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The Role of *N*-Hydroxyphthalimide in the Reaction Mechanism of Liquid-Phase Oxidation of *p*-Cymene

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Abstract—The reaction of the liquid-phase oxidation of *p*-cymene to hydroperoxide with a selectivity of up to 95% at a hydrocarbon conversion of 25–30% has been studied at a reaction temperature of 80–120°C in the presence of *N*-hydroxyphthalimide as the catalyst. The catalytic role of *N*-hydroxyphthalimide has been substantiated. A kinetic model of the liquid-phase oxidation reaction in the presence of the catalyst *N*-hydroxyphthalimide has been developed and adequately described.

Keywords: liquid-phase oxidation, *p*-cymene, *N*-hydroxyphthalimide, *p*-cresol manufacture
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Practical implementation of the "cymene" process for the production of *p*-cresol and acetone is impeded by a low selectivity for *p*-cymene hydroperoxide and, in particular, the difficulty of its concentration. Development of methods for increasing the selectivity of oxidation without catalysis by metal ions would form the real basis for practical implementation of this process. *N*-Hydroxyphthalimide (NHPI), a nonmetallic catalyst for radical oxidation, has recently attracted the attention of researchers [1–4], since it dramatically increases the selectivity of processes, in particular, the *p*-cymene hydroperoxide preparation process [5]. The aforementioned studies have shown that the principal role of *N*-hydroxyphthalimide as a radical oxidation catalyst reduces to duplication of the chain propagation cycle according to Scheme I:

$$R^* \xrightarrow{+O_2,\ k1} ROO^* \xrightarrow{+RH,\ k2} ROOH + R^* \qquad \text{(I)}$$

In this scheme, initial NHPI undergoes a cycle of alternating transformations into the corresponding *N*-oxyphthalimide radical (PINO*) and back (by Scheme II):

$$NHPI + ROO^* \xrightarrow{k21} ROOH + PINO^* \qquad \text{(II)}$$

$$PINO^* + RH \xrightarrow{k22} HNPI + R^* \qquad \text{(IIa)}$$

The new route of reactions (II, IIa) is energetically more favorable than the traditional chain propagation pathway (I) [6]. Calculations show that the enthalpies of reactions (I) and (II) are low, <20 and 80 kJ/mol, respectively [7]. Furthermore, a study of the thermodynamics of the nitroxide radical PINO* [8] showed that the O–H bond energy of NHPI is 375 ± 10 kJ/mol, which is comparable, e.g., with the C–H bond energy (315–400 kJ/mol). It is supposed that the mechanism of chain initiation by the «classical» initiator (In_2)

$$In_2 \xrightarrow{ki} 2In^*. \qquad \text{(III)}$$

can be duplicated as well according to the following reaction:

$$NHPI + O_2 \xrightarrow{kii} PINO^* + HO_2^*. \qquad \text{(IIIa)}$$

It is clear that in the absence of metal ions in the reaction mixture, NHPI additives can facilitate not only the selective production of hydroperoxides, but also a more secure way of their concentration. In this context, studying the kinetics and mechanism of the liquid-phase oxidation of *p*-cymene is of great theoretical and practical importance.

In this study, we investigated the role of *N*-hydroxyphthalimide in various steps of the radical oxidation of *p*-cymene.

EXPERIMENTAL

Oxidation of *p*-cymene (M = 134.22 g/mol; density = 0.8575 g/cm^3, i.e., 1 kg makes 1.166181 L; molarity of the neat liquid is 6.463 mol/L) was carried out with atmospheric oxygen in a continuous-flow closed glass reactor with constant vigorous stirring in the presence of the catalyst *N*-hydroxyphthalimide (M = 163.00 g/mol) taken in an amount of 2.7% of the loaded hydrocarbon mass (0.1656 mol per kg of hydrocarbon). The reaction was monitored by following the oxygen uptake; the oxidation was run in the kinetic regime in which the reaction rate did not depend on the intensity of stirring. The oxidation product was ana-

Table 1. Temperature dependences of change in the current concentrations of hydroperoxide and *p*-cymene with the reaction time

Time (min)	Temperature, °C									
	80	90	100	110	120	80	90	100	110	120
	Hydroperoxide concentration, wt %					*p*-Cymene concentration, wt %				
0	0	0	0	0	0	100	100	100	100	100
5	0.196	0.89	1.4	1.9	2.7	99.8	99.09	98.55	98.01	97.16
10	0.50	3.0	3.7	4.8	7.6	99.49	96.91	96.15	94.96	92
15	0.90	5.2	7.1	9.1	12.4	99.08	94.63	92.59	90.43	86.92
20	1.30	7.7	10.6	13.7	17.8	98.67	92.00	88.9	85.56	81.18
25	1.90	10.9	14.3	19.8	23.2	98.05	88.65	84.98	79.11	75.39
30	2.40	14.1	16.5	26.1	27.8	97.53	85.28	82.63	72.41	70.42

lyzed for *p*-cymene hydroperoxide by iodometric titration.

RESULTS AND DISCUSSION

The oxidation of *p*-cymene in the presence of *N*-hydroxyphthalimide was examined in the temperature range of 80–120°C and until a hydrocarbon conversion of <30%. As shown in Table 1, the hydroperoxide concentration increases and the concentration of *p*-cymene correspondingly decreases with the increasing temperature from 80 to 120°C. Under these conditions, *p*-cymene hydroperoxide can be produced with high selectivity in as large an amount as 27.8% at 120°C for 30 min.

Indeed, the confidence level (R^2, determined by the standard program Excel 93_2003) of linear correlation of experimental values for the concentration of the forming hydroperoxide (wt %) and the corresponding conversion of *p*-cymene (wt %) for all the temperatures was very high ($R^2 = 1$), and the relationship obtained had the form:

$$[\mathrm{ROOH}]_i = \alpha_0^*([\mathrm{RH}]_0 - [\mathrm{RH}]_i) \equiv \alpha_0^*\Delta[\mathrm{RH}]_i, \qquad (1)$$

where $[\mathrm{ROOH}]_i$ is the current hydroperoxide concentration (wt %); α_0 is the proportionality factor (Table 2); and $[\mathrm{RH}]_0$ and $[\mathrm{RH}]_i$ are the initial and current concentrations of *p*-cymene (wt %), respectively.

Table 2. Values for various parameters of the *p*-cymene oxidation reaction, depending on the reaction temperature

Run temperature, °C	Equation (1)	Equations (3), (4)	
	α_0	α_1	α_2
80	0.974	0.983	– 0.0046
90	0.960	0.972	– 0.001
100	0.952	0.964	– 0.0008
110	0.946	0.957	– 0.0005
120	0.943	0.945	– 0.0005

The directly proportional relationship between the hydroperoxide yield and the hydrocarbon consumption shows that there has been no noticeable degradation of ROOH (at least within the accuracy of determination of the reactant concentrations) during the test period. This result might be an indication of constancy of oxidation selectivity (i.e., $\alpha_0 \equiv S_0$) during the experiment. In other words, the proportion of the hydrocarbon that was not consumed for the formation of hydroperoxide (Table 2) depends on the reaction temperature alone, but it remains constant during the reaction and corresponds to the consumption of RH for the formation of chain termination products $[\mathrm{Pr}_0]$:

$$2\mathrm{ROO}^* \xrightarrow{ki} \mathrm{Pr}_0 \qquad (\mathrm{IV})$$

with maintaining the balance (2)

$$\Delta[\mathrm{RH}]_i = [\mathrm{ROOH}]_i + [\mathrm{Pr}_0]_i. \qquad (2)$$

However, the linear regression method used does not allow systematic deviations to be detected in quantities to be matched unless these deviations are large in absolute value. For example, the confidence level (R^2) of a polynomial correlation of the same experimental values of $[\mathrm{ROOH}]_i$ and $\Delta[\mathrm{RH}]_i$ was also very high ($R^2 = 1$). This relationship was as follows:

$$[\mathrm{ROOH}]_i = (\alpha_1 - \alpha_2\,\Delta[\mathrm{RH}]_i)\Delta[\mathrm{RH}]_i. \qquad (3)$$

An analysis of the coefficients (Table 2) for correlation equation (3) shows that the decrease in the integral selectivity (S_i, Eq. (4)) is defined by two terms, of which one is independent of and the other is dependent on the conversion of the hydrocarbon.

$$S_i \equiv [\mathrm{ROOH}]/\Delta[\mathrm{RH}] = (\alpha_1 - \alpha_2\Delta_i). \qquad (4)$$

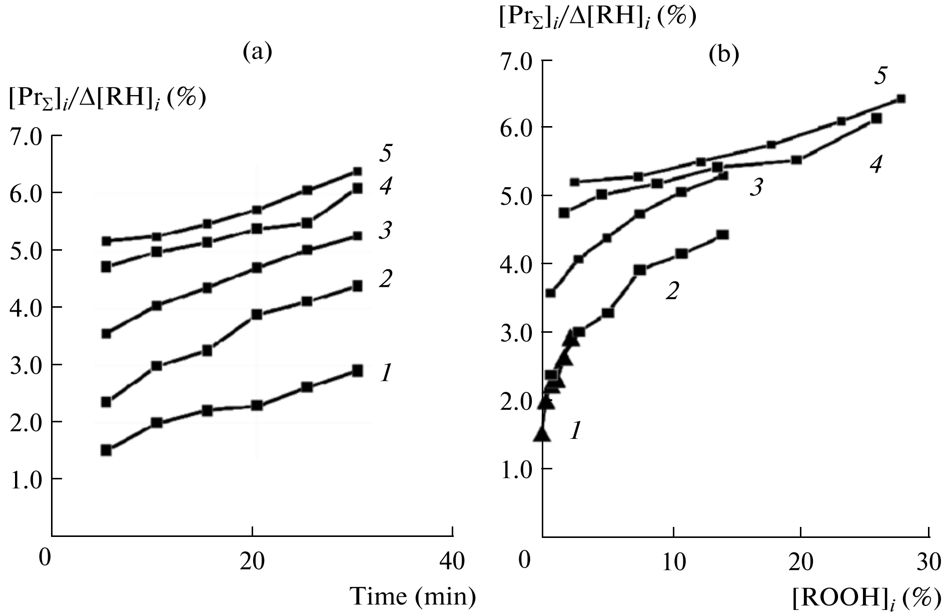

Fig. 1. Change in the proportion of byproducts ($[Pr_\Sigma]_i$) relative to the amount of *p*-cymene consumed in the reaction depending on (a) time and (b) the amount of hydroperoxide formed at different temperatures: (*1*) 80, (*2*) 90, (*3*) 100, (*4*) 110, and (*5*) 120°C.

It can be assumed that the term $\{\alpha 2\Delta[RH]_i\}$ reflects the further consumption of the hydroperoxide via reaction (V) at a rate r_t:

$$2ROOH \xrightarrow{k3} Pr_1(r_t), \qquad (V)$$

The data presented in Table 2 show that the change in the hydroperoxide formation selectivity dependent on the hydrocarbon conversion is very small, being only a few percent. As the temperature increases, the selectivity decreases. However, a certain specific feature of the process should be noted: the selectivity decrement due to hydroperoxide degradation during the reaction depends on the temperature in a manner other than the usual, expected fashion. Evaluating the relative contribution of this hydrocarbon consumption route by a numerical value of α_2, we see (Table 2) that at 80°C, it is an order of magnitude greater than the contribution at 120°C.

Taking into account the high selectivity of the reaction and statistical nondistinguishability of correlation equations (2) and (3), for the further work we selected data on the formation of all byproducts ($[Pr_\Sigma]_i$), since they are the most informative.

$$[Pr_\Sigma]_i = [Pr_0]_i + [Pr_1]_i; \qquad (5)$$

where $[Pr_0]_i$ refers to the byproducts formed via the chain termination reaction,

$[Pr_1]_i$ refers to the byproducts due to the decomposition of hydroperoxide, and

$[Pr_\Sigma]_i$ is the total amount of byproducts.

The share of total byproducts $[Pr_\Sigma]_i$ in *p*-cymene ($[Pr_\Sigma]_i/\Delta[RH]_i$) consumed during the reaction and in relation to hydroperoxide buildup is illustrated in Figs. 1a and 1b, respectively.

Analyzing the data presented in Table 1 and Figs. 1a and 1b, we can come to the following conclusions: (1) there is no induction period of the reaction; (2) the intercepts on the ordinate give the extrapolative ratio of the chain termination products ($[Pr_0]_0$) to the propagation products at a time $t \to 0$, i.e., when the resulting hydroperoxide is not involved in the process; and (3) the proportion of the reaction products, increasing during the process ($[Pr_\Sigma]_i$ – ($[Pr_0]_0$), decreases with the increasing temperature and is much less than $[Pr_0]_0$ at 120°C up to a 25–30% conversion of the hydrocarbon.

Consider the kinetic treatment of the reaction of interest, describing its “classical” propagation mechanism (Eqs. (6)–(9)). The notation of the rate constants for different steps of the process has been given above. In addition, the initiation rate (r_i) responsible for the onset of the process is introduced into the scheme. This rate can be considered an infinitesimal, without which the set of differential equations cannot be integrated. Typically, it is assumed for noncatalytic systems that the chain initiation is determined by reaction (VI), called the “thermal initiation”, with a rate r_i:

$$RH + O_2 \xrightarrow{k_0} R^* + HOO^* \, (r_i) \qquad (VI)$$

The set of differential rate equations is as follows:

$$d[ROOH]/dt = k_2[RH][ROO^*] - k_3[ROOH] \quad (6)$$

$$d[Pr_\Sigma]/dt = k_t([ROO^*])^2 = r_i + 2k_3[ROOH] \quad (7)$$

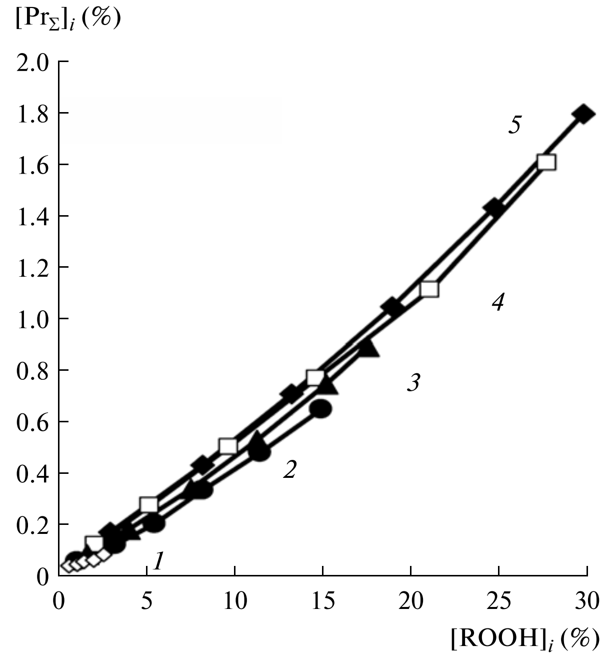

Fig. 2. Experimental data (symbols) and calculated curves for the ratio of byproducts ($[\mathrm{Pr}_\Sigma]_i$) and hydroperoxide formed at different temperatures: (*1*, ◇) 80, (*2*, ●) 90, (*3*, ▲) 100, (*4*, □) 110, and (*5*, ◆) 120°C.

$$-d[\mathrm{RH}]/dt = k_2[\mathrm{RH}][\mathrm{ROO^*}] + k_3[\mathrm{ROOH}] + r_i. \tag{8}$$

Based on the condition that the initiation rate r_i is equal to the termination rate r_t, i.e., the rate of formation of chain termination products (Eq. (7)), we obtain an expression for the concentration of peroxide radicals:

$$[\mathrm{ROO^*}] = \sqrt{r_i} + 2k_3[\mathrm{ROOH}]/\sqrt{k_t}. \tag{9}$$

At the very beginning of the process with extrapolation to a time of $t \to 0$ when the hydroperoxide has not been formed yet, the concentration of the peroxide radical is defined as

$$([\mathrm{ROO^*}])_{t\to 0} = \sqrt{r_i}/\sqrt{k_t}. \tag{9a}$$

The selectivity of the reaction $(S_i)_{t\to 0}$ under these conditions is expressed by Eq. (10):

$$(S_i)_{t\to 0} \equiv (d[\mathrm{ROOH}]/-d[\mathrm{RH}])_{t\to 0} = \frac{k_2[\mathrm{RH}]}{k_2[\mathrm{RH}] + k_t[\mathrm{ROO^*}]} = \frac{k_2[\mathrm{RH}]}{k_2[\mathrm{RH}] + \sqrt{k_t}\sqrt{r_i}}. \tag{10}$$

As can be seen in Figs. 1a and 1b, the initial selectivity $(S_i)_{t\to 0}$ weakly depends on temperature and, after statistical treatment, is expressed by Eq. (11) with a confidence level of $R^2 = 0.975$:

$$(S_i)_{t\to 0} = \exp(4.22 + 135/T)\ (\mathrm{wt}\ \%), \tag{11}$$

where T in the reaction temperature in kelvins.

The ratio of the byproducts to the hydroperoxide formation rates depends much strongly on temperature and is defined by Eq. (12) with a confidence level of $R^2 = 0.942$:

$$(d[\mathrm{Pr}_0]/d[\mathrm{ROOH}])_{t\to 0} = (\sqrt{r_i}\sqrt{k_t}/k_2[\mathrm{RH}]) = \exp(13.15 - 4500/T)\quad (\mathrm{wt}\ \%). \tag{12}$$

We compared this result with similar data on the oxidation of *p*-cymene reported by Makgwane et al. [9], who used another initiator, a phoshovanadate (VPO) complex. It turned out that the numerical values of the product ratio in the initial period of the reaction are almost identical to each other and are satisfactorily described Eq. (12). The results show that the initiation rate r_i is not infinitesimal and is comparable with the rate of initiation by *N*-hydroxyphthalimide ($r_{ii} \equiv r_i$) (Scheme III). The relatively small values of the temperature coefficients for the selectivity and product ratio functions (Eqs. (12) and (13)) indirectly confirm that the catalyst introduced (NHPI) might initiate the generation of radicals.

However, the process characteristics measured at the propagation step in this study are quite different from those obtained in [9]. For example, calculations show that in the case of initiation of the reaction by VPO, the proportion of byproducts $[\mathrm{Pr}_\Sigma]_i/\Delta[\mathrm{RH}]_i$ at 120°C and a *p*-cymene conversion of ≈30% increases from ≈5% to ≈25% (Fig. 8 in the paper cited, curve at 120°C), whereas it varies from ≈5 to 7% in our case (in Fig. 1b, curve *5*). Even if the formation of $[\mathrm{Pr}_\Sigma]$ is attributed to the termination products only, it is evident that the chain length of propagated oxidation in the presence of NHPI is greater in comparison with one of the classical initiators (VPO), i.e., metal ions.

In the case of participation of NHPI in the propagation step (Scheme II), the rate of this step is defined by Eq. (6a)

$$-d[\mathrm{ROOH}]/dt = (k_2[\mathrm{RH}] + k_{21}[\mathrm{NHPI}])[\mathrm{ROO^*}] - k_3[\mathrm{ROOH}]. \tag{6a}$$

The appearance of the new term with a constant k_{21} in Eq. (6a) can be interpreted as an increase in the rate constant of the reaction between the radical {ROO*} and the hydrocarbon. At a constant rate of the termination reaction, the effect of NHPI formally reduces to an increase in the chain length, i.e., a decrease in the yield of undesired products as compared with that of hydroperoxide (Eq. (13)).

$$d[\mathrm{Pr}_\Sigma]/d[\mathrm{ROOH}] = \frac{r_i + 2k_3[\mathrm{ROOH}]}{(k_2[\mathrm{RH}] + k_{21}[\mathrm{NHPI}])[\mathrm{ROO^*}] - k_3[\mathrm{ROOH}]}. \tag{13}$$

It may be assumed that at high temperatures (>100°C), there is a competition between the chain propagation routes defined by Schemes I and II. Theoretical and experimental studies [10, 11] showed that

Table 3. Calculated values for the rate constants K and k_3 of the liquid-phase oxidation reaction of *p*-cymene in the presence of *N*-hydroxyphthalimide and their temperature dependence

Temperature, °C	K, $L^{1/2}\ mol^{-1/2}\ s^{-1}$	k_{3}, s^{-1}
80	0.16 (0.035)*	0.5 (0.5)*
90	0.42	0.63
100	0.50 (0.054)*	0.75 (0.75)*
110	0.60	0.86
120	0.65 (0.071)*	1.02 (1.02)*
80–120	$\exp(7.3–3000/T)$ $R^2 = 0.8$	$\exp(6.14–2400/T)$ $R^2 = 0.996$

* Values of the constants as given in [9].

reactions (II) and (IIa) are thermoneutral or slightly endothermic. As the temperature increases, the replacement of the peroxide radical by the more stable *N*-oxyphthalimide radical (Scheme II) becomes faster and, as a consequence, there is a relative decrease in the increment of the byproduct yield. It is apparently this development that is responsible for the unusual pattern of the curves in Fig. 1b; i.e., the contribution of reactions (II) and (IIa) increases with the increasing temperature as compared with the reactions of Scheme I.

Our experimental data presented above do not allow for the complete kinetic analysis of the process and the determination of the rate constants for each of the reactions. However, to reveal the role of *N*-hydroxyphthalimide (NHPI) in the liquid-phase oxidation reaction of *p*-cymene, we performed a comparative analysis of the description of the system by the set of Eqs. (6)–(8), (8a), and (9) presented above and the description of the oxidation of isopropylbenzene by the mathematical model originally developed by Hattori [12]. Except for minor changes, the kinetics of the process in the work cited is described by identical differential equations. For example, Hattori gives the hydroperoxide formation equation in the following form:

$$-d[\mathrm{ROOH}]/dt = K[\mathrm{RH}]\sqrt{[\mathrm{ROOH}]} - k_3[\mathrm{ROOH}]. \tag{14}$$

It is easy to see that the constant K in Eq. (14) is identical to the ratio of the constants of the set of differential equations (6)–(8):

$$K \cong k_2\sqrt{2k_3}/\sqrt{k_t}, \tag{15}$$

and takes the following form (Eq. (15a)) when the catalyst (NHPI) is used:

$$K \cong (k_2 + k_{21}[\mathrm{NHPI}]/[\mathrm{RH}])\sqrt{2k_3}/\sqrt{k_t}, \tag{15a}$$

According to Hattori [12], Eq. (14) satisfactorily describes the isopropylbenzene oxidation kinetics in the temperature range of 80 to 120°C. Based on the proposed mathematical model of oxidation, the authors of this paper determined the value of the constant K at $T = 120°\mathrm{C}$ as 0.093 $L^{1/2}$ $mol^{-1/2}s^{-1}$. Somewhat later, the Hattori model of isopropylbenzene oxidation was refined by Bhattacharya [13]. The calculated value of K was 0.083 $L^{1/2}mol^{-1/2}s^{-1}$. Finally, Makgwane et al. [9], whose study has been discussed above, attempted to apply the model developed by Hattori and Bhattacharya to the oxidation reaction of *p*-cymene in the presence of a vanadium catalyst. It turned out that the model agrees well with the experimental data and adequately describes the oxidation process. The calculated value of K was 0.071 $L^{1/2}mol^{-1/2}s^{-1}$, which is consistent with the results obtained by Hattori and Bhattacharya. The lower value of K for *p*-cymene is explained in terms of a somewhat lower rate of oxidation of *p*-cymene compared with isopropylbenzene. The rate constant k_3 retains its numerical values in both the cases of isopropylbenzene and *p*-cymene oxidation.

Based on the above considerations, we treated our experimental data in terms of the mathematical model by Makgwane et al. [9]. At the initial step, we used the numerical values of K and k_3 obtained by the cited authors for 80, 100, and 120°C. However, we managed to obtain a good description of the data using the least squares technique, by minimizing the difference between the experimental and calculated values for the hydroperoxide and the undesired products with varying the value of K. The confidence level (R^2) for the correlation of the experimental and calculated data is $R^2 = 0.976$ for the entire set of experiments. The values for the rate constants are given in Table 3.

It turned out that the numerical values of k_3 remained almost unchanged, whereas the calculated values of K were an order of magnitude higher than the value reported by Makgwane et al. [9]. A comparison of the functional dependence of the constant defined by Eqs. (15) and (15a) makes the cause of this discrepancy obvious.

The calculated data on the dependence of the yield of byproducts and the buildup of *p*-cymene hydroperoxide in the temperature range of 80 to 120°C (Fig. 2) are in good agreement with the experimental data.

The results obtained in this study demonstrate the adequacy of the kinetic model in question and the validity of the proposed reaction mechanism for the oxidation of *p*-cymene to hydroperoxide in the presence of *N*-hydroxyphthalimide.

Thus, the analysis of these data leads to the conclusion that the driving force of the catalytic activity of *N*-hydroxyphthalimide are reactions (II) and (IIa), which result in an increase in the chain length of the radical oxidation of *p*-cymene.

REFERENCES

1. O. Fukuda, S. Sakaguchi, and Y. Ishii, Adv. Synth. Catal. **343**, 809 (2001).
2. Y. Ishii, K. Nakayama, M. Takeno, et al., J. Org. Chem. **60**, 3934 (1995).
3. Y. Yoshino, Y. Hayashi, T. Wham, et al., J. Org. Chem. **62**, 6810 (1997).
4. Y. Ishii and S. Sakaguchi, Catal. Surveys Jpn., **3**, 27 (1999).
5. E. A. Kurganova, Yu. B. Rumyantseva, G. N. Koshel', et al., Khim. Prom-st. Segodnya, No. 4, 20 (2012).
6. K. Nobuyoshi, Cai Yang, and E. H. James, J. Phys. Chem. A **107**, 4262 (2003).
7. I. Hermans, L. Vereecken, J. A. Pierre, and J. Peeters, Chem. Commun., 1140 (2004).
8. K. Nobuyoshi, Cai Yang, and H. J. Espenson, J. Phys. Chem. A, 4262 (2003).
9. P. R. Makgwane, N. I. Harmse, E. E. Ferg, and B. Zeelie, Chem. Eng. J. **162**, 341 (2010).
10. Gabriel da Silva and J. W. Bozzelli, J. Phys. Chem. **111**, 5760 (2007).
11. N. Koshino, Cai Yang, and J. H. Espenson, J. Phys. Chem. A **107**, 4262 (2003).
12. K. Hattori, Y. Tanaka, H. Suzuki, et al., J. Chem. Eng. Jpn. **3**, 72 (1970).
13. A. Bhattacharya, Chem. Eng. J. **137**, P. 308 (2008).