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Oxidative C–C coupling of 2,6-di-*tert*-butylphenol in aqueous media *via* catalytically active molybdate surfactants†

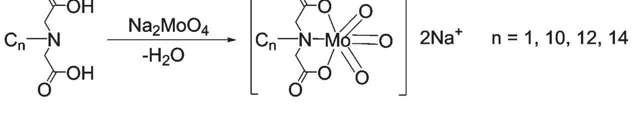
John E. W. Cull, Axel Richard and Jennifer Scott*

Long-chain *N*-alkyliminodiacetatomolybdate catalytic surfactants can be incorporated within a CTAB micellar solution and have shown catalytic activity for the oxidation of 2,6-di-*tert*-butylphenol to the corresponding diphenoquinone in aqueous media.

In an effort to improve our sustainability practices and employ more green chemistry techniques, an increasing number of research groups are turning towards the use of water as a solvent for organic reactions.[1] Although there are numerous obvious benefits to this practice, the main logistical challenges include solubility issues of the non-polar organics and the potential reactivity of water towards the substrates, which can be mitigated by the use of micellar solutions.[2] In addition, functionalization of the micelles using either organic functional groups or catalytically active transition metal complexes can mimic the functionality of enzyme systems, including both the microenvironment and the active site for selective transformation.[3] In fact, several recent reviews highlight the ability of aqueous micelles and metallomicelles to perform selective catalytic organic transformations, including ester hydrolysis, Diels–Alder reactions, and hydrogenations, among others.[2–4]

Although oxidation reactions in micelles have not been explored to the same extent,[5] the oxidation of organic compounds, such as phenol, is of importance from both an environmental standpoint[6] and also in terms of industrial syntheses.[7] In fact, one of the green techniques currently being explored for the oxidation of phenols involves the use of peroxidase enzymes.[8] Due to their greatly reduced cost, peroxidase mimics are a promising substitute for this reaction, combining a micellar medium with a transition metal catalyst, such as those supported by Schiff-base, phthalocyanine, and porphyrin ligands, soluble within the hydrophobic environment of the micelle.[9] Transition metal compounds bearing strongly chelating *surfactant-like* ligands (containing long hydrophobic alkyl chains), on the other hand, have the potential for aggregation into micelles,[10] positioning the catalytically active metal center at the interface between the two phases and acting as an electron-bridge between the water-soluble oxidants and the non-polar organic substrates. Herein, we describe the preparation of *N*-alkyliminodiacetatomolybdate complexes and their incorporation into CTAB micelles. In an effort to explore their oxidative catalysis abilities, preliminary studies are focused on the dimerization of 2,6-di-*tert*-butylphenol (DTBP) to 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone (DPQ). The oxidation of DTBP to DPQ is a relatively well-known reaction,[11] and it is precisely for this reason that it is an excellent candidate for the following proof-of-concept studies. On the other hand, published examples of this transformation occurring in water are few[12,13] and do not involve catalytic surfactants, but rather transition metal catalysts dissolved within the micelle.[12]

Slight modifications to published procedures were used to obtain the long chain *N*-alkyliminodiacetic acids (H_2C_nIDA, where n = 10, 12, 14).[14] Upon reaction with 1 equiv. sodium molybdate in water, the ligand becomes completely solubilized, giving a clear and colourless solution, signifying reaction with the molybdate and generating the 1 : 1 metal–ligand complex (Scheme 1). The analogous reaction using methyliminodiacetic acid was also performed. Previous studies involving mixtures of H_2C_1IDA and molybdate describe the formation of 1 : 1 complexes in solution regardless of the equivalents.[15] Indeed, a combination of NMR, EA, and NAA of an isolated sample of the Mo-C_{12}IDA indicate this to be the case for the



Scheme 1 Synthesis of molybdate surfactants.

Department of Chemistry and Chemical Engineering, Royal Military College of Canada, Kingston, Canada. E-mail: Jennifer.Scott@rmc.ca; Fax: +1-613-542-9489; Tel: +1-613-541-6000 x 3562

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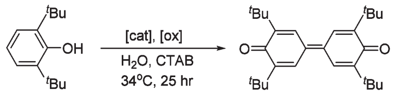
long chain alkyls as well, establishing the identity of the complex as $Na_2MoO_3C_{12}IDA(H_2O)_2$.†

The long chain ionic molybdate complexes are soluble in water in the absence of CTAB. Using conductivity measurements of various solution concentrations, preliminary results suggest the formation of micellar aggregates, with a critical micelle concentration of 1.7 mM.† Studies exploring the physical properties of the metallomicelles are underway and are beyond the scope of this communication.

The catalytic oxidation of DTBP to DPQ was attempted by dissolving DTBP into mixed CTAB-molybdate micellar solutions (4.0 mM CTAB) and monitoring the generation of DQP under varying conditions (temperature, oxidant concentration, nature of the oxidant, concentration of catalyst, and length of the alkyl chain in the ligand) *via* UV-VIS spectrophotometry at 418 nm. As the reactions progressed, the presence of DPQ was visibly witnessed by the appearance of a yellow colour. The results for several trials are shown in Table 1.

Entry 1 lists the results of DPQ formation by Mo-C_{12}IDA (0.2 mM catalyst, 20 mol% catalyst to substrate) at 34 °C after 25 hours, using 10, 100 and 1000 equivalents of H_2O_2 as an oxidant. The highest conversion attained was 80% yield of DPQ using the least amount of oxidant, as measured by UV-VIS. As the oxidant concentration was increased, the amount of DPQ decreased, suggesting perhaps the formation of the over-oxidized benzoquinone (BQ) derivative.[11–13] When the identical larger-scale reaction was performed with 10 equiv. H_2O_2, the residue isolated by extraction displayed a product distribution of 85% DPQ and 7% BQ by NMR, with an additional 8% DTBP remaining unreacted. The conversion shown in entry 1 at 10 equivalents H_2O_2 is significant when compared with the identical run in the absence of molybdate catalyst (entry 2). In this case, trace amounts of DPQ were formed with 10 equivalents of H_2O_2 and only a slight increase was seen with additional oxidant. These results highlight the ability of the molybdate surfactants to afford the C–C coupling of DTBP in an aqueous media, as without the catalyst, only minimal conversion is seen at lower equiv. H_2O_2.

Table 1 Oxidation of DTBP to DPQ[a]



Entry	[cat] mM	Ligand	% Yield DPQ[b] at different equiv. of H_2O_2 10	100	1000
1	0.2	C_{12}	**80**	38	16
2	0	—	Trace	17	13
3	0.2	C_{14}	**99**	21	5
4	0.2	C_{10}	**88**	32	8
5	0.2	C_1	29	**70**	25
6	0.2	—	37	48	25
7	0.6	C_{12}	67	13	7
8	0.4	C_{12}	**72**	14	6
9	0.1	C_{12}	**71**	24	8
10	0.01	C_{12}	68	65	45
11[c]	0.001	C_{12}	10	**99**	18
12	0.0001	C_{12}	Trace	23	5
13[c]	0.2	C_{12}	8	6	Trace
14[d]	0.2	C_{12}	50	—	—
15[e]	0.2	C_{12}	Trace	—	—
16[f]	0.2	C_{12}	Trace	Trace	—
17[g]	0.2	C_{12}	Trace	Trace	Trace

[a] Reaction conditions: 4.0 mM CTAB solution, 1.0 mM DTBP, ox, cat, 25 h in air at 34 °C. [b] Yield determined by UV-VIS absorbance at 418 nm. [c] t = 5 h. [d] T = 50 °C. [e] T = 80 °C. [f] ox = cumene hydrogen peroxide. [g] ox = *tert*-butyl hydrogen peroxide.

Entries 3–6 explore the effect of altering the length of the alkyl chain on the ligand backbone. The other long chain alkyls (C_{14} and C_{10}) show almost quantitative yield of DPQ at 10 equiv. H_2O_2 and a similar pattern to C_{12} of decreasing yield with increasing oxidant concentration (entries 3 and 4). Conversely, when either the C_1 derivative, or no ligand (only Na_2MoO_4), were tested, the yields of DPQ were significantly lower with 10 equiv. H_2O_2, but show respectable yields with increased oxidant (100 equiv., entries 5 and 6). The presence of the long alkyl chain improves the catalyst substantially at lower oxidant concentrations relative to the short chain ligand or the absence of ligand. This is most likely a result of the alkyl chain imbedding itself into the micellar core, positioning the active molybdate center at the interface between the hydrophobic interior and the polar exterior and facilitating electron transfer across the barrier from the hydrophobic DTBP to the water-soluble oxidant to afford the transformation. The fact that increased oxidant is required for the short chain ligand, or free aqueous molybdate, may be merely due to the increased chances of finding an activated molybdate catalyst at the interface for the reaction to occur.

The ratio of catalyst to substrate was altered in entries 7–12, displaying minimal differences when the concentration is increased to 40 or 60 mol% catalyst to DTBP (entries 7 and 8), or even decreased by half to 10 mol% catalyst (entry 9). However, significant changes can be seen when the concentration is decreased by several orders of magnitude. As the concentration decreases to 0.01 and 0.001 mM (entries 10 and 11), increased oxidant becomes more important, culminating in a quantitative yield for 0.1 mol% catalyst with 100 equiv. H_2O_2 after only 5 hours (compared to the analogous conversions seen for the original system after 5 hours, shown in entry 13). This result may be similar to that seen above for the short chain alkyls, in which increased oxidant is necessary to ensure the presence of enough activated molybdate sites to afford conversion. However, decreasing the catalyst concentration further eventually results in lower yields of DPQ (entry 12).

As the temperature of the reaction increases, the amount of DPQ formed with 10 equiv. H_2O_2 decreases (entries 14 and 15), suggesting either the formation of BQ or the further degradation of DPQ to another product at higher temperatures. Additionally, the use of hydrophobic oxidants to afford the transformation proved to be unsuccessful, with both cumene hydrogen peroxide and *tert*-butyl hydrogen peroxide generating only trace amounts of DPQ (entries 16 and 17). More importantly, for all of the tests, no product formation is seen in the absence of oxidant, concluding that air is not a suitable oxidant for this transformation using Mo catalysts.

Conclusions

The results from these tests highlight the ability of the molybdate surfactants to act as catalysts to afford the oxidation of DTBP to DPQ in water using H_2O_2. The mechanism of the C–C bond formation, which most likely involves the formation of phenol radicals and peroxomolybdate intermediates, appears to be facilitated by the ability of the long chain alkyls to position the active site at the boundary layer and is also greatly affected by the concentration of oxidant, where increased concentrations may substantially reduce the selectivity for the dimerized product. These preliminary results emphasize the potential for specially designed catalytic surfactants to afford the oxidation of organic substrates in water by carefully selecting the reaction conditions. Indeed, results involving other transition metal systems will be communicated shortly. Studies are currently underway to explore the mechanism of this reaction in greater detail, as well as to expand the scope of the catalysis towards the oxidation of other substrates of interest, using molybdate and other catalytically active transition metal centers.

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