Kinetic Studies of Acenaphthene Oxidation Catalyzed by N-Hydroxyphthalimide

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ABSTRACT: The acenaphthene oxidation with molecular oxygen in the presence of N-hydroxyphthalimide (NHPI) has been investigated. It is shown that the main oxidation product is acenaphthene hydroperoxide. The phthalimide-N-oxyl (PINO) radical has been generated in situ from its hydroxyimide parent, NHPI, by oxidation with iodobenzenediacetate. The rate constant of H-abstraction ($k_{\rm H}$) from acenaphthene by PINO has been determined spectroscopically in acetonitrile. The kinetic isotope effect and the activation parameters have also been measured. On the basis of the results of our studies and available published literature data, a plausible mechanism for the oxidation process of acenaphthene with dioxygen catalyzed by NHPI was discussed. © 2013 Wiley Periodicals, Inc. Int J Chem Kinet 45: 515–524, 2013

INTRODUCTION

Aerobic oxidation of alkylbenzenes is a promising process in industrial chemistry. One of the most active and selective catalysts in liquid-phase oxidation of alkylbenzenes using molecular oxygen is *N*-hydroxyphthalimide (NHPI) and its mixture with cobalt and manganese salts [1–8]. It has been used to produce hydroperoxides, carboxylic acids, and other oxygen-containing products under moderate conditions in a high yield. In oxidation processes, NHPI acts as a precursor of the phthalimide-*N*-oxyl (PINO) radical, which is the effective species in the reaction of H-atom abstraction from RH.

Polycyclic aromatic hydrocarbons with secondary C-H bonds, for example, acenaphthenes (AcNph) are oxidized by using dioxygen to their corresponding oxygenated derivatives, naphthalic acid and naphthalic anhydride, which are used as intermediates for the synthesis of the important raw materials (such as esters, amides, and imides) for the manufacture of dyes, pharmaceuticals, pesticides, plastics, fibers, curing agents, plasticizers, pigments, fluorescent whiteners, and many other items [9]. Polynuclear hydrocarbons were oxidized during catalysis of NHPI [10], [11], but no literature report has been published on the efficient oxidation of acenaphthene except [10], where authors used the NHPI/anthraquinone system. In this paper, we have reported the kinetic study of the acenaphthene oxidation by molecular oxygen in the presence of NHPI, to better understand the mechanism of the NHPI-catalyzed aerobic oxidation of alkylbenzenes. We have described

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the use of NHPI, in which it acts as a catalyst in the absence of a transition metal compound.

EXPERIMENTAL

NHPI was purchased from Fluka (Sigma-Aldrich Chemie GmbH) and was used as received. Azodiisobutyronitrile (AIBN) and acenaphthene were purified by recrystallizing twice from ethanol. Ethylbenzene, toluene, cumene were purified using a described procedure [12]. An acetic acid was distilled over P_2O_5 . Iodobenzenediacetate (PhI(OAc)₂) was synthesized as described [13]. Acenaphthenone-9, acenaphthenole-9, and acenaphthene quinone were used as received. 9,9,10,10-Tetradeuterated acenaphthene (AcNph- d_4) was synthesized from acenaphthene by means of hydrogen–deuterium exchange with NaH in (CD₃)SO-D₂O by following a literature method [14], and ¹H NMR spectroscopy was used to confirm that 99.8% of acenaphthene was converted into AcNph- d_4 .

Oxidation kinetics was studied at constant oxygen pressure (1 atm) with the gas-volumetric method by measuring the volume of the absorbed oxygen. The intensity of agitation of a reaction vessel was enough to conduct the reaction in kinetic regime. The initial reaction rates were calculated from the slope of the linear plots of the volume of oxygen consumption against time. All kinetic measurements were carried out by using freshly prepared samples.

The rate constant of H-abstraction from acenaphthene by PINO was measured in acetonitrile by UV-vis spectrophotometry, using an Analytic Jena SPECORD S300 spectrophotometer equipped with a thermostated cell holder. PINO was generated by the oxidation of NHPI (7.15 \times 10⁻³ M) with PhI(OAc)₂ (7.15 \times 10⁻⁴ M) in deoxygenated acetonitrile. A solution of the acenaphthene was added into the PINO solution in the cuvette (the acenaphthene concentration is varied in the range (1.35–3.48) \times 10^{-3} M), and the absorbance change was monitored at 382 nm. In all cases, each kinetic trace obeyed a first-order kinetics. Second-order-rate constants were obtained by the plot of the observed rate constant k_{obs} versus the substrate concentration. It was verified that the self-decomposition of PINO, generated by the oxidation of NHPI with PhI(OAc)2 in acetonitrile (10-25°C) was slow enough to allow the study of the reaction of PINO with acenaphthene.

Identification of oxidation products was performed by comparing their chromatograms with those of the authentic samples of acenaphthenenone-9, acenaphthenenole-9, and acenaphthene quinone. Analytical thin layer chromatography (TLC) was



Figure 1 Time dependence curves of O₂ uptake for the oxidation of AcNph (0.1 M) in chlorobenzene (2 mL) at 75°C under atmospheric pressure (1 atm) of dioxygen: 1, [AIBN] = 2.5×10^{-3} M, [NHPI] = 5×10^{-3} M; 2, [AIBN] = 2.5×10^{-3} M; 3, [NHPI] = 5×10^{-3} M.

performed on precoated silica gel "Silufol" plates. A mixture of toluene and ethyl acetate (5:1, v/v) was used as an eluent. Plates were developed by the UV light (365 nm) or KJ treatment.

The concentration of hydroperoxide was measured by the standard iodometric titration.

KINETICS

The oxidation of acenaphthene was carried out in liquid phase under mild reaction conditions (75°C, atmospheric pressure) both in the presence of NHPI and in the absence of NHPI. The oxidation was followed by monitoring the oxygen consumption in a monostatic system built in our laboratory. The experiments were carried out at 75°C in chlorobenzene solutions containing acenaphthene (0.02–1.54 M), AIBN (0–0.05 M) as an initiator, and NHPI (0–0.005 M). Figure 1 shows, as an example, the time-dependence curves of the O₂ uptake during the oxidation of acenaphthene.

After an initial induction period of several minutes, the oxygen absorption is observed (Fig. 1). In the oxidation of substrate by NHPI or AIBN alone, the rates of oxidation were low, or almost no O_2 uptake was observed. The oxidation in the presence of the NHPI/AIBN system discloses a synergistic effect.

In the following experiments, the influence of the concentration of the catalyst, initiator, and substrate on the maximum reaction rate was studied. The oxidation was carried out at 75°C in chlorobenzene solutions containing AIBN (2.5×10^{-3} M), NHPI (5×10^{-3} M), and variable amounts of acenaphthene (Fig. 2).

The influence of the initiator concentration on the oxidation rate at 75°C was studied. The variation of the AIBN concentration at constant concentrations of acenaphthene (0.1 M) and catalyst NHPI (5×10^{-3} M) show that the rate of oxidation increases linearly



Figure 2 Dependence of the oxygen consumption rates for the oxidation of AcNph catalyzed by NHPI (5×10^{-3} M) and AIBN (2.5×10^{-3} M) in chlorobenzene (2 mL) at 75° C on the AcNph concentration.



Figure 3 Dependence of the oxygen consumption rates for the NHPI (5×10^{-3} M) catalyzed oxidation of AcNph (0.1 M) in chlorobenzene (2 mL) at 75°C on the AIBN concentration.

with the square root of the initiator concentration (Fig. 3).

A series of experiments were performed where the catalyst concentration was changed at constant concentrations of acenaphthene and AIBN. As illustrated in Fig. 4 a plot of the oxidation rates versus the NHPI concentration is linear.



Figure 4 Dependence of the oxygen consumption rates for the AIBN (2.5×10^{-3} M) initiated oxidation of AcNph (0.1 M) at 75°C in chlorobenzene (2 mL) on the NHPI concentration.

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Figure 5 Dependence of the induction period of oxidation rates of AcNph in chlorobenzene (2 mL) at 75°C on the concentration of the inhibitor; [AcNph] = 0.1 M; [AIBN] = 2.5×10^{-3} M; [NHPI] = 5×10^{-3} M.

The rate of initiation was determined using the inhibitor method, using butylated hydroxytoluene (BHT) as the inhibitor: $W_i = 2[BHT]/\tau$, where τ , the induction period, is taken to be a time obtained using extrapolation of the oxygen consumption rates—a time curve at zero of the oxygen consumption rates. The rate of acenaphthene oxidation after complete consumption of the inhibitor is equal to the rate of acenaphthene oxidation in the absence of the inhibitor. As illustrated in Fig. 5 the induction period linearly depends on the concentration of the inhibitor.

Analysis of the data of Fig. 5 provides the $W_i = (2.71 \pm 0.11) \times 10^{-7} \text{ M s}^{-1}$. The initiation rate calculated using the equation $W_i^{\text{calc}} = 2k_d$ [AIBN] (where k_d is the rate constant of the AIBN decomposition at 75°C and [AIBN] is the AIBN concentration) agrees with the experimental initiation rate W_i ($W_i^{\text{calc}} = (2.66 \pm 0.11) \times 10^{-7} \text{ M s}^{-1}$). This fact shows that PINO does not participate in the initiation stage.

REACTION PRODUCTS

The iodometric titrations of reaction mixtures during acenaphthene oxidation catalyzed by NHPI showed the presence of peroxides. Acenaphthene was oxidized easily to the corresponding hydroperoxide in high yield, by the NHPI/AIBN system. Acenaphthene-9-hydroperoxide is the main oxidation product, but as shown in Fig. 6 the change in the concentration of hydroperoxide does not follow the curve of the absorption of O_2 . The yield of hydroperoxide decreases with time. NHPI does not accelerate the hydroperoxide decomposition reaction [15], but it is found that the oxidation of acenaphthene for 5 h leads to the formation of a mixture of acenaphthenone, acenaphthenole, acenaphthene quinone, and acenaphthene-9hydroperoxide. The products were separated by TLC.



Figure 6 Concentration profiles for hydroperoxide and O_2 observed during the oxidation of AcNph (0.1 M) in the presence of NHPI (5 × 10⁻³ M) and AIBN (2.5 × 10⁻³ M) in chlorobenzene (2 mL) at 75°C and 1 atm.

FORMATION OF PINO

The formation of the PINO radicals in oxidation processes of organic substrates catalyzed by NHPI has been described [16,17]. PINO can be generated by treating NHPI with inorganic [15,18-20], organic, and organometallic [21-23] oxidants. Usually, on a preparative scale, PINO is generated from a precursor NHPI by the oxidation with $Pb(OAc)_4$ in the acetic acid solution [24]. It should be noted that lead tetraacetate has a strong influence on the NHPI reactivity and induces two different channels for the reaction pathway, radical and nonradical reactions [25]. As an experimental alternative to use of Pb((OAc)₄ for the oxidation of NHPI to PINO, iodobenzenediacetate ((PhI(OAc)₂) was studied. We report here the generation of PINO from its precursor NHPI by the oxidation with PhI(OAc)₂ in the acetonitrile solution and show an electron spectrum with maximum absorbance at 382 nm. The UVvis spectra of the solution of NHPI and PhI(OAc)₂ in acetonitrile are shown in Fig. 7.

The absorption spectrum of 7.15×10^{-3} M solution of NHPI in acetonitrile is presented in Fig. 7



Figure 7 UV–vis spectrum of NHPI $(7.15 \times 10^{-3} \text{ M})$ in acetonitrile in the absence of PhI(OAc)₂ (1) and in the presence of PhI(OAc)₂ (7.15 × 10⁻⁴ M) ((2), 1200 s after mixing; (3), 7200 s after mixing).

$$PINO^{\bullet} + RH \xrightarrow{k_{H}} NHPI + R^{\bullet}$$
(1)

$$NHPI + R^{\bullet} \xrightarrow{k_2} PINO^{\bullet} + RH$$
 (2)

$$PINO^{\bullet} + R^{\bullet} \xrightarrow{\kappa_3} PINOR$$
(3)

Scheme 1 The mechanism of H-abstraction from molecule of substrate by PINO.

(trace 1). Following the addition of 7.15×10^{-4} M of PhI(OAc)₂ in acetonitrile at 25°C, a new and broad absorption band in the 360–460 nm develops (trace 2), having λ_{max} at 382 nm and $\varepsilon = 1360$ M⁻¹ cm⁻¹. The λ_{382} absorption decreases according to an exponential first-order curve ($k_d = 1.3 \times 10^{-3} \text{ s}^{-1}$ in acetonitrile at 25°C). The same value of k_d we obtained by generating PINO by Pb(OAc)₄ in acetic acid at 25°C [26]. The mechanism of the spontaneous decay of PINO is unknown. Espenson et al. [27] and Masui et al. [28] have confirmed the second-order self-decay of PINO in both acetonitrile and acetic acid. This different observed behavior may be due to different conditions of experiments: concentrations of PINO and methods of generation of radicals.

RATE CONSTANT OF H-ABSTRACTION AT 25°C

The reaction of PINO in the hydrocarbon medium (RH) under inert atmosphere can be described by the following Eqs. (1)-(3) (Scheme 1) [29]–[32].

The contribution from each step to the kinetics of the process can depend on the structure of R^{\bullet} . It was necessary to study the effect of each step on the kinetics of PINO consumption under our experimental conditions.

The kinetics of the reaction of the PINO with a series of alkylarenes with primary, secondary, and tertiary benzyl C–H bonds (toluene, ethylbenzene, acenaphthene, and cumene) was studied, and the reaction rate constants were determined. The scheme of the process was examined, and the applicability boundaries of the simplification during the analysis were shown.

Kinetic studies described above were carried out in chlorobenzene, because a catalytic oxidation based on NHPI in apolar solvents is expected to be more effective [33]. However, owing to the low solubility of acenaphthene in chlorobenzene, the rate of hydrogen abstraction from the acenaphthene was investigated in acetonitrile in the presence of an excess of substrate.

PINO was generated in a 3-mL spectrophotometric quartz cuvette by quickly mixing NHPI (7.15 × 10^{-3} M) with PhI(OAc)₂ (7.15 × 10^{-4} M) in acetonitrile at 25°C under an argon atmosphere, and their UV– vis absorption spectra were recorded at $\lambda_{max} = 382$ nm.



Figure 8 Decomposition of PINO generated from $[NHPI] = 7.15 \times 10^{-3}$ M in the absence (1) and in the presence (2) of different amounts of AcNph in acetonitrile at 25°C. Readings were at 382 nm.

At reaction time, the increase in the peak intensity was observed. This result indicates the formation of PINO radicals. Fast addition of a solution of acenaphthene into the PINO solution, at an initial substrate concentration 8–15 times higher than that of PINO, marked the beginning of the kinetic experiment. The concentrations of alkylarenes were selected in such a way that the half-life of PINO would be 10–60 s. Preliminary experiments showed that PINO was slowly consumed in a pure solvent. The half-life of PINO would be 760 s at 25°C. The consumption of PINO strongly accelerated in the presence of acenaphthene, following clean pseudo–first-order kinetics in the presence of an excess of substrate (Fig. 8).

The decay traces are nicely described in Eq. (4) (Fig. 9), where *A* is the absorbance, k_d is the first-order-rate constant for spontaneous decay, and k_H is the second-order-rate constant for hydrogen abstraction from RH:

$$\ln \frac{(A_t - A_{\infty})}{(A_o - A_{\infty})} = -(k_{\rm d} + 2k_{\rm H} \, [\rm RH])t \tag{4}$$

The factor 2 before $k_{\rm H}$ indicates that PINO takes part in two reactions: The PINO radical abstracts a hydrogen atom from a C–H bond of hydrocarbon (RH); this step is followed by a radical recombination reaction of the carbon-centered radical (R[•]) with the PINO radical to form a radical adduct PINO-R.

In the O₂ atmosphere, alkyl radicals (\mathbb{R}^{\bullet}) are captured by oxygen to form ROO[•] radicals. In this case, the chain termination step is the self-reaction of the peroxyl radical, because there are no likely termination channels for PINO radicals at high enough [O₂] to capture \mathbb{R}^{\bullet} radicals. PINO radicals also do not terminate with peroxyl radicals [34]. Therefore, the factor before $k_{\rm H}$ in Eq. (4) must be 1 if the reaction is carried out in the O₂ atmosphere.



Figure 9 Logarithmic anamorphoses of the kinetic curves of PINO consumption in the reactions with acenaphtene (1), ethylbenzene (2), toluene (3), and cumene (4) at 25° C.



Figure 10 Pseudo–first-order rate constants of the Habstraction from AcNph by PINO at various concentrations of AcNph. The slope of the plot gives the $k_{\rm H}$ value.

The experimentally determined values of the pseudo–first-order rate constant $k_{obs} = k_d + 2k_H$ for the decay of the PINO radical are plotted in Fig. 10 as a function of the acenaphthene concentration, and the second-order rate constants (k_H) for the reactions of PINO with acenaphthene were obtained from the slopes of these plots. The initial concentrations of RH was (2.0–3.7) × 10⁻³ M.

The simulation using differential equations was chosen to analyze Scheme 1. To apply successfully this method, one has to estimate the boundaries of probable variation of the rate constant values for each of the steps and to choose a reliable method of integration of the resulting system of differential equations.

The data on the k_2 values are obtained at 294–298 K ($k_2 \sim 10^3-10^4$ L mol⁻¹ s⁻¹) [29,30]. The k_3 values change from 10^7 to 10^9 L mol⁻¹ s⁻¹ [35–37]. The $k_{\rm H}$ values change from 10^{-4} to 10^3 L mol⁻¹ s⁻¹ [17]. Thus, a probable interval of variation of the rate constants of reactions (1)–(3), considering the obtained estimates and measured observed rate constants of PINO consumption, is $10^{-4}-10^9$ L mol⁻¹ s⁻¹, and the system of differential equations corresponding to reactions (1)–(3) is stiff. We chose the Gear method for numerical integration of such systems. We compared the results of calculations obtained by this method for an ideal case (when the reaction of PINO with RH is described only by Eq. (1)) and for the general case (Eqs. (1)–(3)) to determine the error, which is the result of reaction (2).

It was found out that the error depends on values of k_2 , k_3 , [NHPI]_o, and [PINO]_o, but the error is independent of product $k_{\rm H}$ ·[RH]. The complete coincidence of the results of numerical integration and calculation by algebraic equations was obtained for Scheme 1 (see reactions (1)–(3)) with integral equations).

If [RH] = constant and $[NHPI]_0 = \text{constant} (k_H [RH] = k_{He} \text{ and } k_2[NHPI]_0 = k_{2e})$, Scheme 1 is simplified (as shown below):

$$\operatorname{PINO}^{\bullet} \xrightarrow{\kappa_{\operatorname{He}}} \mathbb{R}^{\bullet} \tag{5}$$

$$\mathbf{R}^{\bullet} \stackrel{\kappa_{2e}}{\longrightarrow} \mathbf{PINO}^{\bullet} \tag{6}$$

$$PINO^{\bullet} + R^{\bullet} \xrightarrow{k_3} PINOR$$
 (7)

$$\frac{\mathrm{d}[\mathrm{PINO}^{\bullet}]}{\frac{\mathrm{d}t}{\frac{\mathrm{d}[\mathrm{R}^{\bullet}]}{\frac{\mathrm{d}}t}}} = -k_{\mathrm{He}}[\mathrm{PINO}^{\bullet}] - k_{3}[\mathrm{PINO}^{\bullet}][\mathrm{R}^{\bullet}] + k_{2e}[\mathrm{R}^{\bullet}]$$

If in our system, the steady-state condition $[\mathbb{R}^{\bullet}]/dt = 0$ is fulfilled, then

$$[\mathbf{R}^{\bullet}] = \frac{k_{\mathrm{He}}[\mathrm{PINO}^{\bullet}]}{k_{3}[\mathrm{PINO}^{\bullet}] + k_{2e}}$$

Taking into account the latter one, we can obtain the next equation:

$$\frac{d[\text{PINO}^{\bullet}]}{dt} = -k_{\text{He}}[\text{PINO}^{\bullet}] - k_{3}[\text{PINO}^{\bullet}]$$
$$\times \frac{k_{\text{He}}[\text{PINO}^{\bullet}]}{k_{3}[\text{PINO}^{\bullet}] + k_{2e}}$$
$$+ k_{2e} \frac{k_{\text{He}}[\text{PINO}^{\bullet}]}{k_{3}[\text{PINO}^{\bullet}] + k_{2e}}$$

The solving of the latter equation gives the next equation:

$$\ln \frac{[\text{PINO}^{\bullet}]}{[\text{PINO}^{\bullet}]_{o}} - \frac{k_{2}[\text{NHPI}]_{o}}{k_{3}} \left(\frac{1}{[\text{PINO}^{\bullet}]} - \frac{1}{[\text{PINO}^{\bullet}]_{o}}\right)$$
$$= -2k_{\text{H}}[\text{RH}]t \tag{8}$$

The second term of Eq. (8) is related to the contribution of steps (2) and (3) of Scheme 1 and might lead



Figure 11 The regions of 5% error in coordinates [PINO]₀ – [NHPI]₀ at different values of k_2/k_3 .

to an error when determining $k_{\rm H}$, the first-order kinetic equation is used. In the ideal case, Eq. (8) is simplified:

$$\ln \frac{[\text{PINO}^{\bullet}]}{[\text{PINO}^{\bullet}]_{o}} = -2k_{\text{H}}^{\text{id}}[\text{RH}]t \tag{9}$$

Thus, the error of experimental determination of $k_{\rm H}$ is described by the following equation:

$$\text{Error} = \left| \frac{k_{\text{H}}^{\text{id}} - k_{\text{H}}}{k_{\text{H}}^{\text{id}}} \right|$$

Taking into account Eqs. (8) and (9), one can obtain the equation for the error:

$$\operatorname{Error} = \frac{k_2[\operatorname{NHPI}]_{o}}{k_3} \cdot \frac{\left(\frac{1}{[\operatorname{PINO}^{\bullet}]} - \frac{1}{[\operatorname{PINO}^{\bullet}]_{o}}\right)}{\ln\frac{[\operatorname{PINO}^{\bullet}]_{o}}{[\operatorname{PINO}^{\bullet}]_{o}}}$$
(10)

The calculations were conducted taking into account that [PINO[•]] = $0.5 \cdot [PINO^{•}]_{o}$. Conditions for the 5% experimental error were obtained by the variation of the values of the ratio k_2/k_3 , [NHPI]_o, and [PINO]_o.

In Fig. 11, a line in the coordinate $([NHPI]_o/[PINO]_o)$ at different values of (k_2/k_3) represents the border of the area with 5% error. The area above the line is the area in which the error is $\leq 5\%$ and the area under the line is the area of $\geq 5\%$ error.

ACTIVATION PARAMETERS

Rate constants of H-abstraction from a molecule of acenaphthene have been measured at various temperatures (in the 10–25°C range). Each second-order $k_{\rm H}$ value is derived from averaging of five pseudo–firstorder rate constants, determined at different initial concentrations of the substrate. The initial concentration of PINO was 2.5×10^{-4} M and that of acenaphthene

1	L.
<i>T</i> (K)	$k_{\rm H} ({ m M}^{-1} { m s}^{-1})$
283	4.6 ± 0.1
288	5.4 ± 0.1
293	6.6 ± 0.1
298	7.7 ± 0.1

Table IRate Constants $k_{\rm H}$ of H-abstraction fromAcNph by PINO in Acetonitrile at Different Temperatures

ranged between 2×10^{-3} M and 3.7×10^{-3} M. From the Arrhenius equation (ln $k_{\rm H} = \ln A - E_{\rm a}/RT$), ln A and $E_{\rm a}$ parameters were obtained.

The $k_{\rm H}$ values for all temperatures are reported in Table I.

Analysis of the data of Table I provides the $E_a = 24.4 \pm 0.2$ kJ/mol and $A = (1.47 \pm 0.05) \times 10^5$ M⁻¹ s⁻¹. It is not easy to explain low pre-exponential factor for the reaction of PINO with AcNph, and we do not have the necessary data to explain this problem. As to our point of view, the most likely cause may be a specific interaction (hydrogen bond or others) of the substrate molecules and the radical with the medium that prevents reaching the required structure (geometry) of the transition state.

strates and obtained large values of KIE. They proposed that quantum mechanical tunneling takes part in the PINO radical reactions.

The value $W_{\rm H}/W_{\rm D}$ for the oxidation of acenaphthene was measured by performing an experiment with 0.1 M AcNph- d_4 , 2.5 × 10⁻³ M AIBN, and 5 × 10⁻³ M NHPI. The value $W_{\rm H}/W_{\rm D}$ = 2.2 indicates that the catalytic cycle also involves hydrogen abstraction in the propagation reaction (ROO• + RH).

REACTION MECHANISM

The liquid-phase oxidation of acenaphthene proceeds according to a widely known free radical chain mechanism, and it is a typical example of consecutive reaction. Amorati et al. have carried out an in-depth research on the catalytic mechanism of NHPI [33]. On the basis of our experimental observations and published literature data, the following reaction scheme, for the oxidation process of acenaphthene with dioxygen catalyzed by NHPI, has been suggested. The scheme shows the oxidation reactions of acenaphthene to its hydroperoxide on the radical pathway. The initial stage is being the formation of the PINO radicals in the reaction of NHPI with initiator radicals:



KINETIC ISOTOPE EFFECT

The kinetic isotope effect (KIE) was calculated from the ratio of the $k_{\rm H}$ and $k_{\rm D}$ rate constants of the reaction of acenaphthene and AcNph- d_4 with PINO. The The highly reactive PINO radicals can abstract the hydrogen atom from the acenaphthene to produce the carbon-centered radicals of acenaphthene and regenerate the NHPI:



reactions of the PINO radical with acenaphthene show KIEs $(k_{\rm H}/k_{\rm D})$ of 11.7 in acetonitrile at 25°C, which accounts for a hydrogen atom abstraction mechanism. Koshino et al. [27] measured the KIE for various sub-

The alkyl radicals react with oxygen to form the important peroxyl radical (ROO[•]), which can abstract hydrogen from the molecule of acenaphthene to form the alkyl radical and hydroperoxide:



The peroxyl radical can also abstract a hydrogen atom from the NHPI:



The chain termination step is the self-reaction of the peroxyl radical. Secondary peroxyl radicals react in a nonradical way, leading to the formation of equal yields of alcohol and ketone [38]. PINO radicals do not terminate with each other or with peroxyl radicals [34]: Amorati et al. report, experimentally, that $d[O_2]/dt$ changes linearly with the low concentration of NHPI, with the square root of the initiator concentration, and the rate of catalyzed oxidation does not significantly depend on the cumene concentration [33]. Such



Secondary alkylbenzenes cannot be selectively converted to their corresponding alcohols or ketones because the products posses higher reactivity than the starting hydrocarbons. Acenaphthene quinone can form consequently of deep product oxidation, for example,

dependences were observed in acenaphthene oxidation in the presence of NHPI. All these observations can be described on the basis of the Ishii [1] mechanism.

$$\begin{array}{c} & & & \\ &$$

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Table II Results of Oxidation of AcNph by O_2 in the Presence of NHPI at 75°C and 1 atm in Chlorobenzene

$\overline{W_{\rm i} \times 10^7 ({\rm M}{ m s}^{-1})}$	2.71 ± 0.11
$k_{\rm p}/\sqrt{k_{\rm t}}$	0.012 ± 0.001
$k_{\rm f}/\sqrt{k_{\rm t}}$	5 ± 0.2
$k'_{\rm H} \ ({ m M}^{-1} \ { m s}^{-1})$	7.7 ± 0.1

According to the proposed kinetic model [33], the rate of oxidation described by Eq. (20) is

$$- d[O_2]/dt = k_p \cdot (W_i/2k_t)^{1/2} \cdot [RH] + k_f \cdot (W_i/2k_t)^{1/2} \cdot [R_2NOH].$$
(20)

where k_p is the propagation rate constant, k_t is the rate constant of termination of the peroxyl radicals, W_i is the rate of initiation, and k_f is the rate constant for the hydrogen atom abstraction from NHPI by the peroxyl radical.

It is interesting to apply Eq. (20) to our kinetic data for the oxidation of acenaphthene in the presence of NHPI. On the basis of this equation, the slope of the plot reporting $-d[O_2]/dt$ against [NHPI] will provide $k_f(W_i/2k_1)^{1/2}$. The results of acenaphthene oxidation with the NHPI catalyst are listed in Table II.

The k_t value is unknown, but from Table II it can be seen that the reactivity of NHPI with the peroxyl radical (k_f) is larger than that of acenaphthene (k_p).

CONCLUSIONS

We have developed metal-free acenaphthene oxidation catalyzed by NHPI. The developed catalytic system allows obtaining the desired hydroperoxide in high yield by the oxidation of the acenaphthene. We also suggested a possible mechanism of this catalytic method, which undergoes a radical process. Kinetic studies carried out to investigate the catalytic behavior of NHPI on the oxidation of acenaphthene are consistent with a simple kinetic model.

The H-abstraction rate constant and KIE for the reaction of PINO with acenaphthene are determined. The value of KIE is 11.7. This finding further supports that quantum mechanical tunneling plays a role in the hydrogen abstraction of the PINO radicals. The activation parameters are determined for this reaction.

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