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Kinetics and Mechanism of Liquid-Phase Nitration of 2, 4, 6-Tri-*t*-Butylphenol

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Rates of reaction of 2,4,6-Tri-*t*-butylphenol with nitrogen dioxide (1000 ppm) have been determined in a batch reactor. The kinetics of reaction has qualitative distinctions according to the initial phenol concentration in the hexadecane solution. The phenol decay proceeds with fixed rate in time depending on the flow rate of NO₂ at [PhOH]₀ = 4.0·10⁻⁴–3.5·10⁻³ M. At [PhOH]₀ = 6.0·10⁻⁵ M the kinetics is controlled by the first order law. The rate constant of the phenolic hydrogen atom abstraction by NO₂ is $k_1 = 5.9 \cdot 10^3 \exp(-10 \text{ kJ/RT})$, M⁻¹s⁻¹. At 22°C the rate constant of NO₂ and phenoxy radical recombination is 76.5 M⁻¹s⁻¹. The formation of the reaction products has been studied by UV spectroscopy. The mechanism of nitration and side reactions in a batch reactor has been discussed.

Keywords: Nitration; Tri-*t*-Butylphenol; kinetics; mechanism; side reactions

INTRODUCTION

Nitrogen dioxide is the efficient initiator of the different free radical processes [1], specifically of the hydrocarbon liquid-phase oxidation [2]. In connection with this the detailed elucidation of the mechanism of reactions with space hindered phenols is of profound importance because of these compounds can be used to stabilized different materials, for instance the engine oil, from nitrogen oxides forming during combustion [3]. It was shown in works performed previously that the

nitrogen dioxide reactions with the hindered phenols are differs radically from those with phenol or cresols [4], [5]. These distinctions are primarily exhibited by the composition of the ultimate products. Whereas the NO₂ reaction with phenol results in the formation of the aromatic ring nitration products, hindered phenols yield nitrocyclohexadienones in the similar conditions. The latter are the sufficiently unstable compounds and can initiate a sequence of the side reactions during its conversion.

Both NO₂ and the hindered phenols present the important constituents of different chemical processes. The revealing of the kinetic peculiarities of reactions of NO₂ with phenols in the liquid phase is required to realize the mechanism in conditions modeling the environmental exposures. From this viewpoint it is appropriate to conduct reactions at reasonably low concentrations of NO₂ in a mixtures with the balance nitrogen using a batch reactor described previously [6]. The application of this technique enables the reaction mechanism to be investigated under changes over a wide range of the phenol concentrations and the flow rates of the gas mixture (FR). In the work the kinetic characteristics of NO₂ reaction with 2,4,6-Tri-*t*-butylphenol (TTBP) in hexadecane (HD) have been examined and the mechanism of the reaction product formation has been discussed.

EXPERIMENTAL

The reactions were performed in a batch reactor in the temperature range from 25°C to 100°C at TTBP concentrations in HD of $3.0 \cdot 10^{-5}$ – $3.5 \cdot 10^{-3}$ M. HD (45 ml) was pre-bubbled for hour by the gas mixture (1000 ppm NO₂) at FR of 100 ml/min to a limiting concentration of NO₂ and than 5 ml of TTBP in HD solution was added. The changes of the TTBP concentration during reaction at FR of 50–300 ml/min were registered periodically by the optical density at 280 nm on spectrophotometer UV/VIS Perkin Elmer Lambda 18 using 0.1 and 1 cm cells. The kinetics of NO₂ solubility in HD at different FR was also determined by spectrophotometer. To do this HD saturated with the gas mixture for different time was inserted in 5 cm cell and NO₂ concentration was measured by the optical density at 410 nm [7]. The radiospectrometer ESP 300 Bruker was used to

measure the free radical concentration. In some experiments the kinetics of TTBP decay was studied immediately in optical cell. In this case the mixture of HD saturated by NO_2 to a limit in reactor and TTBP solution HD low initial concentration ($\approx 3.0 \cdot 10^{-5} \text{ M}$) were added to 1 cm cell.

RESULTS AND DISCUSSION

Solubility of NO_2 in HD

The determination of NO_2 solubility has a prime importance to carry out the kinetic measurements in a batch reactor. It is apparent that the rate of NO_2 dissolving in the reaction mixture at a given temperature must play a decisive role in TTBP conversion. Figure 1a gives the kinetic curves of the NO_2 concentration in HD at different FR. From these curves it will be obvious that at different initial rates of dissolving a limiting concentration of NO_2 in HD is roughly the same for all FR ($\approx 6.0 \cdot 10^{-5} \text{ M}$).

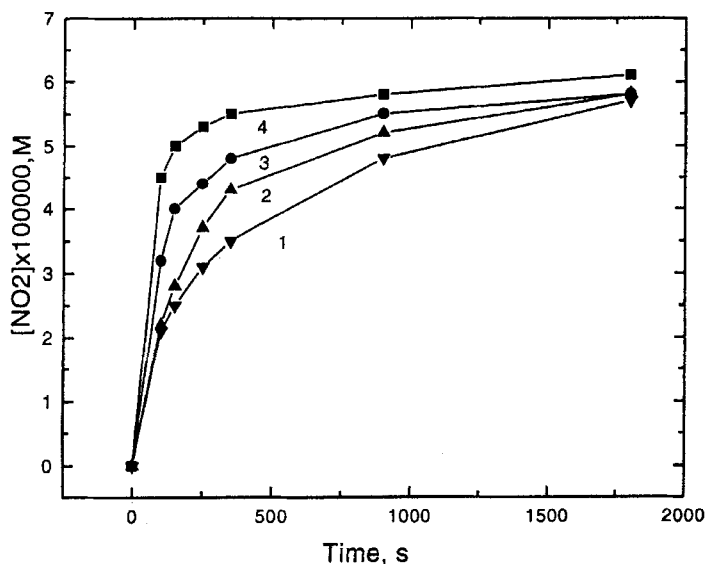


FIGURE 1 Kinetics of NO_2 solubility in HD (a) and anamorphosises (b) at FR: 1-50 ml/min, 2-100 ml/min, 3-200 ml/min, 4-300 ml/min.

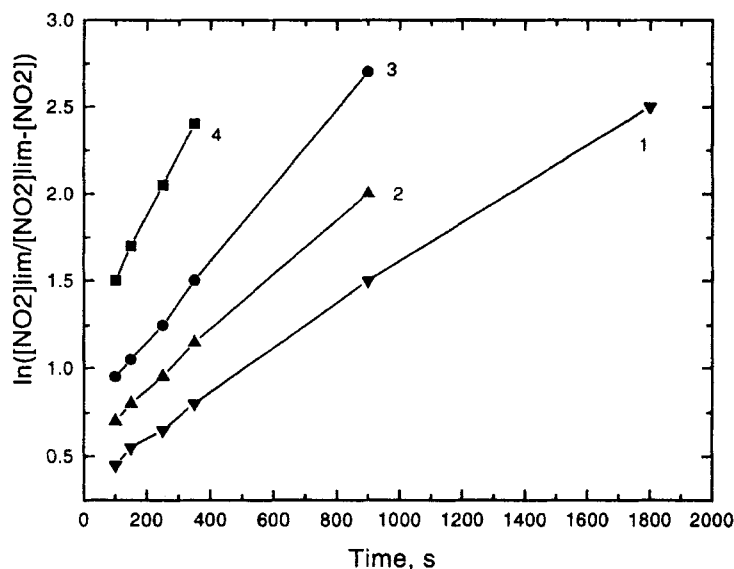


FIGURE 1b (Contd.)

The experimental plots were analyzed to define the kinetic parameter characterizing the rate of the NO_2 dissolving. Formally these curves can be described by equation

$$[\text{NO}_2] = [\text{NO}_2]_{\text{lim}} [1 - \exp(-k_s t)] \quad (1)$$

where $[\text{NO}_2]_{\text{lim}}$ is a limiting concentration, k_s is the constant depending on FR. This conclusion is confirmed by anamorphosises of curves in co-ordinates of (1) shown in Figure 1b. It turns out that the k_s values obtained are linearly FR dependent at the constant temperature.

Kinetics of TTBP Decay

The experiments performed show that kinetics of TTBP conversion has qualitative distinctions according to the initial phenol concentration in solution. The phenol decay predominantly proceeds with the fixed rate in time depending strongly on FR at reasonable TTBP concentrations ($5.0 \cdot 10^{-4} - 3.5 \cdot 10^{-3} \text{ M}$) which much superior to those of NO_2 . This is demonstrated in Figure 2a. In the wake of some initial

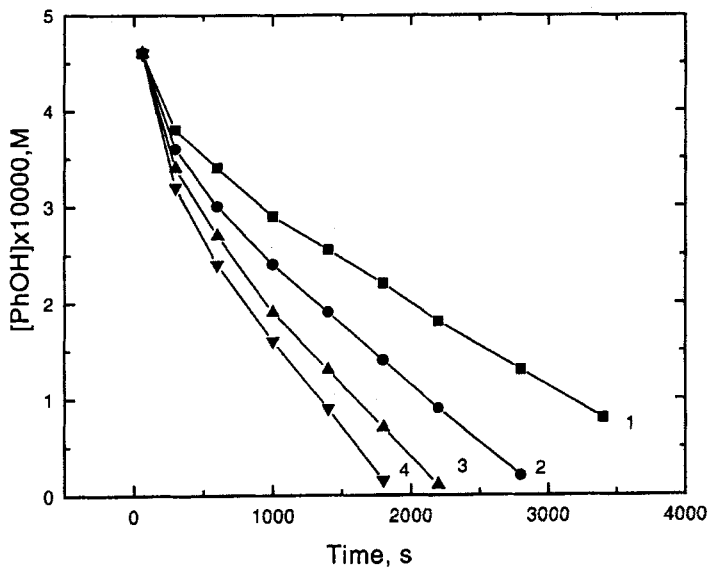


FIGURE 2 Kinetics of TTBP decay at FR 1-50 ml/min, 2-100 ml/min, 3-200 ml/min, 4-300 ml/min (a) and the decay rate dependence on NO_2 solubility (b) $[\text{PhOH}]_0 = 5.0 \cdot 10^{-4} \text{M}$.

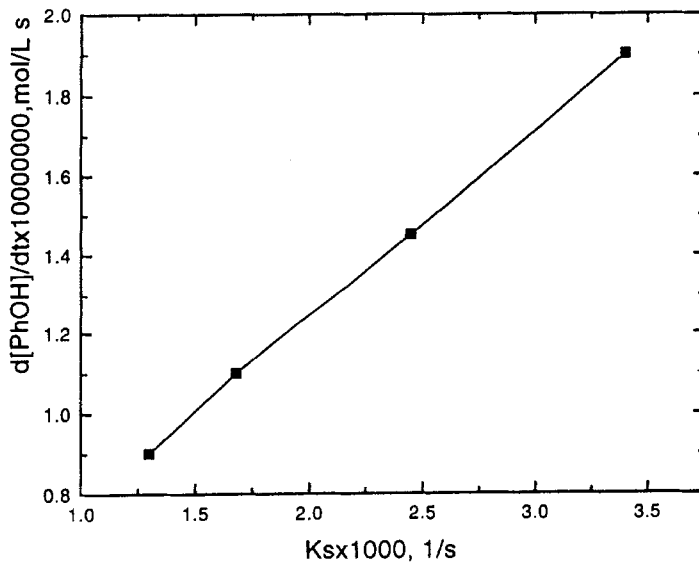
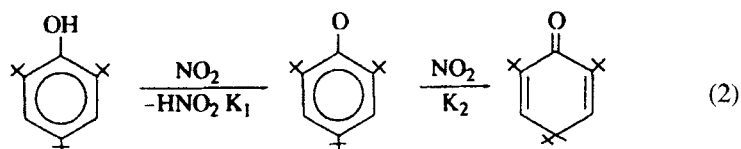


FIGURE 2b (Contd.)

part the rate ceases to depend on the TTBP concentration. As this taken place, the directly proportional reaction rate- k_s relationship is observed (Fig. 2b).

The kinetic curves match actually at the low initial phenol concentration comparable with $[\text{NO}_2]_{\text{lim}}$ (Fig. 3a). Under these conditions the kinetics of TTBP decay is governed by the first order law over all time (Fig. 3b).

These results can be explained by the following model based on the reaction scheme put forward in works [4, 5]



HNO_2 is decomposed with NO_2 formation

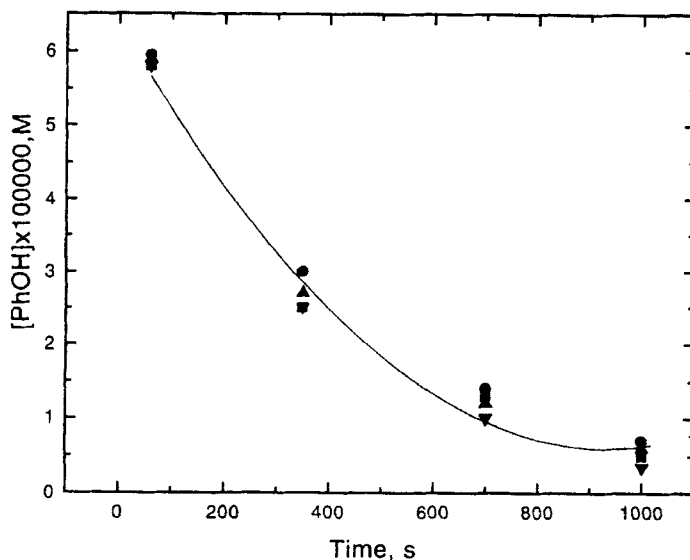
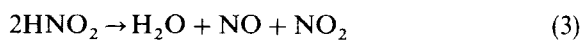


FIGURE 3 Kinetics of TTBP decay at FR 50-300 ml/min, (a) and its straightening (b) $[\text{PhOH}]_0 = 6.0 \cdot 10^{-5} \text{M}$.

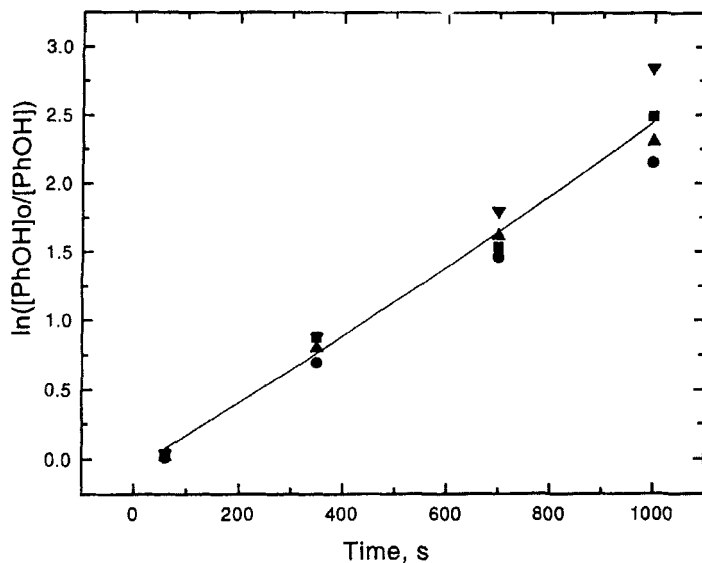


FIGURE 3b (Contd.)

Assume a steady state for the phenoxy radical concentration and HNO_2 . Then the rate of NO_2 concentration change upon addition of TTBP in terms of the found experimentally relationship (1) is determined by equation

$$\frac{d[\text{NO}_2]}{dt} = k_s([\text{NO}_2]_{\text{lim}} - [\text{NO}_2]) - k_1[\text{PhOH}][\text{NO}_2] \quad (4)$$

In so doing three cases are possible as required by the TTBP concentration in solution. If $k_1[\text{PhOH}] \gg k_s$ the rate of the TTBP decay is constant and proportional to k_s on the attainment of a steady concentration of

$$[\text{NO}_2]_{\text{st}} = \frac{k_s[\text{NO}_2]_{\text{lim}}}{k_s + k_1[\text{PhOH}]}$$

$$\frac{d[\text{PhOH}]}{dt} \approx -k_s[\text{NO}_2]_{\text{lim}} \quad (5)$$

The example of such kinetics is shown in Figure 2a, b. The deviation from linearity on the initial portions of kinetic dependencies is involved probably the attainment of a steady-state of NO_2 concentration. Really, the time of these portions is approximately coincident with that when NO_2 concentration flattens out at dissolving in HD (Fig. 1a). The decrease of TTBP concentration in the early stage correlates with a limiting concentration of NO_2 pre-dissolved in HD. It should be pointed out that k_s values for NO_2 in TTBP solution can be differed from those in a pure HD. Unfortunately, we could not appraise the concentration change of NO_2 in the phenol solution by the spectrophotometric method because of the absorbance band overlapping.

Other kind of relationship of TTBP decay is observed if $k_1[\text{PhOH}] \ll k_s$. Then $[\text{NO}_2]_{\text{st}} \approx [\text{NO}_2]_{\text{lim}}$ and

$$\frac{d[\text{PhOH}]}{dt} \approx -k_1[\text{NO}_2]_{\text{lim}}[\text{PhOH}] \quad (6)$$

The rate does not depend on FR in a batch reactor and corresponds to the first order law. The similar regulation is inherent in kinetics shown in Figure 3a, b. The estimation of k_1 from the plot of Figure 3 gives $k_1 = 36.5 \text{ M}^{-1}\text{s}^{-1}$ at 22°C .

The intermediate variant is possible when $k_1[\text{PhOH}] \approx k_s$ for a substantial range of the phenol concentrations

$$\frac{d[\text{PhOH}]}{dt} = -\frac{k_1 k_s [\text{NO}_2]_{\text{lim}} [\text{PhOH}]}{k_s + k_1 [\text{PhOH}]} \quad (7)$$

As it was established, such case is realized at $[\text{PhOH}]_0 \approx 2.0 \cdot 10^{-4} \text{ M}$.

The k_1 value obtained in the batch reactor conditions has been related to the corresponding value determined from the kinetics of the phenol decay measured at once in cell of UV spectrophotometer. On mixing of solutions of TTBP and NO_2 in HD the starting concentrations of phenol and NO_2 were respectively $3.1 \cdot 10^{-5} \text{ M}$ and $3.4 \cdot 10^{-5} \text{ M}$. When the reagent initial concentrations of the bimolecular reaction are dissimilar, the difference of two concentrations is independent of time. Although it follows from (2) that two NO_2 molecules are required for the product formation, the possibility should be allowed for the nitrogen dioxide regeneration from HNO_2 by reaction (3). Then kinetic

curve of TTBP decay must be straightened out in co-ordinates of following equation

$$\ln \frac{[\text{PhOH}] + [\text{NO}_2]_0 - [\text{PhOH}]_0}{[\text{PhOH}]} - \ln \frac{[\text{NO}_2]_0}{[\text{PhOH}]_0} = ([\text{NO}_2]_0 - [\text{PhOH}]_0) k_1 t \quad (8)$$

The kinetics in these conditions and the straightening are shown in Figure 4a, b. The k_1 obtained in this case is $10.7 \text{ M}^{-1} \text{ s}^{-1}$ and close in order to value measured for reaction in a batch reactor. It is possible that k_1 obtained at bubbling is somewhat overestimated so far as the value of $[\text{NO}_2]_{\text{lim}}$ for pure HD has been used for its evaluation. The fact is that a limiting solubility of NO_2 can be raised in the presence of polar molecules of TTBP and products of its conversion resulting in k_1 apparent increase.

To determine the activation parameters the reaction was studied at 60–100°C at constant FR (100 ml/min). The measurements have been carried out at the relatively low phenol original concentrations when

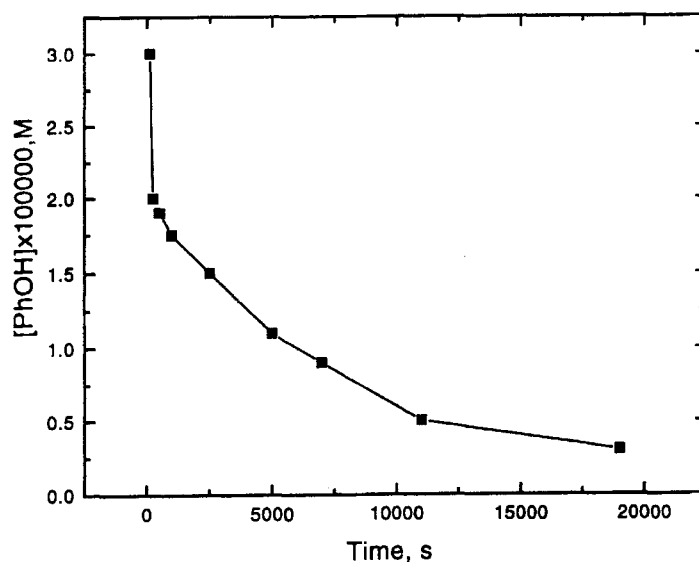


FIGURE 4 Kinetics of TTBP decay in UV cell (a) and its straightening (b).

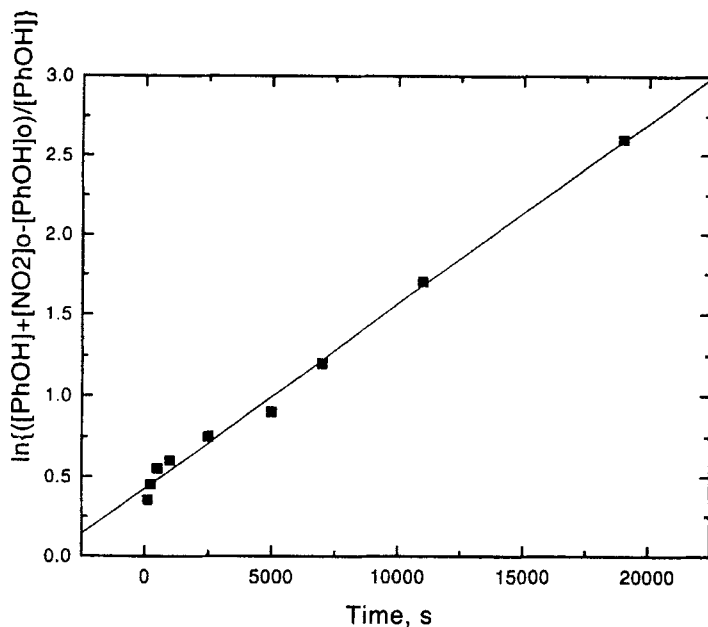


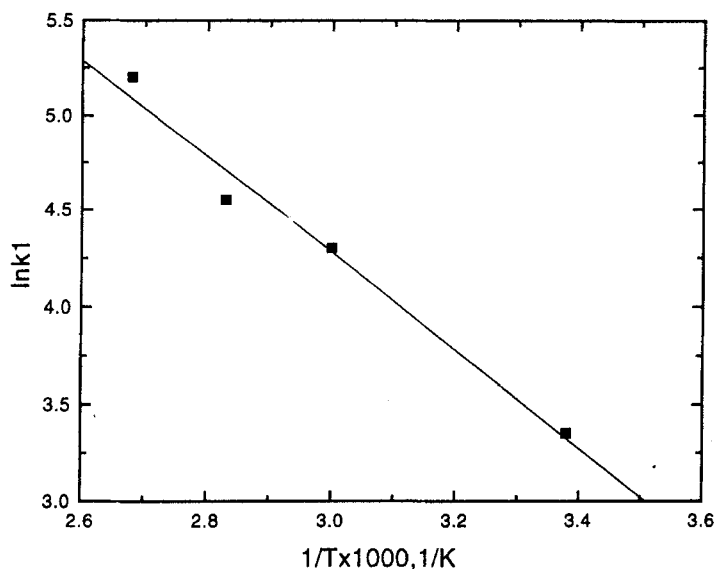
FIGURE 4b (Contd.)

reaction is controlled by the first order law. It was found that this rule is also obeyed at elevated temperatures. To make an estimate of k_1 the measurements of $[\text{NO}_2]_{\text{lim}}$ were performed over studied temperature interval. The values of $[\text{NO}_2]_{\text{lim}}$ are essentially decreased with a rise of temperature. So these values are $1.9 \cdot 10^{-5} \text{M}$ at 60°C and $1.6 \cdot 10^{-5} \text{M}$ at 100°C . The magnitudes of k_1 obtained at different temperatures are tabulated in Table I.

The Arrhenius plot of k_1 is shown in Figure 5. From this dependence the values of the activation energy and the pre-exponential factor were determined: $k_1 = 5.9 \cdot 10^3 \exp(-10 \text{ kJ/RT})$, $\text{M}^{-1}\text{s}^{-1}$. The activation energy for this reaction is rather close to the relevant values of the

TABLE I The temperature dependence of k_1 for TTBP decay in a batch reactor

T, K	293	333	353	373
$k_1, \text{M}^{-1}\text{s}^{-1}$	36.5	72.7	96.2	179.5

FIGURE 5 The k_1 Arrhenius dependence.

phenolic hydrogen atom abstraction by peroxy radicals in the liquid phase [8,9] but pre-exponent is order of magnitude lower.

Estimation of the Rate Constant of the NO_2 and 2,4,6-Tri-*t*-Butylphenoxy Radical Recombination

The formation of phenoxy radicals in reaction of NO_2 with TTBP has been detected before [5]. In our experiments (22°C) the stationary concentration of these radicals was measured during bubbling of NO_2 with FR or 300 ml/min in solution with $[\text{PhOH}]_0 = 3.5 \cdot 10^{-3} \text{M}$. As this takes place, the maximum concentration of PhO^\cdot is $3.5 \cdot 10^{-4} \text{M}$ within a half hour and TTBP concentration reduced to $2.5 \cdot 10^{-3} \text{M}$. The phenoxy radicals disappear completely after decay of TTBP. On the basis of steady-state condition

$$[\text{PhO}^\cdot] = \frac{k_1}{k_2} [\text{PhOH}] \text{ one can estimate } k_2. \text{ Taking into}$$

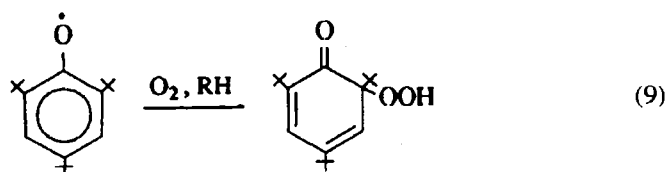
account $k_1 = 10.7 \text{ M}^{-1} \text{s}^{-1}$, we get

$k_2 = 76.5 \text{ M}^{-1}\text{s}^{-1}$ at 22°C . This value is much less than the rate constant of recombination of PhO^\cdot and peroxy radicals (as an example, $4.7 \cdot 10^8 \text{ M}^{-1}\text{s}^{-1}$ for cumylperoxy radicals [10]). Because of this the stationary concentration of PhO^\cdot in the studied system reaches a comparatively high level (about 10% of initial TTPB concentration).

On the Mechanism of the Product Formation at TTBP Conversion in a Batch Reactor

The main product of reaction of TTBP with NO_2 in liquid phase is 2,4,6-Tri-*t*-butyl-4-nitro 2,5-cyclohexadienone (I) forming by scheme (2). This compound is easily identified by the absorbance intensive band with $\lambda = 240 \text{ nm}$ [4], [5]. But in parallel with (I) the appearance of new absorbance bands at 320 nm (II) and 380 nm (III) is observed during bubbling (Fig. 6.1). The form and the intensity ratio of these bands are changed with time. So the optical density at 320 nm drops after total decay of TTBP and the fine structure with the 10 nm distance between lines (IV) is developed on the background of the 380 nm band. (Fig. 6.2). The changes of the optical densities for (I), (II) and (III) are shown in Figure 7. One can see that the (I) concentration is slowly decreased after its peak. In doing so the 240 nm band decrease takes place in solution with the same rate also outside reactor.

The distinctive features of the 320 nm band (II) are that its intensity passes through a maximum when TTBP disappears and noticeably increases upon termination of NO_2 bubbling (Fig. 6.3) but this band is decreased again by repeat treatment of solution in reactor. These facts provide a possibility to attribute 320 nm band to *o*-quinolide hydroperoxides which have the absorbance peak with enough extinction ($\lg \epsilon \approx 3$) just in this spectral region [11]. The formation of (II) at the stage of TTBP decay evidently occurs as a result of the phenoxy radical oxidation



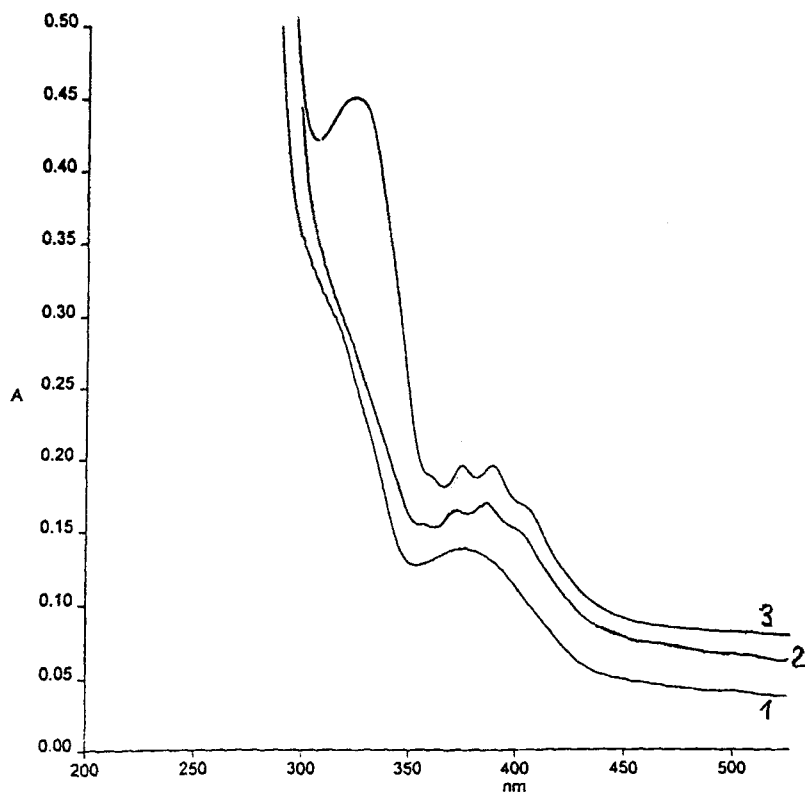
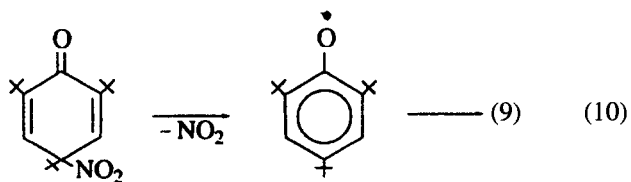


FIGURE 6 UV spectra of TTBP solution during bubbling (1), after total TTBP decay (2) and after 12 hours upon the bubbling termination (3).

The nonstability of (I) has been mentioned in work [4]. The slow decomposition of (I) after bubbling of NO_2 with a simultaneous growth of the (II) concentration (Fig. 6.3) may be therefore presented as follows



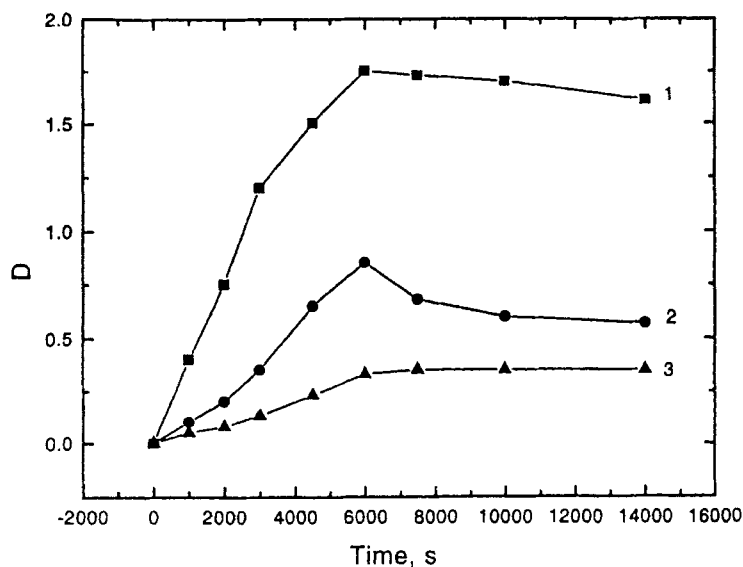
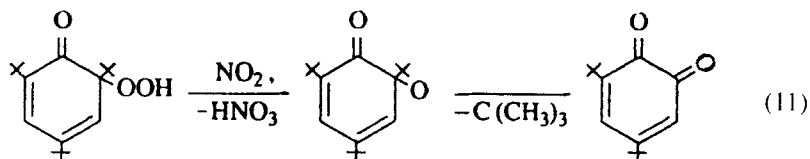


FIGURE 7 The optical density changes at 240 nm (1), 320 nm (2) and 380 nm (3): (1)–0.1 cm cell, (2) and (3)–1 cm cell.

It seems likely that formation of *p*-quinolide hydroperoxides also proceeds by analogous reaction. But these hydroperoxides have high absorbance only in region of 240 nm [11] and its band is overlapped with the absorbance of main product (I). The tentative estimate using known extinction coefficient shows that at 22°C the content of (II) does not exceed 8% with respect to $[\text{PhOH}]_0$. But the limiting content of (II) grows at elevated temperatures. At 60°C in the reactor conditions this value amounts up to 25%. This result also serves as a support of the (II) formation owing to oxidative process (7).

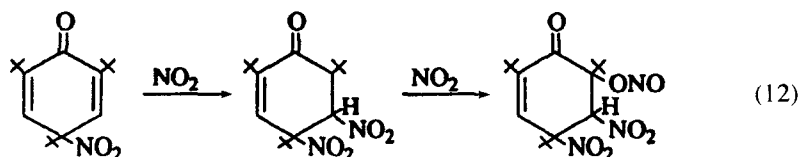
The appearance of (III) can be explained by decomposition of (II) in reaction with NO_2



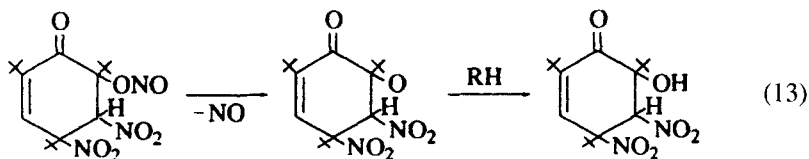
In consequence of this process *o*-quinone is obtained which has UV absorbance at 380–390 nm ($\lg \epsilon = 3.2$) [12, 13]. The formation of *o*-quinone as a terminal product of consecutive reactions of TTBP oxidation is supported by kinetic data. Referring to Figure 7, the kinetics of accumulation of (III) has clearly defined S-type shape. The *p*-quinone can be generated analogously in reaction of NO_2 with *p*-quinolide hydroperoxides. But *p*-quinones have very small absorbance at 430 nm ($\lg \epsilon = 0.3$) and this band must be overlapped by the *o*-quinone band. It was shown before [14], the reaction of NO_2 with hydroperoxides happens with much efficiency in a similar way.

The quinolide peroxides of space-hindered phenols are typical products of inhibited oxidation [10]. The reactions (9–11) become dominant if to perform the heating of solution at 60–100°C without NO_2 bubbling. In this case (I) is quantitatively transformed into (III) and the band at 590 nm characteristic of *o*-quinones is also observed.

The band with fine structure at 380 nm resulting after TTBP conversion into (I) (Fig. 6.2) is typical for nitrites. The nitrite formation in reaction of *p*-nitrocyclohexadienone with NO_2 was proposed in [5]. For (I) this process can be exhibited as follows



The structure of (IV) is confirmed by exact match between the band of (IV) and the spectrum of tertiary nitrites [15]. There appears to be formation of nitrites rather than appropriate nitrocompounds is favoured of steric hindrance by *t*-butyl groups [5]. Unfortunately the nitrite concentration is difficult to measure because of superposition of (III) and (IV) absorbance bands. The nitrite band dies out in solution outside a batch reactor within a few days. This is in agreement with reaction of decomposition with corresponding hydroxycyclohexanone formation assumed in work [5].



CONCLUSION

The interaction of TTBP with NO_2 in liquid phase is the multistage free radical process in which a number products are produced. The initial reactions involving the phenolic hydrogen atom abstraction and recombination of NO_2 and phenoxy radical are fairly slow if to compare with similar reactions of peroxy radicals. The reactions are accompanied by side oxidation process in the batch reactor conditions. The oxidation is maximized by heating with the quinone formation as a major resulting product and is competitive with the nitration reactions.

References

- [1] Titov, A. I. (1963). *Tetrahedron*, **19**, 557–580.
- [2] Johnson, M. D. and Korcek, S. (1991). *Lubrication Science*, **3**, 95–118.
- [3] Korcek, S., Johnson, M. D. and Jensen, R. K. (1992). Book of Abstracts, Sixth Intern. Symposium on Organic Free Radicals, Noordwijkerhout, *The Netherlands*.
- [4] Cook, C. D. and Woodworth, R. C. (1953). *J. Amer. Chem. Soc.*, **75**, 6242–6244.
- [5] Brunton, G., Cruse, H. W., Riches, K. M. and Whittle, A. (1979). *Tetrahedron Letters*, **12**, 1093–1094.
- [6] Jensen, R. K., Korcek, S., Mahoney, L. R. and Zinbo, M. (1979). *J. Amer. Chem. Soc.*, **101**, 7574–7584.
- [7] Hall, T. C. and Blacet, F. E. (1952). *J. Chem. Phys.*, **20**, 1745–1749.
- [8] Howard, J. A. and Ingold, K. U. (1962). *Can. J. Chem.*, **40**, 1851–1864.
- [9] Howard, J. A. and Furimsky, E. (1973). *Can. J. Chem.*, **51**, 3738–3745.
- [10] Burtsov, V. I., Roginskii, V. A. and Miller, V. B. (1979). *Polymer Science USSR*, **20**, 1022–1030.
- [11] Bickel, A. F. and Kooyman, E. C. (1953). *J. Chem. Soc.*, 3211–3218.
- [12] Nagakura, S. and Kuboyama, A. (1954). *J. Amer. Chem. Soc.*, **76**, 1003–1005.
- [13] Mason, H. S. (1948). *J. Amer. Chem. Soc.*, **70**, 138–140.
- [14] Pryor, W. A., Castle, L. and Church, D. F. (1985). *J. Amer. Chem. Soc.*, **107**, 211–217.
- [15] Ungrade, H. E. and Smiley, R. A. (1956). *J. Org. Chem.*, **21**, 993–997.