nitroxyl radicals. The recombination of **4** and NO_2 yields nitro compounds or nitrites [eqn. (3)].


5 **6**

(3)

The nitroso groups in **5** and **6**, having an α-hydrogen atom, undergo isomerisation into oximes[12] which react with NO_2 to produce iminoxyl radicals **7** [eqn. (4), Fig. 1(a)].

Simultaneously to the reaction given in eqn. (3), acyl radicals **4** can be transformed into acyl(alkyl)nitroxyl radicals, for instance, by attaching to the nitroso groups of **5** or **6** with the

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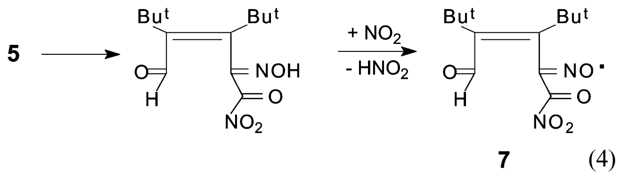
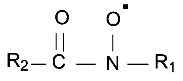
‡ The IUPAC name for phorone is 2,6-dimethylhepta-2,5-dien-4-one.



7 (4)

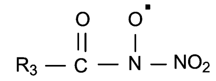


$$R_2-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle O^{\bullet}}{|}}{N}-R_1$$

8

formation of structures in which the substituents R^1 and R^2 are fragments of the quinone molecules.

On heating samples from room temperature up to 307 K, the proportion of radicals **1** in the EPR spectrum decreases considerably with a corresponding increase of the signal due to radicals **8** (Fig. 1(c)). On further heating to 339 K, radicals **1**, **7** and **8** disappear, and the EPR spectrum shown in Fig. 1(d) is obtained. This spectrum may be considered as a triplet ($a_{N(1)}$ = 0.85 mT) of triplets ($a_{N(2)}$ = 0.47 mT) with g = 2.0060. The value of $a_{N(1)}$ approximately coincides with that for acyl(alkyl)-nitroxyl radicals; the g-value is also in agreement with this conclusion.[10] As for the value of $a_{N(2)}$, it nearly corresponds to the splitting of 0.35 mT observed in nitroxyl radicals containing an α-nitroso group.[13] The EPR spectrum in Fig. 1(d) shows radical **9** to be sufficiently stabilised at high temperatures. However insufficient data concerning the nature of the substitutents at the radical centres means that the structures of acyl(alkyl)-nitroxyl radicals **8** and **9** and possible mechanisms for their formation from **1** have not been explored in the present work.



$$R_3-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle O^{\bullet}}{|}}{N}-NO_2$$

9

The composition of radicals generated in liquid solutions of TBQ, for example in benzene, is in essence identical to that in solid samples. However, the concentrations of radicals reach their maximum levels practically at the onset of the nitrogen dioxide admission which is in contrast to the solid samples. The signals of radicals **1**, **7** and **8** are also seen in the spectrum given in Fig 1(e), and yet some quantitative distinctions are noticeable. The fraction of iminoxyl radicals **7** is rather insignificant in TBQ with aerosol. In this case the value of a_N = 3.21 mT characterises *E*-isomers of these radicals.[1] In solution, an intense signal due to the *Z*-isomer of radical **7** is observed, with only a small amount of the *E*-isomer. The EPR spectrum parameters of the *Z*-isomers (a_N = 2.95 mT, g = 2.0046) are similar to those of radical **1**. Besides, the additional signal belonging to the dialkylnitroxyl radical **10** has a value of a_N = 1.34 mT and g = 2.0046. These radicals appear presumably from the addition of a certain alkyl radical to the nitroso compounds **5** or **6**. For instance, alkyl radicals in TBQ can arise due to hydrogen atom abstraction from Bu^t by alkoxyl radicals formed in eqn. (1). It is possible that the reaction of an exchange of alkoxyl to alkyl radicals proceeds more effectively in solution than in the solid samples.

Molecular products of TBQ nitration

The detection of some molecular products using IR spectra can serve to some extent as confirmation of the free-radical processes taking place in *p*-benzoquinones under the action of nitrogen dioxide. The significant changes associated with the appearance of new bands were observed in spectral region of 1100–1800 cm^{-1} (Fig. 2). Two bands at 1560 and 1340 cm^{-1} are due to the asymmetric and symmetric stretches of NO$_2$ groups in nitro compounds such as **5** or those obtained by nitration of double bonds of quinones. The formation of nitroso groups connected with the decomposition of radical **1** can also be traced in the IR spectrum. The typical band at 1560–1570 cm^{-1} for isolated nitroso compounds overlaps, apparently, with the band for nitro compounds. However, the band at 1120 cm^{-1} implies the presence of the nitroso *trans*-dimers.[12] Evidence for the conversion of radical **1** according to eqns. (1–3) is provided by the appearance of the absorption band at 1704 cm^{-1} which can be assigned to the carbonyl stretch in α,β-unsaturated aldehydes. The formation of these products could be the reason for the "melting" of quinones shown by the reduction of anisotropy in the EPR spectra.

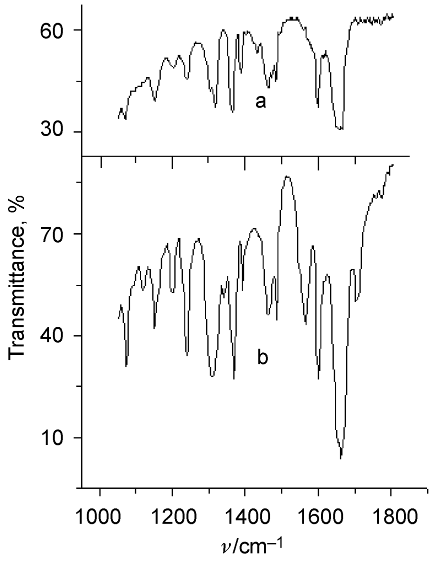


Fig. 2 IR spectra of TBQ (a) and after exposure to NO$_2$ (b).

Kinetic features of oxynitroxyl radical formation

As is evident from Fig. 1 the radicals **1** are rather sensitive to temperature; a stationary concentration of the radicals varies reversibly with changes in temperature in an atmosphere of nitrogen dioxide. The resolution of the EPR spectra is sufficiently good to allow changes in the concentrations of **1** to be estimated using the amplitude of the low-field component of their signal. The corresponding temperature dependencies are given in Fig. 3. As can be seen, the concentrations increase sharply with decreasing temperature in the range 285 < T < 300 K. However, after attainment of a maximum, the concentrations decrease with further lowering of temperature.

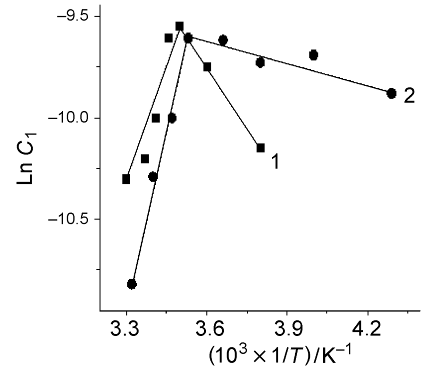


Fig. 3 Temperature dependencies of stationary concentrations of radicals **1** in TBQ (1) and TBQ with aerosol (2).

In view of their rather low thermal stability, radicals **1** quickly disappear at room temperature within several minutes after pumping out nitrogen dioxide from the samples. It can be assumed that there are two differing kinetic pathways for the radical decay in the absence of NO_2. One pathway is concerned with the splitting out of NO_2; in this case the kinetics of decay could be governed by the first-order law on the concentration of radicals. The other possible mechanism involves recombination of radicals **1** with the resulting formation of N_2O_4 and two molecules of TBQ.

For confirmation of which mechanism occurs, the kinetic measurements of the decay of **1** at room temperature were carried out on samples representing composites of AC, TBQ and aerosol in different ratios. The use of the chemically inert polymer with nitrogen oxides in the composites has allowed radical decay to be slowed down after pumping out nitrogen dioxide and the kinetics of this process to be measured. As shown in Fig. 4, the kinetics are well described by the second-order rate law and significant distinctions in the rate of radical decay are visible depending on the molecular organisation of the samples which is controlled by the amount of polymer present. If the concentration of radicals is dependent on the TBQ weight in such composites, the effective rate constants are 31.0 kg mol^{-1} s^{-1} and 18.4 kg mol^{-1} s^{-1} in the samples with weight ratios of aerosol : AC : TBQ of 1 : 1 : 1 and 1 : 1 : 0.3, respectively. Apart from the form of the EPR spectra, these kinetic features suggest that molecular mobility plays an important role in the radical process. Only rather rapid molecular motion allow radicals to approach and undergo bimolecular decay. Such conditions are realised in "liquid" sites containing products of the quinone free-radical conversions. The amount of a polymeric component in the samples essentially influences their molecular organisation and hence molecular dynamics, as is reflected in the significant changes of rates of radical decay.

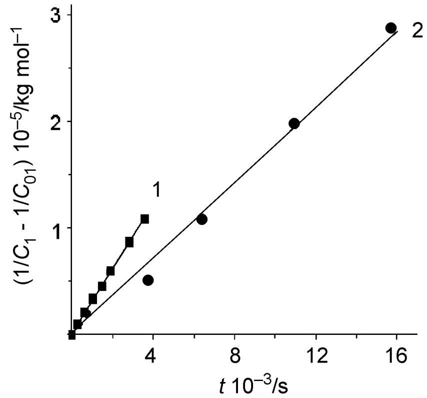


Fig. 4 Kinetics of the decay of radical **1** at 293 K after pumping out NO_2 in composites of aerosol, AC and TBQ with weight ratios 1 : 1 : 1 (1) and 1 : 1 : 0.3 (2).

It is assumed that the increase in the stationary concentration of radicals **1** with decreasing temperature in the range from 285 K to 300 K occurs due to the formation of the nitrogen dioxide dimer, as the equilibrium for $2NO_2 \rightleftharpoons N_2O_4$ is also shifted to the right with decreasing temperature.[14] The decisive role of N_2O_4 in the mechanism of the formation of **1** is confirmed by the results of kinetic measurements at various pressures of nitrogen dioxide. The kinetic curves for the accumulation of **1** are shown in Fig. 5. The radical formation rates are nearly constant at this stage of the reaction and strongly depend on the nitrogen dioxide concentration in the gas phase. The constancy of the initial rates corroborates the mechanism of formation of radicals **1**, by the one-step addition of nitrogen dioxide in the dimer form to the double bonds of the quinones. From other mechanisms associated with reactions of nitrogen dioxide with products of nitration, these radicals should be formed, probably, with autoacceleration. The relationships between the initial rates and partial pressures of NO_2 and N_2O_4 calculated from known equilibrium constants[14] are shown in Fig. 6, from which it is clear that the experimental values of the initial rates depend linearly on the partial pressures of N_2O_4 and not of NO_2.

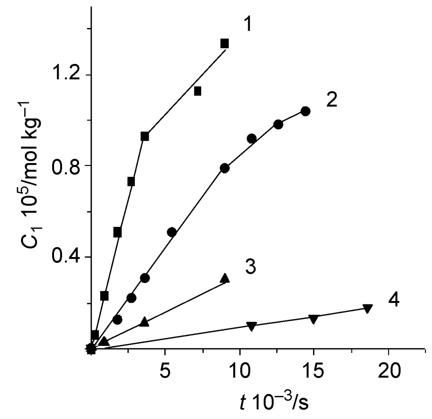


Fig. 5 Kinetics of accumulation of radicals **1** at various pressures of NO_2: 1.45 × 10^4 (1); 0.63 × 10^4 (2); 0.43 × 10^4 (3); 0.25 × 10^4 Pa (4).

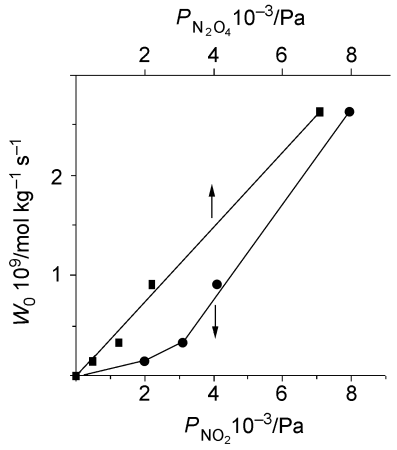
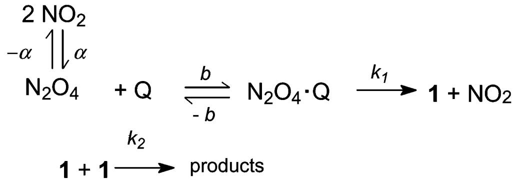


Fig. 6 Dependencies of initial rates of accumulation of radicals **1** at 293 K on partial pressures of NO_2 and N_2O_4.

Relying on the kinetic data obtained, the formation and decay of **1** can be formally presented by the following reactions as shown in eqn. (5).



$$\begin{array}{l} 2\,NO_2 \\ -\alpha \Big\uparrow\!\Big\downarrow \alpha \\ N_2O_4 + Q \underset{-b}{\overset{b}{\rightleftharpoons}} N_2O_4{\cdot}Q \xrightarrow{k_1} \mathbf{1} + NO_2 \\ \mathbf{1} + \mathbf{1} \xrightarrow{k_2} \text{products} \end{array} \qquad (5)$$

If it is believed that $-b \gg k_1$ and $-a \gg b$, then the expression for the concentration of **1** at the steady state takes the form, eqn. (6).

$$C_1 = \left[\frac{k_1 ab}{k_2(-a)(-b)}\right]^{1/2} [NO_2] \qquad (6)$$

Then the temperature dependence of the concentration of radical **1** in these conditions can be determined by eqn. (7),

$$\ln C_1 = A + (E_2 - E_1 + \Delta H_a + \Delta H_b)/2RT \qquad (7)$$

where A is a parameter dependent on the nitrogen dioxide pressure, E_1 and E_2 are activation energies of the formation and decay of radicals **1**, ΔH_a is the heat of equilibrium dissociation of N_2O_4 dissolved in the quinone samples and ΔH_b is the dissociation heat of an intermediate complex of N_2O_4 with quinone molecules Q. An estimation of the temperature coefficient $E_2 - E_1 + \Delta H_a + \Delta H_b$ in eqn. (7) at 285–300 K (Fig. 3) gives 64 kJ mol^{-1} for pure TBQ and 96 kJ mol^{-1} for TBQ with aerosol. At 230–290 K the equilibrium is practically completely shifted towards N_2O_4·Q, and the temperature coefficient of the dependencies takes the opposite sign. The change in the stationary concentrations of radicals **1** is determined in this temperature range, apparently, just from the $E_2 - E_1$ values which are −32 kJ mol^{-1} for TBQ and −16 kJ mol^{-1} for TBQ with aerosol. Then using these values, we obtain $\Delta H_a + \Delta H_b =$ 96 kJ mol^{-1} for TBQ and 112 kJ mol^{-1} for TBQ with aerosol.

As is already known, the enthalpy of the N_2O_4 equilibrium dissociation in the gas phase is 60 kJ mol^{-1}.[14] An increase to 64–68 kJ mol^{-1} was found for the apparent enthalpy of N_2O_4 dissociation in some coordinating solvents, for example, acetonitrile.[15] In all likelihood this phenomenon results from the complexation of N_2O_4 with solvent molecules. To account for the observed temperature dependencies, we assume that the complexes involving quinone molecules act as spin traps for NO_2 in the irreversible dissociation of N_2O_4. The appearance of such complexes must, probably, be accompanied by an essential heat effect ΔH_b. If it is supposed that ΔH_a in TBQ falls within the range 60–70 kJ mol^{-1}, then values of 26–52 kJ mol^{-1} for ΔH_b can be estimated for different samples.

The available data [2,16] show that nitrogen tetraoxide is capable of reacting with unsaturated compounds in solution by different mechanisms depending on the polarity of the solvent. These two mechanisms because of the existence of N_2O_4 in the planar form and as nitrosyl nitrate, which dissociate respectively by homolytic and heterolytic pathways. The heterolytic pathway leads to the formation of nitroso nitrates as the main products of alkene nitration, while homolytic dissociation gives dinitro compounds and nitro nitrites. Generation of the quinone radicals is also dependent on the homolytic dissociation of nitrogen tetraoxide. The features of this process appear to be the formation of an intermediate complex involving N_2O_4 coordination with two double bonds of the quinone compound. This conclusion follows from the analysis of temperature dependencies of the stationary concentration of radicals. In such complexes the configuration of reagents is favourable to the generation of NO_2adduct radicals owing to the addition of NO_2 immediately after N_2O_4 dissociation.

Conclusions

The paper illustrates the use of quinones as model compounds for the generation of oxynitroxyl radicals by their interaction with nitrogen dioxide. The effectiveness of this process depends appreciably on the equilibrium concentrations of the monomer and dimer forms of nitrogen dioxide in the gas phase. The reactive oxynitroxyl radicals in the presence of nitrogen dioxide are capable of initiating the free-radical transformations of quinones with the resulting formation of relatively stable acyl(alkyl)nitroxyl radicals along with various molecular products. In this connection the free-radical processes considered may be of use as a specific test for similar quinone structures in various chemical and biological systems. The selective reactions of these types of compounds with nitrogen dioxide give in essence specific spin labels. On the other hand, the insertion of quinone fragments into polymers and polymer composites in certain amounts can provide in principle a way of studying the structural–physical effects on the reactivity of free radicals. As has been shown in the results obtained (Figs. 3 and 4), the thermodynamic characteristics and the kinetic behaviour of the oxynitroxyl radicals depend strongly on the structural organisation of the media.

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