The Oxidation of Methylbenzenes and Naphthalenes to Quinones with H_2O_2 in the Presence of Palladium Catalyst

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Methylbenzenes and naphthalenes were oxidized to quinones with aqueous(60%) H_2O_2 in acetic acid in the presence of a 0.24 wt% Pd(II)-sulfonated polystyrene type resin. The selectivities to quinones were higher in naphthalenes than in methylbenzenes. Among the naphthalenes used, 2-methylnaphthalene, 2,3-dimethylnaphthalene, and 2,6-dimethylnaphthalene gave 1,4-quinones in good yields(50—64%). The increase in the reaction temperature increased the selectivity to quinones from 40% at 20 °C to 70% at 70 °C.

The oxidation of 2-methylnaphthalene with chromium trioxide to 2-methyl-1,4-naphthoquinone (vitamin K_3) is known to be a practical process.[1] Recently, various quinones have been prepared from aromatic hydrocarbons with chromium trioxide by the addition of 18-crown-6 ether.[2] However, catalytic oxidation is valuable since the use of a large amount of chromium trioxide gives rise to problems in the treatment of waste water. Along this line, the oxidation of aromatic hydrocarbons to quinones with H_2O_2 in the presence of acid catalysts has been claimed.[3] As for metal-ion catalysts, naphthalenes and anthracenes have been oxidized with ammonium peroxodisulfate under the coexistence of ammonium cerium(IV) sulfate and silver(I) nitrate[4] in an emulsified solution. From a practical standpoint, a solid catalyst is useful in the separation of the catalyst from the reaction products.

In the oxidation of 2-methylnaphthalene to 2-methyl-1,4-naphthoquinone, we have found a palladium catalyst supported on sulfonated polystyrene type resins.[5] In this work palladium catalysts were applied to the oxidation of methylbenzenes and naphthalenes since several quinone compounds showed antitumor or antibiotic activities.

The reaction rates and selectivities to the quinones differed widely with the substituents on methylbenzenes and naphthalenes.

Experimental

Reagents and Preparation of the Catalyst. Methyl benzenes, naphthalenes, 1,2-naphthoquinone, 1,4-naphthoquinone, 2-methyl-1-naphthol, 2,3,5-trimethylhydroquinone, 2-methyl-1,4-naphthoquinone, 2,5-dimethyl-p-benzoquinone, and 2,3,5,6-tetramethyl-*p*-benzoquinone, were purchased commercially. Aqueous (60%) H_2O_2 was obtained from Mitsubishi Gas Chemical Co. The conditioning of sulfonated polystyrene type(SP) resin (DOWEX 50w-x8, 200-400 mesh, H-form, 1 g, water content 50%) was carried out by allowing it to stand for 1 h in 30 ml of acetic acid. The solvent was removed and the SP resin was washed with acetic acid; then, a 0.24 wt% Pd(II)–SP resin catalyst was prepared from 5 mg of $Pd(AcO)_2$ and the SP resin (1 g) by stirring in 20 ml of acetic acid for 5 h at 50 °C. The catalyst was separated and washed three times with acetic acid. Melting points were determined with a Yanagimoto micro melting-point apparatus and were uncorrected.

2,3-Dimethyl-1,4-naphthoquinone. 2,3-Dimethyl-naphthalene (385 mg, 2.5 mmol) was oxidized with 60% H_2O_2 (0.7 ml, 15.6 mmol) at 50 °C for 8 h in 10 ml of acetic acid in the presence of the 0.24 wt% Pd(II)–SP resin catalyst (1 g). After the catalyst had been separated, the reaction mixture was diluted with water to 40 ml and poured into the separating funnel with hexane to extract the quinone from the reaction mixture. The hexane layer was washed with water, dried, and evaporated. The quinone was crystallized from methanol; mp 126—127 °C. Lit,[6] mp 127 °C. Found: C, 77.68; H, 5.46%. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41%.

2,6-Dimethyl-1,4-naphthoquinone. 2,6-Dimethylnaphthalene (768 mg, 5.0 mmol) was oxidized with 60% H_2O_2 (1.05 ml, 23.4 mmol) at 50 °C for 8 h in 20 ml of acetic acid in the presence of the 0.24 wt% Pd(II)–SP resin catalyst (2 g). The quinone was obtained from the reaction mixture in the same way as 2,3-dimethyl-1,4-naphthoquinone; mp 137—138 °C. Lit,[7] mp 136—137 °C. Found: C, 77.30; H, 5.41%. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41%.

2,3,5-Trimethyl-*p*-benzoquinone. 2,3,5-Trimethyl-*p*-benzoquinone was prepared from 2,3,5-trimethyl-*p*-hydroquinone with chromium trioxide in dichloromethane/diethyl ether according to a method described in the literature[2]; mp 30 °C. Lit,[2] mp 32 °C. Found: C, 71.41; H, 6.92%. Calcd for $C_9H_{10}O_2$: C, 71.98; H, 6.71%.

2-Methyl-1,4-naphthalenediol. 2-Methyl-1,4-naphthalenediol was prepared by reducing 2-methyl-1,4-naphthoquinone with sodium dithionite according to a method from the literature[1]. Mp 150—160 °C. Found: C, 75.94; H, 5.57%. Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79%.

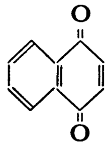
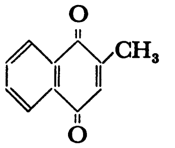
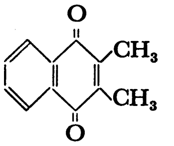
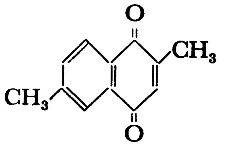
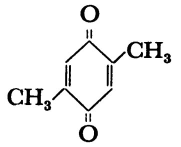
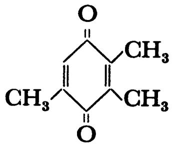
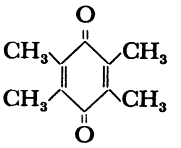
General Procedure for the Oxidation of Methylbenzenes and Naphthalenes. Naphthalenes (2.5 mmol), acetic acid (10 ml), and the 0.24 wt% Pd(II)–SP resin catalyst (1 g) were added to a 50 ml flask. Oxidation was initiated by the addition of 60% H_2O_2 (0.35 ml, 7.8 mmol) under magnetic stirring. After 4 h, an additional 0.35 ml of 60% H_2O_2 was added and the solution was heated until the oxidation was almost completed. The products were analyzed by high-performance liquid chromatography (HPLC) (M & S pack C-18, 4.6×150 mm column, Gilson Co. model 302) using $MeOH–H_2O$ (100:15) as the eluent (flow rate, 0.5 ml min^{-1}; detector, UV at 285 nm). 2,6-Dimethylnaphthalene or 2-methylnaphthalene was used as an internal standard. Retention times were 1,2-naphthoquinone 3.9 min, 1,4-naphthoquinone 4.6 min, 2-methyl-1,4-naphthoquinone 5.5 min, 2,3-dimethyl-1,4-naphthoquinone 7.0 min, 2,6-dimethyl-1,4-naphthoquinone 6.6 min, 2,5-dimethyl-*p*-benzoquinone 4.4 min, 2,3,6-trimethyl-*p*-benzoquinone 5.2 min, 2,3,5,6-tetramethyl-*p*-benzoquinone 6.8 min, naphthalene 7.2 min, 2-methylnaphthalene 9.6 min, 2,3-dimethylnaphthalene 12.9 min, 2,6-dimethylnaphthalene 13.8 min, *p*-xylene 7.8 min, 1,2,4-trimethylbenzene 10.7 min, and 1,2,4,5-tetramethylbenzene 14.0 min, respectively.

Results and Discussion

Oxidation of Methylbenzenes and Naphthalenes. In the oxidation of 2-methylnaphthalene to 2-methyl-1,4-naphthoquinone, the composition of the catalysts and the reaction conditions such as metal ions, anions, the supports of palladium, and solvents have been studied previously.[5] The best catalyst was prepared from palladium salts and sulfonated polystyrene-type resins in acetic acid by an ion-exchanging procedure at 50 °C for a 5-h heating. When a 0.24 wt% palladium-sulfonated polystyrene type resin (SP resin) was used, the conversion of 97% and the selectivity of 55% were attained at 50 °C for 8 h. Though the SP resin itself catalyzed the oxidation, the activity was poor; a conversion of 54% and a selectivity of 37% were obtained under the same reaction conditions. Acetic acid was an effective solvent for the oxidation. In our oxidation system 2-methyl-1,4-naphthoquinone was sufficiently stable in separated experiments; a quinone of 9.9% was decomposed after 8 h at 50 °C.

In this report, the oxidation of methylbenzenes and naphthalenes was carried out with aqueous 60% H_2O_2 by using palladium catalysts. Results are shown in

Table 1. Oxidation of Methylbenzenes and Naphthalenes to Quinones

Substrate	Quinone	Temp °C	Time h	Conv %	Yield %
Naphthalene		50	8	67.9	12.6
2-Methylnaphthalene		60	8	92.9	59.9
2,3-Dimethylnaphthalene		50	6	95.1	51.2
2,6-Dimethylnaphthalene		50	8	97.9	64.7
p-Xylene		70	8	37.2	6.6
1,2,4-Trimethylbenzene		70	10[a]	77.6	3.3
1,2,4,5-Tetramethylbenzene		70	8	74.8	8.4

Substrate (2.5 mmol), 60% H_2O_2 (0.7 ml, 15.6 mmol), 0.24 wt% Pd(II)-SP resin (DOWEX 50 w-x8, 200—400 mesh) 1 g, and AcOH 10 ml were used. a) H_2O_2 of one equivalent to 1,2,4-trimethylbenzene was added each at 0 h, 4 h, and 7 h.

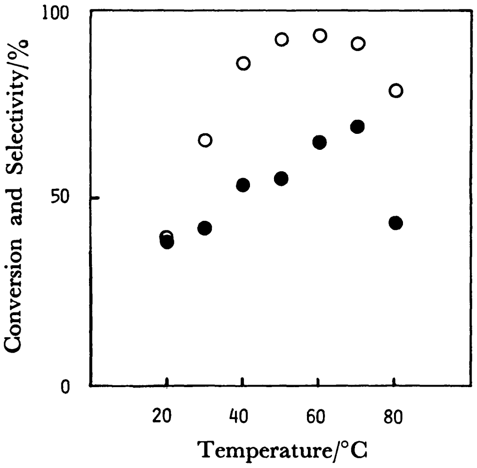


Fig. 1. Effect of the temperature on the conversion and the selectivity of the oxidation of 2-methylnaphthalene to 2-methyl-1,4-naphthoquinone with H_2O_2. 2-Methylnaphthalene 0.35 g(2.5 mmol), 60% H_2O_2 0.7 ml(15.6 mmol), 0.24 wt% Pd(II)-SP resin (DOWEX 50w-x8, 200—400 mesh) 1 g, and AcOH 10 ml were used. The oxidation was carried out for 8 h. ○: Conversion, ●: Selectivity.

Table 1. Methylbenzenes such as *p*-xylene, 1,2,4-trimethylbenzene, and 1,2,4,5-tetramethylbenzene were oxidized to give 2,5-dimethyl-*p*-benzoquinone, 2,3,5-trimethyl-*p*-benzoquinone, and 2,3,5,6-tetramethyl-*p*-benzoquinone, respectively, with poor yields of 3—8% at 70 °C. On the other hand, naphthalenes were oxidized easily to give methylnaphthoquinones; 2-methyl-, 2,3-dimethyl-, and 2,6-dimethylnaphthalene gave corresponding 1,4-quinones from naphthalenes with selectivities of 54, 53, and 66%, respectively. The only quinone from naphthalene was 1,4-naphthoquinone, since the decomposition of 1,2-naphthoquinone occurred vigorously.

Figure 1 shows the effect of the reaction temperature on the conversion and the selectivity in the oxidation of 2-methylnaphthalene. The conversion increased upon increasing the reaction temperature up to 50 °C and a constant value of around 90% was attained. However, a further increase in the reaction temperature (80 °C) collapsed the catalyst and the activity decreased drastically.

The selectivity also increased linearly upon increasing the reaction temperature to 70 °C. Therefore, we carried out the oxidation at temperatures between 50 and 70 °C. Usually, a higher selectivity is expected when mild reaction conditions are employed. Our results were contrary to the general tendency. For this complicated result, the presence of two different types of active species working under different temperature ranges are considered, i.e., hydroxyl cations[8] worked mainly at higher temperatures to give quinones and hydroxyl radicals at lower temperatures to afford polymerized compounds as by-products.[9]

Table 2. Oxidation Rates of 2-Methylnaphthalene, 2-Methyl-1-naphthol, and 2-Methyl-1,4-naphthalenediol

Substrate	Initial rate[a)]	Select.[b)]
	$\times 10^{-4}$ mol dm^{-3} min^{-1}	%
2-Methylnaphthalene	5.9	55
2-Methyl-1-naphthol	72.2	61
2-Methyl-1,4-naphthalenediol	1500	100

Substrate (5.0 mmol), 60% H_2O_2 (one equivalent to the substrates), 0.24 wt% Pd(II)-SP resin (DOWEX 50w-x8, 200—400 mesh) 2 g, and AcOH 20 ml were used. The oxidation was carried out at 50 °C. a) The rate of formation of 2-Methyl-1,4-naphthoquinone. b) The selectivity to 2-methyl-1,4-naphthoquinone.

The Oxidation of Various Substituted Benzenes and Naphthalenes. The yields of quinones varied with the position and the number of the methyl groups attached to benzenes and naphthalenes (Table 1). As a tendency, electron-donating substituents, such as methyl and methoxyl groups at carbon-2, accelerated the oxidation. On the other hand, nitro groups greatly retarded the oxidation; the ratios for the initial oxidation rates were $MeO:Me:H:Cl:NO_2=11.1:3.4:1.0:0.6:0.1$. The large substituent effect and an ionic media of our reaction system suggested that an electrophilic attack of peroxigenated palladium at the 1-position of naphthalenes to give 1-naphthols is a key step for the quinone formation followed by the hydroxylation to carbon-4. 2-Methyl-1-naphthol and 2-methyl-1,4-naphthalenediol, the supposed intermediates, were easily oxidized to give quinones as shown in Table 2.

The nature of the palladium catalysts in the oxidation with peroxides is still ambiguous. Recently, a peroxidized palladium complex has been prepared from *t*-BuOOH and $Pd(AcO)_2$ and used for the oxidation of olefins to ketones.[10] In our catalyst, *t*-BuOOH was inactive to the oxidation of 2-methylnaphthalene.

The oxidations of methoxybenzenes with chromium trioxide have afforded benzoquinones selectively.[11] Also, 1,2,3-trimethoxybenzene has been oxidized to give dimethoxy-*p*-benzoquinones with H_2O_2 in acetic acid in the presence of hexacyanoferrate.[12] On the other hand, the palladium–SP resin catalyst easily oxidized *o*-, *m*-, and *p*-dimethoxybenzenes with H_2O_2 to give polymerized tars.

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