Nanoclusters

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Aerobic Oxidation of Hydroquinone Derivatives Catalyzed by Polymer-Incarcerated Platinum Catalyst**

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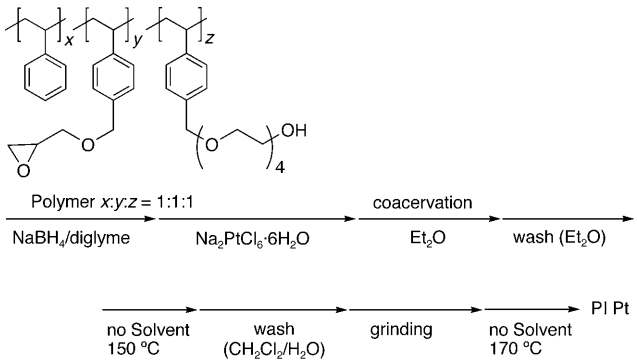
Quinones constitute an important group of substrates. Their structure is often found in naturally occurring compounds and is incorporated into synthetic biologically active compounds.[1] They are also useful in the construction of polycyclic molecules by Diels–Alder reactions.[1,2] The most important property of quinones is the ease in which they undergo redox transformations between hydroquinones and quinones. In organic chemistry, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and chloranil are among the most common oxidizing and dehydrogenating reagents.[3] In biology, ubiquinones and plastoquinones play critical roles in energy production based on the quinone–hydroquinone redox reaction.[4]

The oxidation of hydroquinones is one of the most direct ways to prepare the corresponding quinones. Although various oxidizing agents have been used for this purpose, reduced oxidants inevitably remain as co-products in stoichiometric reactions. With increasing interest in atom economy and environmental concerns, methodologies for catalytic oxidation that use molecular oxygen are highly desirable. In this context, catalysts such as $(NO)_x$,[5] Pt/C or Pt/alumina,[6] supported metalated phthalocyanine,[7] $[VO(acac)_2]$ (acac = acetylacetonate),[8] Fe^{III}–EDTA (EDTA = ethylenediaminetetraacetate),[9] $CuSO_4/Al_2O_3$,[10] dinuclear Cu or Pt catalysts,[11,12] (dibenzo[b,i]-1,4,8,11-tetraazacyclotetradecianato) cobalt(II),[13] NPV_6Mo_6/C,[14] *N*,*N*′-bis(2′-pyridinecarboxamido)-1,2-benzene]cobalt(II),[15] and copper/amine/cellulose polymers[16] have been previously reported, although substrate scope remains to be improved. In particular, the oxidation of hydroquinones substituted with electron-withdrawing groups (EWGs), such as chlorohydroquinone, was either reported to be difficult or was not described, presumably because of its high redox potential.[2,3]

Recently we have reported that styrene-based polymer-incarcerated Au nanoclusters (PI Au) efficiently catalyze the aerobic oxidation of hydroquinone derivatives.[17] While various alkyl-substituted hydroquinones were smoothly oxidized, reactions with EWG-substituted hydroquinones in the presence of PI Au either did not proceed or proceeded slowly with the aid of an added base. Herein we report the aerobic oxidation of hydroquinones and their derivatives catalyzed by polymer-incarcerated platinum nanoclusters (PI Pt). In this catalytic system, a wide range of hydroquinone and catechol derivatives, including tetrachlorohydroquinone, are smoothly oxidized under ambient conditions with low catalyst loading (0.05–2 mol%).

PI Pt was prepared following the previously reported procedure for PI Au (Scheme 1).[18] Different platinum loading values, approximately 0.05 mmol Pt g^{-1} and approximately 0.1 mmol Pt g^{-1}, did not result in a significant difference in catalytic activity and the particle size, as derived from transmission electron microscopy (TEM) images.



Scheme 1. Preparation of PI Pt.

The results of the oxidation reaction on a range of substrates under various reaction conditions are summarized in Table 1. When tetrachlorohydroquinone was left in an O_2 atmosphere in the absence of any catalyst only a negligible

Table 1: Optimization of reaction conditions.

1,4-tetrachlorohydroquinone —[Pt catalyst (1 mol% as Pt); gas (1 atm), RT, 3 h, $CHCl_3/H_2O$]→ *p*-chloranil

Entry	$CHCl_3/H_2O$ (mL mmol substrate^{-1})	Gas	Yield [%][b]
1[a]	27/1.0	O_2	<1
2[c]	27/0	O_2	23
3	0/27	O_2	9
4	27[d]/1.0	O_2	60
5	27/1.0	O_2	>99
6	27/1.0	Air	73
7	27/1.0	N_2	6

[a] Without PI Pt. [b] Determined by GC analysis (internal standard: anisole), standard curve method. [c] $MgSO_4$ (1 equiv) was added as a dehydrating agent. [d] THF was used instead of $CHCl_3$.

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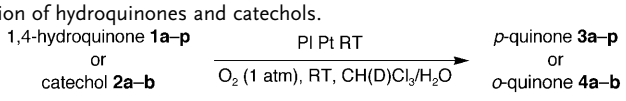
amount of *p*-chloranil was obtained (Table 1, entry 1). While PI Pt-catalyzed reactions in either chloroform or water alone afforded the oxidized product only in low yield (Table 1, entries 2 and 3), homogeneous media such as THF/H_2O resulted in an improved yield (Table 1, entry 4). Gratifyingly, carrying out the reaction in a biphasic solvent system of chloroform/water (27:1) led to the quantitative formation of the desired product (Table 1, entry 5). Oxidation occurred even under atmospheric oxygen (Table 1, entry 6), but a poor yield was obtained when the reaction was carried out under nitrogen (Table 1, entry 7). These observations indicate that molecular oxygen is indispensable for the reaction and that oxidation does not occur through H_2 elimination. Inductively coupled plasma (ICP) analysis showed that no platinum had leached into the reaction mixture (Table 1, entry 5). To the best of our knowledge, this is the first example of truly efficient catalytic aerobic oxidation of electron-deficient hydroquinone derivatives such as tetrachlorohydroquinone.

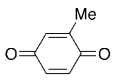
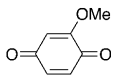
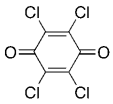
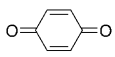
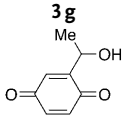
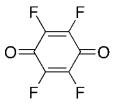
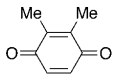
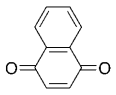
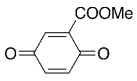
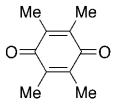
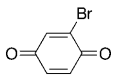
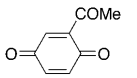
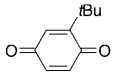
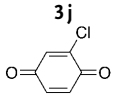
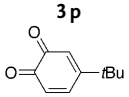
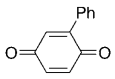
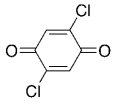
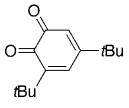
The results of aerobic oxidation catalyzed by PI Pt are summarized in Table 2. All the hydroquinones examined were oxidized readily (within 1–8 h) in good to excellent yields, under additive-free conditions at room temperature. Catalyst loading was decreased to as low as 0.05 mol% (**1a**), and a maximum turnover frequency (TOF) of at least 1000 h^{-1} was observed (**1a**). Catalytic activity was not inhibited by acid (**1a**). PI Pt catalyzed the oxidation not only of hydroquinones substituted with electron-donating groups (EDGs; **1a–i**) but also EWG-substituted hydroquinones (**1j–p**). Catechols were also found to be good substrates (**2a**, **2b**). The reaction was very clean and selective for all substrates, no significant by-products were detected and complete consumption of the starting materials was observed. Lower yields in a few cases (**1b**, **1g**, **1n**) may arise from the inherent tendency of quinones to sublime, which could cause a loss of products during the reaction. Analytically pure products could be isolated by simply removing the catalyst from the reaction mixture by filtration followed by conventional phase separation and solvent removal, which simplifies the experimental procedure. It is noted that alcohols remain unchanged in this catalytic system (**1h**). *p*-Methoxyanisole and *p*-methoxyphenol were not oxidized, and starting materials were recovered.[19] These results indicate high chemoselectivity of PI Pt, which could be useful in further applications.

Quantitative measurement of the O_2 uptake with a gas burette confirmed 0.5 mol of O_2 uptake per mole of substrate conversion (11.8 mL of O_2 for 1 mmol substrate, Scheme 2). This finding indicates that H_2O is the sole net co-product, although H_2O_2 may be formed as an intermediate.[20]

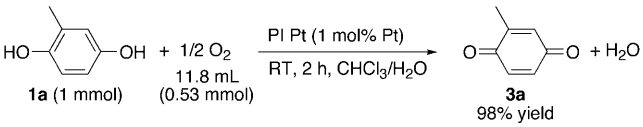
The recovery and reuse of PI Pt was studied using *tert*-butylhydroquinone as a substrate (Scheme 3). When the PI Pt collected by filtration was reused after only drying, a gradual

Table 2: PI Pt-catalyzed aerobic oxidation of hydroquinones and catechols.

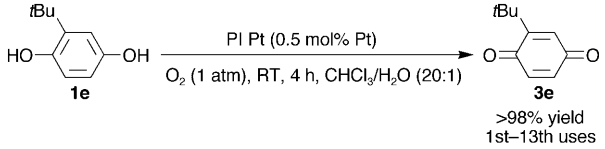


Product	Amount PI Pt [mol% Pt]	*t* [h]	Yield [%]	Product	Amount PI Pt [mol% Pt]	*t* [h]	Yield [%]	Product	Amount PI Pt [mol% Pt]	*t* [h]	Yield [%]
	0.1 0.05	1 5 1	>99[b] 90[b] >99[b,d]		0.1	1	75[a]		1 0.5	3 3	99[b] 90[a]
3a				**3g**				**3m**			
	0.1	2	75[b]		1	3	76[c]		1	3	65[b]
3b				**3h**				**3n**			
	0.2%	3.75	89[a]		0.1	2	>99[a]		2	3	92[c]
3c				**3i**				**3o**			
	0.1	2	93[a]		1	0.5	80[b]		2	6	88[a]
3d				**3j**				**3p**			
	0.1	3.5	>99[b]		0.5	7	93[b]		1	3	98[c]
3e				**3k**				**4a**			
	0.1	1	94[b]		1	3	99[b]		1	8	>99[a]
3f				**3l**				**4b**			

[a] Yield of isolated product. [b] Yield determined by GC (internal standard: anisole), standard curve method. [c] Yield was determined by ^{1}H NMR analysis (internal standard: acetophenone). [d] HCl (1 equiv) was added.



Scheme 2. Quantitative measurement of O_2 uptake.



Scheme 3. Recovery and reuse of the catalyst.

decline of catalytic activity was observed,[21] although no leaching of platinum into the reaction mixture was detected by ICP analysis in each run. However, treatment of the recovered catalyst with base was found to be effective in preventing its deactivation. When the filtered catalyst was washed with $CHCl_3$/0.5 M aqueous NaOH after each use, the PI Pt could be reused at least 13 times to catalyze oxidation reactions in almost quantitative yield.

In conclusion, we have developed an aerobic oxidation of hydroquinone derivatives that is catalyzed by polymer-incarcerated platinum nanoclusters. A remarkably wide substrate scope has been achieved, including EWG-substituted hydroquinones, which are unprecedented substrates for catalytic oxidation. The oxidation proceeded smoothly with as little as 0.05 mol% PI Pt under ambient conditions, with high selectively for the hydroquinone structure. Water is the sole co-product and the catalyst could be reused at least 13 times without any loss of catalytic activity. This methodology provides not only a synthetically useful but also an environmentally benign route for the preparation of quinone derivatives.

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[19] PI Pt (1 mol%), O_2 (1 atm), RT, 3 h, $CHCl_3$ (20 mL mmol^{-1} substrate), H_2O (1 mL mmol^{-1} substrate).
[20] Vigorous emission of O_2 gas was observed upon treatment of an aqueous solution of H_2O_2 with PI Pt.
[21] When the catalyst was reused after recovery by simple filtration and drying, the yields were >99% (1–5th), 96% (6th), 84% (7th), and 63% (8th).

