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Electronic Effect of Substituent of Quinones on their Catalytic Performance in Hydrocarbons Oxidation

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Abstract Quinones with electron-withdrawing F, Cl or Br groups and *N*-hydroxyphthalimide (NHPI) were used as catalysts in selective oxidation of hydrocarbons with molecular oxygen as oxidant. The catalytic activity in the selective oxidation of ethylbenzene to oxygenation products was in the following order: *p*-benzoquinone < tetrafluoro-*p*-benzoquinone ≈ tetrachloro-*p*-benzoquinone < tetrabromo-*p*-benzoquinone (*p*-TBBQ). Moderate electron-withdrawing power of substituent was suitable for quinone abstracting hydrogen from NHPI to generate reactive phthalimido-*N*-oxyl (PINO). The catalytic activity of *p*-TBBQ/NHPI, the best catalyst in our study, was also tested in the selective oxidation of alkylarenes, alkenes and alkanes.

Keywords Quinones · Substituent effects · Hydrocarbons · Oxidation · *N*-hydroxyphthalimide

1 Introduction

Quinones are ubiquitous in nature [1]. This kind of compounds, such as coenzyme Q10 [2], tryptophan tryptophylquinone in bacterial dehydrogenase, and 2,4,5-trihydroxyphenylalanine quinone in the copper amine oxidases [3], are a common type of cofactors found in enzymes and redox proteins [4]. They are apt to form various odd-electron intermediates in different types of biochemical redox processes. It is known that the substituents of quinones play a major role in modulating the kinetics of the electron- and proton-transfer reactions associating with the redox chemistry and the electronic properties of quinones [5]. Halogen substituents can enhance the half-wave reduction potential of quinones and thus increase their ability of abstracting hydrogen atom [6]. Therefore, the study of the catalytic performance of quinones with different substituents is necessary.

Ishii and coworkers developed an efficient catalytic system composing of *N*-hydroxyphthalimide (NHPI) and metal mediators (cobalt, manganese, etc.), which exhibited excellent catalytic activity in oxidation processes [7]. Since then, a number of catalysis systems containing NHPI and various mediators have been developed in the oxidation of different kinds of organic compounds [8]. In the past decades, many researchers put their interest in metal-free catalysis systems to avoid the toxicity of the metals [9]. We have reported a metal-free catalysis system combining anthraquinone with NHPI for the oxygenation of hydrocarbons, which gives good activity and selectivity in the oxidation of various hydrocarbons such as ethylbenzene, cyclohexane, and toluene [10, 11]. In these systems, reactive phthalimido-*N*-oxyl (PINO) was formed in situ via quinone abstracting a hydrogen atom from NHPI, and at the same time, quinone was reduced to semiquinone radical (QH). QH was abstracted H atom to return quinone by other radicals such as alkyl peroxide radical. PINO radical is highly electrophilic species and can efficiently promote hydrocarbon oxyfunctionalization with O_2. Scheme 1 shows the mechanism of the oxidation reaction of hydrocarbon catalyzed by *p*-benzoquinone/NHPI [11].

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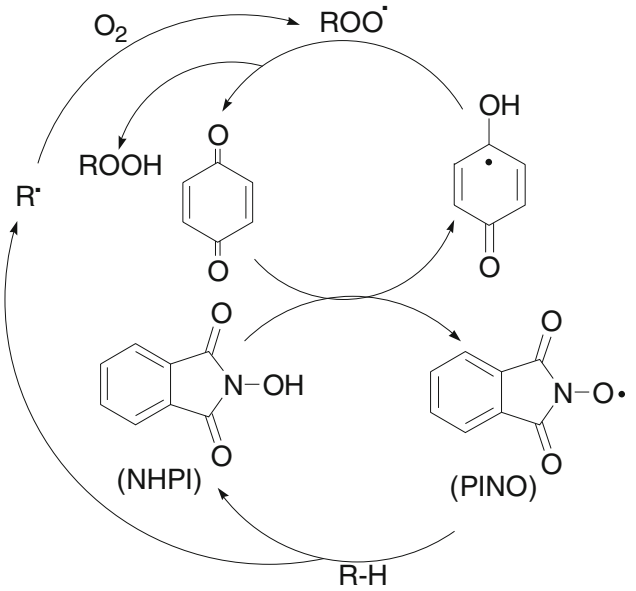


Scheme 1 The mechanism of hydrocarbon oxidation catalyzed by *p*-benzoquinone/NHPI

In this paper, we studied the electronic effect of different halogen substituents on the quinones' catalytic properties. Quinones combined with NHPI were used as catalysts in the oxidation of hydrocarbons with molecular oxygen as oxidant.

2 Experimental

2.1 Materials

The compounds tetrafluoro-*p*-benzoquinone (*p*-TFBQ, 95%), tetrachloro-*p*-benzoquinone (*p*-TCBQ, 97%), and tetrabromo-*p*-benzoquinone (*p*-TBBQ, 95%) were purchased from Alfa Aesar (Fig. 1). *p*-Benzoquinone (*p*-BQ, A.R.) was purified by vacuum sublimation prior to use. Ethylbenzene (99.5%), cyclohexane (99.5%), and acetonitrile (99.5%) were of analytic grade. Cyclohexene (98%) and tetralin were of chemical grade. Fluorene was industrial grade and was purified by recrystallization from ethanol. All the other chemicals were of analytic grade without any purification.

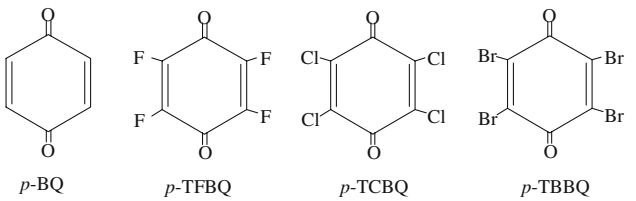


Fig. 1 The structures of quinones

2.2 Catalytic Studies

Catalytic reactions were performed in an 80 mL autoclave reactor. Typically, 2 mL (16 mmol) ethylbenzene, 10 mL CH_3CN, desired amount of quinone and NHPI were added into the reactor. After sealing the reactor, the atmosphere over the mixture was replaced with O_2 for three times. The reactor was heated to the desired temperature with agitation by means of a magnetic stirrer. Then, the reactor was charged with 0.3 MPa of O_2, and the pressure was kept constant during the reaction by feeding O_2. When the reaction was finished, the reactor was cooled to the ambient temperature.

The reaction products were identified by comparison with authentic products and GC-MS. For ethylbenzene oxidation, acetophenone (AcPO), 1-phenylethanol (PEA) and benzoic acid (BA) were determined using toluene as the internal standard. The yield of 1-phenylethyl hydroperoxide (PEHP) could not be directly measured by gas chromatography (GC) because of the decomposition of PEHP to AcPO in GC analysis [12]. In addition, PEHP can be converted quantitatively to PEA with excessive Ph_3P at room temperature, thus PEHP can be quantified via measuring the change of PEA. For the oxidation mixture of cyclohexane, the quantitative analyses of cyclohexanol and cyclohexanone were carried out by GC using toluene as the internal standard, and the cyclohexyl hydroperoxide was calculated by the methods described by Shul'pin [13]. For all the other hydrocarbons oxidation, the conversion and selectivity were calculated by GC area normalization.

3 Results and Discussion

3.1 Catalytic Activity of Substituted Benzoquinone in Ethylbenzene Oxygenation

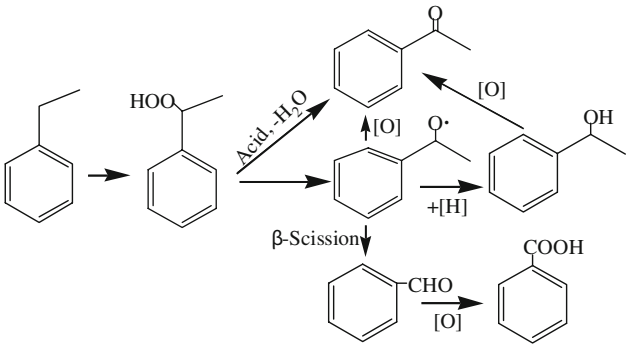
First, the catalytic properties of quinones were investigated in the selective oxidation of ethylbenzene using quinone and NHPI as catalyst. The main products were AcPO, PEA, PEHP and BA. Table 1 gives the reaction results. When NHPI was used alone, 23.2% conversion of ethylbenzene was obtained with 54.8, 12.0 and 33.2% selectivity to AcPO, PEA and PEHP, respectively. The results were in accordance with the previous literature [14]. Among H-, F-, Cl-, and Br-substituted benzoquinone, which combined with NHPI as catalyst system, the conversion of ethylbenzene varied in the following order: H- $<$ F- $\approx$ Cl- $<$ Br-. The conversion of ethylbenzene and products distribution were almost same when benzoquinone/NHPI was used as catalyst compared with that of NHPI alone (Table 1, entry 2). The lower performance of benzoquinone/NHPI suggested that benzoquinone could not accelerate the

Table 1 Oxidation of ethylbenzene with different catalysts

Entry[a]	Catalyst	Conversion (%)	Selectivity (%)			
			AcPO	PEA	PEHP	BA
1	NHPI	23.2	54.8	12.0	33.2	0
2	*p*-BQ/NHPI	23.7	49.0	16.9	34.1	0
3	*p*-TFBQ/NHPI	35.7	51.6	16.7	31.7	0
4	*p*-TCBQ/NHPI	31.9	74.7	16.6	2.3	6.4
5	*p*-TBBQ/NHPI	49.6	80.7	13.6	0.4	5.2

[a] Reaction conditions: 16 mmol ethylbenzene, 1.5 mol% quinone, 10 mol% NHPI, 10 mL CH_3CN, 0.3 MPa O_2, 80 °C, 6 h

generation of PINO from NHPI. This might be caused by the lower redox potential of benzoquinone [6], which results in the difficulty of hydrogen atom transfer from NHPI to benzoquinone. From Table 1, it can be seen that quinone can effectively accelerate the oxidation of ethylbenzene by introducing of electron-withdrawing group F-, Cl-, or Br-. Using benzoquinone substituted by F- or Cl- combined with NHPI as catalyst system, the conversion of ethylbenzene was similar, which was of 35.7 and 31.9%, respectively. *p*-TBBQ/NHPI showed the highest activity with ethylbenzene conversion of 49.6% (Table 1, entry 5). However, the potential of *p*-TBBQ is the lowest among F-, Cl-, and Br-substituted benzoquinone. The above results revealed that there were some other factors influencing the reaction besides the redox potential of quinone. The process of electron transfer between *p*-BQ and NHPI should be a proton-coupled electron transfer (PCET) process because the energy of the transition structure of PCET is lower than that of the conventional radical hydrogen atom abstraction mechanism [15–17]. In this pathway, NHPI interacted with quinone to give a hydrogen-bond complex, and then electron proton transfer occurred. An electron and a proton transferred from NHPI to quinone while PINO and semiquinone radicals were formed. The stability of the hydrogen-bond complex between NHPI and quinone will affect the proton-coupled electron transfer, and further influence the catalytic properties of the combined NHPI and quinone catalyst system. It has been reported by Andrews et al. that quinone can coordinate with donors to form a stable bimolecular or trimolecular complexes [18]. Therefore, the electron-withdrawing substituents on quinone stabilize not only the semiquinone radical but also the hydrogen-bond complex in view of the electronic effect. The different electron-withdrawing power of F, Cl and Br probably changed the relative stability of the hydrogen-bond complex and the semiquinone radical. Because F or Cl has the strong electron-withdrawing power, the stability of the hydrogen-bond complex of *p*-TFBQ or *p*-TCBQ with NHPI is high and thus the formation of PINO is retarded. Although the potential of *p*-TBBQ was lower than *p*-TFBQ and *p*-TCBQ, the



Scheme 2 The reaction pathway of catalytic oxidation of ethylbenzene

electron-withdrawing power of Br was the best suitable for the PCET process, and thus *p*-TBBQ/NHPI catalyst system exhibited the highest activity. From above results, it can be concluded that moderate electron-withdrawing power of substitutes for quinone was suitable for hydrogen atom transfer reaction.

Scheme 2 shows the pathway of oxidation of ethylbenzene. PEHP was the initial product that can decompose to AcPO in the reaction process [10]. As shown in Table 1, the selectivity of PEHP varied in the following order: *p*-BQ > *p*-TFBQ > *p*-TCBQ > *p*-TBBQ. The selectivity of PEHP was only 0.4% with *p*-TBBQ/NHPI as catalyst. In addition, the selectivity of AcPO increased in the order of *p*-BQ < *p*-TFBQ < *p*-TCBQ < *p*-TBBQ. The positive correlation between the selectivity of PEHP and AcPO clearly shows that quinone could accelerate the decomposition of PEHP to AcPO. It has been reported that the acidity of catalyst plays an important role for dehydration of peroxide to ketone [10, 19]. The electron-withdrawing substituents render the electron density of quinone deficient, which increases Lewis acidity of quinone. Though the acid strength of *p*-TFBQ was the highest, it formed more stable complex with NHPI as discussed above. Therefore, the selectivity of AcPO was lower with *p*-TFBQ/NHPI than those with *p*-TCBQ/NHPI and *p*-TBBQ/NHPI, respectively. Meanwhile, the homolytic cleavage of O-O bond of PEHP could occur in the process of reaction [20]. PEA was formed through RO abstracting a H atom from NHPI, QH or alkane [10]. On the other hand, BA can be obtained through the further oxidation of benzaldehyde which was formed via the *β*-scission of RO.

3.2 Influence of Reaction Conditions on the Oxidation of Ethylbenzene Catalyzed by *p*-TBBQ/NHPI System

Since *p*-TBBQ/NHPI presented the best catalytic performance in the oxidation of ethylbenzene, we chose this catalyst for the more detailed study. First, we investigated

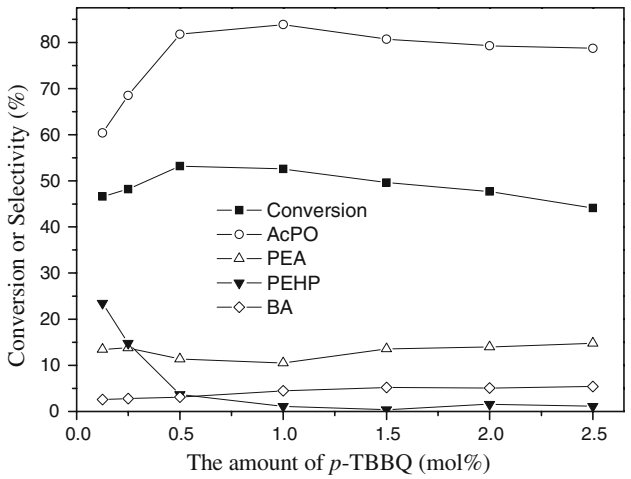


Fig. 2 Results of ethylbenzene oxygenation catalyzed by *p*-TBBQ/NHPI system with different feed amount of *p*-TBBQ. Reaction conditions: 16 mmol ethylbenzene, 10 mol% NHPI, 10 mL CH_3CN, 0.3 MPa O_2, 80 °C, 6 h

the effect of the ratio between the *p*-TBBQ and ethylbenzene on the oxidation reaction. The results are given in Fig. 2. When the *p*-TBBQ amount was as low as 0.125 mol%, the *p*-TBBQ/NHPI system yet catalyzed the oxidation of ethylbenzene efficiently, and the conversion of ethylbenzene was 46.6%. The conversion increased with the increasing of the *p*-TBBQ amount and reached its maximum 53.2% at 0.5 mol% *p*-TBBQ. But if the *p*-TBBQ amount exceeded 0.5 mol%, the activity decreased gradually. The characters of quinone may cause the inhibition of the superfluous *p*-TBBQ for the oxygenation of ethylbenzene. As mentioned above, quinone can abstract a hydrogen atom from NHPI and accelerate the generation of the free radical PINO. On the other hand, quinone was also a radical scavenger [21] and inhibited the reaction. Therefore, a proper amount of quinone can accelerate the reaction, but excessive quinones probably scavenge free radicals and inhibit the free radical chain process.

Second, the temperature dependence of ethylbenzene oxidation, employing *p*-TBBQ/NHPI as the catalyst, is displayed in Table 2. Ethylbenzene was obviously oxidized at 60 °C and the conversion was 20.2%. When the temperature was increased to 70 °C, the conversion of ethylbenzene was significantly improved to 46.3%. The conversion of ethylbenzene was further increased to 53.2% at 80 °C, but the over-oxidation product BA began to appear. Moreover, the amount of BA increased remarkably once the reaction temperature was higher than 90 °C. The results show that the temperature is another key factor for the decomposition of PEHP to AcPO or BA. Therefore, the appropriate temperature for ethylbenzene oxygenation catalyzed by *p*-TBBQ/NHPI system should be 80–90 °C.

Table 2 Temperature dependence of ethylbenzene oxygenation catalyzed by *p*-TBBQ/NHPI system

Entry[a]	Temperature	Conversion (%)	Selectivity (%)			
			AcPO	PEA	PEHP	BA
1	60	20.2	24.1	15.7	60.2	0
2	70	46.3	61.4	14.7	24.0	0
3	80	53.2	81.8	11.4	3.7	3.1
4	90	59.4	80.5	8.8	5.2	5.5
5	100	66.3	80.8	6.0	3.9	9.3

[a] Reaction conditions: 16 mmol ethylbenzene, 0.5 mol% *p*-TBBQ, 10 mol% NHPI, 10 mL CH_3CN, 0.3 MPa O_2, 6 h

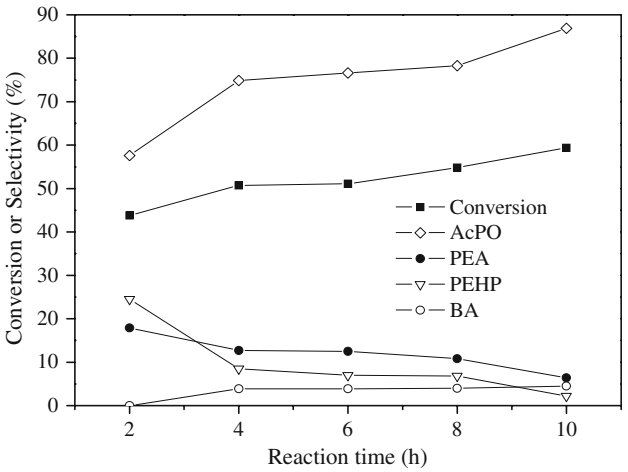


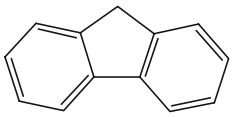
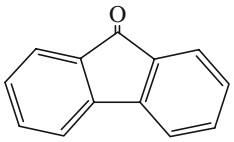
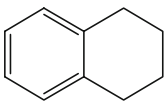
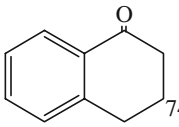
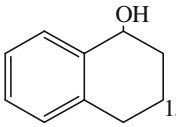
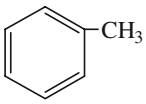
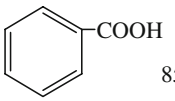
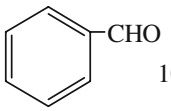
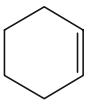
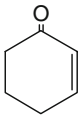
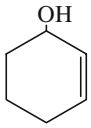
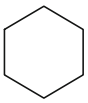
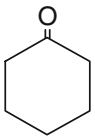
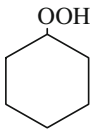
Fig. 3 Effect of the reaction time on the oxygenation of ethylbenzene catalyzed by *p*-TBBQ/NHPI system. Reaction conditions: 16 mmol ethylbenzene, 0.5 mol% *p*-TBBQ, 10 mol% NHPI, 10 mL CH_3CN, 0.3 MPa O_2, 80 °C

Third, the influence of the reaction time on the oxygenation of ethylbenzene catalyzed by *p*-TBBQ/NHPI system at 80 °C is illustrated in Fig. 3. The conversion of ethylbenzene and the selectivity of AcPO were both increased with the increase of the reaction time, whereas the selectivity of both PEA and PEHP were decreased. The results also prove that PEHP was the initial product and PEHP and PEA could be further converted to AcPO. At the reaction time of 10 h, 59.4% conversion of ethylbenzene with 86.9% selectivity to AcPO was obtained.

3.3 Oxidation of Various Hydrocarbons Catalyzed by *p*-TBBQ/NHPI

After having established the best conditions for the oxidation of ethylbenzene, we focused our attention on the substrate scope. The results of oxidation of various hydrocarbons catalyzed by *p*-TBBQ/NHPI are presented in Table 3. Fluorene was oxygenated to fluorenone with a good selectivity (96.9%), although the conversion was only moderate

Table 3 Oxidation of various hydrocarbons catalyzed by *p*-TBBQ/NHPI[a]

Entry	Substrate	Time (h)	Conversion (%)	Selectivity (%)	
1		6	49.0		96.6
		10	61.1		97.8
2		5	83.1	 74.1	 15.2
3[b]		10	26.6	 85.2	 10.5
4		5	85.6	 64.4	 8.4
5		4	12.6	 6.2	 32.8

[a] Reaction conditions: 2 mL of liquid substrates or 2 mmol of solid substrate in 10 mL CH_3CN, 1.5 mol% *p*-TBBQ, 10 mol% NHPI, 0.3 MPa O_2, 80 °C

[b] *p*-TCBQ instead of *p*-TBBQ was used

(49.0%). When the reaction time lasted to 10 h, the conversion increased to 61.1% with 97.8% selectivity of fluorenone. At 80 °C for 5 h, 83.1% of tetralin was converted to 1-tetralone and 1-tetralol with 74.1 and 15.2% selectivity, respectively. The main product of cyclohexene oxygenation was 2-cyclohexen-1-one. 85.6% of cyclohexene was converted with 64.4% selectivity to 2-cyclohexen-1-one at 80 °C for 6 h. More challenging selective oxidation of fully saturated cyclohexane was also attempted. 12.6% conversion of cyclohexane with cyclohexanone and cyclohexyl hydroperoxide as main products was obtained. Benzoic acid was an important intermediate for synthesizing ε-caprolactamin in Snia-Viscosa process [22] and fine chemicals. By using *p*-TCBQ/NHPI as catalyst, 26.6% conversion of toluene with 85.2% selectivity to benzoic acid was obtained.

4 Conclusions

In conclusion, the introduction of F, Cl or Br into benzoquinone increased its redox potential. In the selective oxidation of ethylbenzene catalyzed by quinone and NHPI, the conversion of ethylbenzene varied in the order of H- < F- ≈ Cl- < Br-. The moderate electron-withdrawing power of the substituent was the most suitable for hydrogen atom transfer reaction, and thus promoted the oxidation of ethylbenzene. Additionally, a proper amount of quinone could accelerate the reaction, but excessive quinone probably scavenged free radicals and inhibited the reaction. *p*-TBBQ/NHPI can also effectively catalyze the oxidation of alkylarenes, alkenes and alkanes.

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