Organocatalytic Oxidative Dehydrogenation of Dihydroarenes by Dioxygen Using 2,3-Dichloro-5,6-dicyano-benzoquinone (DDQ) and NaNO₂

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Abstract: The oxidative dehydrogenation of dihydroarenes catalyzed by 2,3-dichloro-5,6-dicyano-benzoquinone (DDQ) and NaNO₂ with dioxygen is reported. The combination of DDQ and NaNO₂ showed high efficiency and high selectivity, compared with other benzoquinones and anthraquinones, e.g., >99% conversion of 9,10-dihydroanthracene with 99% selectivity for anthracene can be obtained at 120 °C under 1.3 MPa O₂ for 8 h. Excellent results were achieved in the oxidative dehydrogenation of variety of dihydroarenes.

Keywords: Oxidative dehydrogenation; DDQ; Dioxygen; Redox couples.
Introduction

The dehydrogenation of hydrocarbons to various alkenes and aromatic olefins is an important project in modern chemical manufacture and scientific research [1, 2]. A very attractive approach is oxidative dehydrogenation. Oxidants such as dioxygen, halogens, sulfur compounds, etc., could accept hydrogen and thus the thermodynamics of the dehydrogenation process shifts to the right side. These exothermic oxidation reactions also provide necessary process heat to compensate for the endothermic dehydrogenation and thus dehydrogenation can be successfully operated under moderate conditions [3]. On the other hand, the selectivity is difficult to control in the presence of oxidants, and byproducts are thus generated. Recently, noble-metal catalysts such as Ru(OH)₃/Al₂O₃ and Ru(TMP)(O)₂ have been found to readily catalyze oxidative dehydrogenation reactions with high selectivity [4, 5], but unfortunately the need for noble metals makes such a dehydrogenation process uneconomic. There is strong incentive for developing new cheaper oxidative dehydrogenation catalysts which simultaneously employ dioxygen as oxidizing agent.

High-potential quinones such as DDQ are usually used as hydrogen acceptors in many types of reactions such as dehydrogenation of hydrocarbons and benzylic alcohols, oxidation of alcohols and allylic ethers, and direct cross-dehydrogenative-coupling reactions, etc [6-9]. Unfortunately, quinones are often used with stoichiometric amount because they are converted into quinols after accepting hydrogen and can not be recycled to the initial state. In order to solve the above problem, efforts have been made to regenerate the quinones. Several reagents such as Mn(OAc)₃, HClO₄, HIO₄, and HNO₃ showed efficiency in converting quinols to quinones [10, 11]. But in most cases these reagents were still required in stoichiometric or in excess amounts.

In a previous study at our laboratory, anthraquinones and NHPI were coupled to form an efficient organocatalytic system in the aerobic oxidation of hydrocarbons under moderate reaction conditions. The redox transformation between anthraquinones and anthraquinols can be cycled by NHPI/PINO [12-15]. Recently, we have designed a novel DDQ/NaNO₂ catalytic system for dehydrogenation of 9,10-dihydroanthracene (Scheme 1) [16]. In the present work, benzoquinones and anthraquinones combined with NaNO₂ were studied in terms of activity and selectivity. Further, the detailed operation conditions including catalyst loading, reaction time, and temperature for DDQ/NaNO₂ were optimized. Moreover, its application in the oxidative dehydrogenation of variety of dihydroarenes was investigated. At last the redox catalytic cycle was proposed. The redox couples quinone/quinol and NO₂/NO were expected to create a catalytic cycle in the presence of O₂ in the dehydrogenation. This novel organocatalytic system offers new thoughts for design of highly selective catalyst for oxidative dehydrogenation of aromatic hydrocarbons.

Scheme 1. Catalytic oxidative dehydrogenation of 9,10-dihydroanthracene to anthracene.
Results and Discussion

Comparison of different benzoquinones and anthraquinones combined with NaNO2

The effect of a variety of benzoquinones and anthraquinones (Figure 1) including BQ, TCQ, DDQ, AQ, CAQ, and TCAQ combined with NaNO2 in the oxidative dehydrogenation of 9,10-dihydroanthracene was explored (Figure 2).

Figure 1. The studied benzoquinones and anthraquinones.

BQ: benzoquinone; TCQ: 2,3,5,6-tetrachloro-1,4-benzoquinone; AQ: anthraquinone; CAQ: 2-chloroanthraquinone; TCAQ: 1,4,5,8-tetrachloroanthraquinone

Figure 2. The oxidative dehydrogenation of 9,10-dihydroanthracene with different quinones and NaNO2 a.

a Reaction conditions: 10 mL toluene, 0.5 mmol 9,10-dihydroanthracene, 0.05 mmol quinone, 0.05 mmol NaNO2, 120 °C, 1.3 MPa O2, 8 h. When using AQ/NaNO2, the amount of by-product AQ is the difference between the GC measurement value and the loading amount in AQ/NaNO2. ATC: anthracene
The results showed that both benzoquinones and anthraquinones exhibited considerable activity. It was notable that DDQ/NaNO₂ showed high catalytic efficiency. The conversion of 9,10-dihydroanthracene was >99% and selectivity to anthracene was 99%. Besides DDQ/NaNO₂, TCQ/NaNO₂ also showed good results. The selectivity to anthracene was 96% with 47% conversion. Comparably, BQ/NaNO₂ was low active but high selective. The conversion only reached 15% and the selectivity to 9,10-dihydroanthracene was >99%. Traces of AQ were detected as the sole by-product by GC-MS measurement. The activity of benzoquinones varied following the order: DDQ>TCQ>BQ. These activity results coincide with the reduction potential order of benzoquinones [17-19]. The electron-withdrawing group can increase the reduction potential and thus the dehydrogenation ability increases. In case of different anthraquinones (AQ, CAQ, and TCAQ), the results were not satisfactory, as both anthracene and considerable amounts of AQ were produced. The occurred oxidative side-reaction suggested anthraquinones have catalytic ability in catalyzing aerobic oxidation of 9,10-dihydroanthracene to AQ. On the basis of these results, it could be concluded that DDQ combined with NaNO₂ was the highest active and selective among the quinones investigated.

**Optimization of the catalyst loading amounts, reaction time, and temperature for DDQ/NaNO₂**

Performing as an excellent oxidative dehydrogenation catalyst, DDQ combined with NaNO₂ was further studied under detailed conditions. The results of oxidative dehydrogenation with different catalyst loading amount are listed in Table 1. The loading amounts of DDQ and NaNO₂ were equal and increased simultaneously from 1 mol% to 10 mol%. Obviously, the conversion is low at lower catalyst loading (1 mol%, 2 mol%, and 3 mol%), and then increased to >99% at 5 mol% and 10 mol%. So 5% DDQ and 5% NaNO₂ are selected as the optimum loading amounts. Furthermore, we examined the efficiency of air. With 5% DDQ and 5% NaNO₂, it only gave 64% conversion and >99% selectivity to anthracene under 1.3 MPa air. By increasing the catalyst loading amount to 10% DDQ and 10% NaNO₂, the conversion was increased to >99% with >99% selectivity to anthracene, similar to that under 1.3 MPa O₂. The results indicated that oxidative dehydrogenation can perform under air, but the efficiency is lower than that under O₂.

**Table 1.** Effect of catalyst loading amount on the oxidative dehydrogenation of 9,10-dihydroanthracene to anthracene

| Entry | Catalyst loading (mol%) | Conversion (%) | Products and selectivity (%) |
|-------|--------------------------|---------------|------------------------------|
|       | DDQ | NaNO₂ |                   | ATC | AQ |
| 1     | 1   | 1    | 19               | >99 | -  |
| 2     | 2   | 2    | 35               | >99 | -  |
| 3     | 3   | 3    | 56               | >99 | -  |
| 4     | 5   | 5    | >99              | 99  | 1  |
| 5     | 10  | 10   | >99              | 99  | 1  |
| 6ᵇ    | 5   | 5    | 64               | >99 | -  |
| 7ᵇ    | 10  | 10   | >99              | >99 | -  |

ᵃ Under the same reaction conditions as described in Figure 2;ᵇ 1.3 MPa air.
Table 2. Effect of reaction time on the catalytic oxidative dehydrogenation of 9,10-dihydroanthracene to anthracene a.

| Entry | Catalyst loading (mol%) | Time (h) | Conv. (%) | Products and selectivity(%) |
|-------|------------------------|----------|-----------|----------------------------|
|       | DDQ | NaNO₂ |       | ATC | AQ |
| 1     | 5   | 5     | 1     | 42  | >99 | -   |
| 2     | 5   | 5     | 3     | 47  | >99 | -   |
| 3     | 5   | 5     | 5     | 54  | >99 | -   |
| 4     | 5   | 5     | 8     | >99 | 99  | 1   |
| 5     | 5   | 0     | 5     | 10  | >99 | -   |
| 6     | 0   | 5     | 5     | 8   | >99 | -   |
| 7     | 0   | 0     | 5     | 3   | >99 | -   |
| 8 b   | 0   | 0     | 5     | n.d.| -   | -   |

a Under the same reaction conditions as described in Figure 2; b under N₂ atmosphere.

In order to further study the process, the influence of reaction time on the catalytic performance of DDQ/NaNO₂ was investigated. As illustrated in Table 2, the conversion of 9,10-dihydroanthracene increased very rapidly in the initial 1 h (entry 1). When the reaction time was up to 8 h, the conversion of 9,10-dihydroanthracene reached >99%. In the whole reaction process, the selectivity for anthracene was extremely high, especially in the initial 1-5 h, and no oxidative by-products were detected (entries 1-3). To identify the characteristics of each component of DDQ/NaNO₂ and function of O₂, further study was carried. The reactions were run for 5 h, avoiding the disturbance of further slight oxidation occurring at long reaction times. It was observed that 54% of 9,10-dihydroanthracene was dehydrogenated with DDQ/NaNO₂ (entry 3). When 5 mol% DDQ was used individually, the conversion was decreased dramatically from 54% to 10% (entry 5). It suggested NaNO₂ can promote DDQ dehydrogenate 9,10-dihydroanthracene. Only using 5 mol% NaNO₂, dehydrogenation reaction can proceed to a limited extent with 8% conversion (entry 6). Moreover, without DDQ/NaNO₂, only a small amount of anthracene was produced (entry 7). This indicated that 9,10-dihydroanthracene is difficult to dehydrogenate with NaNO₂ or O₂. In this system, NaNO₂ readily decomposes to NO. NO can be rapidly oxidized to NO₂ in the presence of O₂, and the generated NO₂ can oxidize 2,3-dichloro-5,6-dicyano-1,4-hydroquinone (DDQ-H₂) to DDQ. Similarly, the quick oxidation of NO to NO₂ by O₂ was observed in aerobic oxidation of alcohols using TEMPO/Br₂/NaNO₂ catalyst [20], and also found in CH₄ oxidation with Pd/C/NaNO₂/BQ [21]. It cannot proceed without the organocatalytic system in the absence of O₂ (entry 8). This proved the indispensability of O₂.

The effect of temperature on the rate of reaction was examined with DDQ (5 mol%) and NaNO₂ (5 mol%) for 8 h (Figure 3). It can be seen that elevating the reaction temperature from 60 °C to 120 °C barely affected the selectivity to anthracene, which remained at high values (>99% at 60 °C-100 °C, and 99% at 120 °C). On the other hand, the conversion of 9,10-dihydroanthracene was significantly increased when enhancing the reaction temperature. At 120 °C, the conversion of 9,10-dihydroanthracene achieved >99%. The results indicated that the optimized temperature for oxidative dehydrogenation with DDQ/NaNO₂ was 120 °C.
Figure 3. Effect of reaction temperature on the oxidative dehydrogenation of 9,10-dihydroanthracene.

| Entry | Substrates | Conversion (%) | Product and selectivity/yield (%) |
|-------|------------|----------------|-----------------------------------|
| 1     | ![9,10-dihydroanthracene](image1) | >99 | ![9,10-dihydroanthracene](image2) 99/99 |
| 2     | ![1,4-cyclohexadiene](image3) | >99 | ![1,4-cyclohexadiene](image4) >99/99 |
| 3     | ![acenaphthene](image5) | 91 | ![acenaphthene](image6) >99/91 |
| 4     | ![9,10-dihydrophenanthrene](image7) | 77 | ![9,10-dihydrophenanthrene](image8) >99/77 |
| 5     | ![1,2-dihydronaphthalene](image9) | 68 | ![1,2-dihydronaphthalene](image10) >99/68 |
| 6b    | ![iminodibenzyl](image11) | 32 | ![iminodibenzyl](image12) 74/24 |

Table 3. Oxidative dehydrogenation of different dihydroarenes with DDQ/NaNO₂.

Oxidative dehydrogenation of variety of dihydroarenes with DDQ/NaNO₂

To explore the application scope of this organocatalytic system, oxidative dehydrogenation of variety of dihydroarenes including 9,10-dihydroanthracene, 1,4-cyclohexadiene, acenaphthene, 9,10-dihydrophenanthrene, 1,2-dihydronaphthalene, and iminodibenzyl by DDQ/NaNO₂ were investigated (Table 3).

Table 3. Oxidative dehydrogenation of different dihydroarenes with DDQ/NaNO₂.

| Entry | Substrates | Conversion (%) | Product and selectivity/yield (%) |
|-------|------------|----------------|-----------------------------------|
| 1     | ![9,10-dihydroanthracene](image1) | >99 | ![9,10-dihydroanthracene](image2) 99/99 |
| 2     | ![1,4-cyclohexadiene](image3) | >99 | ![1,4-cyclohexadiene](image4) >99/99 |
| 3     | ![acenaphthene](image5) | 91 | ![acenaphthene](image6) >99/91 |
| 4     | ![9,10-dihydrophenanthrene](image7) | 77 | ![9,10-dihydrophenanthrene](image8) >99/77 |
| 5     | ![1,2-dihydronaphthalene](image9) | 68 | ![1,2-dihydronaphthalene](image10) >99/68 |
| 6b    | ![iminodibenzyl](image11) | 32 | ![iminodibenzyl](image12) 74/24 |

* Reaction conditions: 0.5 mmol substrate; other conditions were the same as described in Figure 2; *b* the main by-product cannot be confirmed.

a 0.025 mmol quinone, 0.025 mmol NaNO₂; other conditions were the same as described in Figure 2.
This organocatalytic system exhibited high selectivity. In the cases of 9,10-dihydroanthracene, 1,4-cyclohexadiene, and 1,2-dihydonaphthalene, yields to anthracene, benzene, naphthalene were 99%, 99%, and 91%, respectively. For other substrates, moderate yields (around 70%) were achieved under the same reaction conditions (entries 4, 5). When iminodibenzyl was reacted, it only gave 32% conversion with 74% selectivity to iminostilbene. It is worthwhile to note that Thummel et al. had examined the DDQ-induced dehydrogenation rates in the aromatization of 1,4-dihydrobenzocycloalkenes and 1,4-dihydronaphthocycloalkenes. They provided evidence to support that a positively charged intermediate was involved in an initial rate-limiting hydride transfer to DDQ. The intermediate carbonium ion would be destabilized by electron-withdrawing groups and stabilized by the electron-donating groups, which causes different hydride losing rates [22]. Here the phenomenon that iminodibenzyl showed low activity was consistent with their findings. It may probably because the electron-withdrawing effect of a N atom destabilized the intermediate carbonium ion, and thus the activity of iminodibenzyl was reduced.

The proposed catalytic cycle

Based on the above results, the functions of the DDQ and NaNO₂ are as follows. (1) DDQ can dehydrogenate 9,10-dihydroanthracene to anthracene. (2) NaNO₂ is suggested to act as a convenient nitrogen oxide source, and to readily decompose to NO. NO will rapidly react with O₂ to form NO₂. The released NO₂ can abstract hydrogen from 9,10-dihydro-anthracene to produce anthracene. Since it is difficult to dehydrogenate 9,10-dihydroanthracene with NO₂, the reaction is kept at low conversion. In the absence of O₂, NO can not be oxidized to NO₂, and thus dehydrogenation can not occur. (3) O₂ may be responsible for the recovery of NO₂ from NO, and NO₂ will abstract hydrogen from DDQ-H₂ to generate DDQ, and thus the dehydrogenation by DDQ can proceed. In our previous work, the suggestion was proven by two additional experiments [16]. When 0.5 mmol DDQ and 0.5 mmol 9,10-dihydroanthracene were stirred at 120 °C for 8 h without O₂, it was found that 99% of 9,10-dihydroanthracene was converted to anthracene and considerable amounts of DDQ-H₂ were detected by HPLC measurements. This demonstrated that DDQ can stoichiometrically dehydrogenate 9,10-dihydroanthracene to anthracene. Then 0.5 mmol NaNO₂ and 0.5 mmol DDQ-H₂ were mixed and stirred under 1.3 MPa O₂, DDQ-H₂ was fully oxidized to DDQ. It revealed that in the presence of O₂, NO can be oxidized to NO₂, and NO₂ can readily oxidize DDQ-H₂ to DDQ.

A tentative mechanism for the catalytic cycle is proposed in Scheme 2. The substrate 9,10-dihydroanthracene is readily dehydrogenated by DDQ to produce anthracene. After abstracting hydrogen, DDQ is reduced to DDQ-H₂. DDQ-H₂ is re-oxidized to DDQ again by NO₂ generated in-situ, and NO is produced. In the presence of O₂, NO is readily oxidized to NO₂. Thus the dehydrogenation can proceed. The net reaction is: 9,10-dihydroanthracene reacted with O₂ to form anthracene and H₂O.
Scheme 2. The proposed catalytic cycle of DDQ/NaNO₂ for oxidative dehydrogenation of 9,10-dihydroanthracene to anthracene.

Conclusions

In conclusion, a quinone-based organocatalytic system was developed for the oxidative dehydrogenation of 9,10-dihydroanthracene with dioxygen under mild conditions. Compared with other quinones, DDQ combined with NaNO₂ showed high efficiency. It gave >99% conversion of 9,10-dihydroanthracene with 99% selectivity for anthracene at 120 °C under 1.3 MPa O₂ for 8 h. The organocatalytic system was also efficient for the oxidative dehydrogenation of variety of dihydroarenes. Two redox couples – DDQ/DDQ-H₂ and NO₂/NO – were combined to create a catalytic cycle in the presence of O₂. DDQ/NaNO₂ is highly effective and economical. It may be one of the substitutions for the conventional oxidative dehydrogenation catalyst.

Experimental

General

BQ (99%), TCQ (99%), DDQ(98%), AQ (99%), CAQ (99%), TCAQ (99%), 9,10-dihydroanthracene (98%), anthracene (99%), 1,4-cyclohexadiene (97%), acenaphthene (99%), 9,10-dihydrophenanthrene (95%), 1,2-dihydronaphthalene (>98%), and iminodibenzyl (97%) were purchased from J&K Chemical Ltd. NaNO₂ (99%) and toluene (99.5%) were purchased from Tianjin Kermel Chemical Reagent Development Center.

Oxidation reaction and products analysis

The typical catalytic reaction was performed in a 50 mL stainless steel autoclave equipped with a magnetic stirrer. Toluene (10 mL), 9,10-dihydroanthracene (0.5 mmol), quinine (0.05 mmol), and NaNO₂ (0.05 mmol) were placed in the autoclave. After the desired temperature was reached, O₂ was pressurized (ca. 1.3 MPa) into the reactor and the pressure was kept constant by supplying dioxygen during the reaction. The oxidation products were identified by Agilent 6890N GC/5973 MS detector and quantitated by Agilent 4890D GC equipped with FID detector.
Acknowledgements

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**Sample availability:** Samples of the compounds presented in this paper are available from the authors.

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