Selective N-oxidation of aromatic amines to nitroso derivatives using a molybdenum acetylide oxo-peroxo complex as catalyst

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Abstract

The molybdenum acetylide oxo-peroxo complex obtained in situ by the treatment of the corresponding molybdenum acetylide carbonyl complex, $CpMo(CO)_3(C\equiv CPh)$; $Cp = \eta^5\text{-}C_5H_5$ with H_2O_2, has been used as an efficient catalyst for selective N-oxidation of primary amines to nitroso derivatives. Excellent amine conversion (up to 100%) and very high selectivity for nitroso compounds (99%) have been obtained using 30% hydrogen peroxide as an oxidant. The oxo peroxo Mo(VI) complex has also been found to be very active for the oxidation of various substituted primary aromatic amines with electron donating as well as electron withdrawing substituents on the aromatic ring.

Catalytic oxidation of amines is an important functional transformation in organic synthesis.[1,2] Amongst the possible amine oxidation products (hydroxyl, nitroso, nitro, azo and azoxy), aromatic nitroso compounds are utilized extensively as chemical feedstocks for a wide range of useful materials such as dyes, pharmaceuticals, perfumes and plastics.[3] Oxidation of amines pose problems due to nonregioselective or over-oxidation of amines and competitive oxidation of substrates. General methods for the preparation of nitroso compounds have been addressed by Gowenlock et al.[4] Several organo catalysts[5,6] as well as metal catalysts[7] are reported for the oxidation of amines. However, mainly the nitro compounds are obtained in many cases. $FeCl_2–Py_4$ complex is reported to give selectively nitroso or nitro product depending on the oxidant used and also the oxidant used is a limiting agent leading to a very low TON for the product.[8] TS-1 is reported to give high selectivity (73%) for nitroso compound at very low conversions (7.3%).[9]

Amongst the early transition-metal complexes, molybdenum(VI) complexes have functional as well as structural similarity with molybdo-enzymes and have the ability to catalyze a variety of oxidation reactions.[10,11] Various molybdenum organometallic complexes and oxides are known to be very good homogeneous and heterogeneous catalysts for the oxidation/epoxidation reactions.[12–14] Preyssler's catalysts (W and mixed W/Mo) have been reported to oxidize anilines with maximum selectivity (82%) for the azoxy compound.[15] Several Mo catalysts with acac[16] or hmpa[17] ligands as well as Mo- and W-based coordination polymers[18] have been used for aniline oxidation. Recently, we have used molybdenum acetylide complex, $CpMo(CO)_3(C\equiv CPh)$; $Cp = \eta^5\text{-}C_5H_5$ complex, (**1**) as oxidation catalyst for cis-dihydroxylation of various olefins.[19] In continuation of our efforts to find out the catalytic activity of this catalysts for the oxidation of other substrates, selective N-oxidation of amines to nitroso derivative has been investigated. To our knowledge there are no reports on the use of a molybdenum acetylide complex for the oxidation of amines. This study is particularly interesting since it offers the possibility of extending the usually

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versatile catalytic potential of organometallic complexes to aqueous media.

The molybdenum acetylide complex, $CpMo(CO)_3$-(–C≡CPh), was prepared according to the literature method.[20] The oxidant used was hydrogen peroxide and hence to confirm the stability of the catalyst and to study the nature of the catalytically active species under the reaction conditions, catalyst **1** was treated with H_2O_2 and characterized by FTIR. On treatment of complex **1** with 30% aqueous hydrogen peroxide, the corresponding oxo peroxo Mo(VI) acetylide complex was formed after loss of the carbonyl ligands (Scheme 1).

The FTIR spectrum of **1** after the addition of H_2O_2 confirmed the formation of the oxo peroxo species. The IR band at 953 cm^{-1} indicates the presence of a Mo=O terminal bond. The band at 858 cm^{-1} corresponds to the O–O stretching vibration of the peroxo species. The weak bands at 664 and 577 cm^{-1} can be assigned to the Mo–O$_2$ (peroxo) asymmetric and symmetric stretching vibrations, respectively. The IR positions for the Mo oxo and peroxo moieties are in good agreement with the literature reports for various Mo oxo peroxo complexes.[21] The acetylide moiety remained intact even after the addition of H_2O_2, as confirmed by broad low intensity band centred at 2100 cm^{-1} assigned to ν(C≡C). The bands due to C–H stretching vibrations of the phenyl ring were observed in the range 2854–2955 cm^{-1} and the C=C stretching vibrations of the ring were observed at 1464 and 1377 cm^{-1}. The bands due to the carbonyl stretching vibrations (1940, 2031 cm^{-1}) disappeared after the addition of H_2O_2. This clearly indicates the elimination of all the CO ligands and the formation of a higher oxidation state Mo(VI) complex with the retention of the acetylide moiety attached to the Mo centre.

The applicability of the oxo peroxo Mo(VI) catalyst for amine oxidation was initially investigated for aniline oxidation (Scheme 2).[22] Based on our previous experience,[19] the liquid-phase catalytic oxidation of aniline was carried out
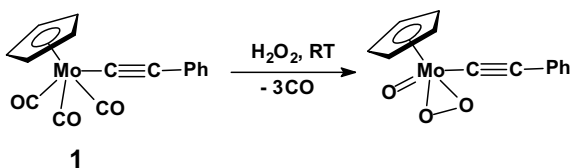
Scheme 1. In situ generation of the oxo-peroxo Mo(VI) acetylide complex.
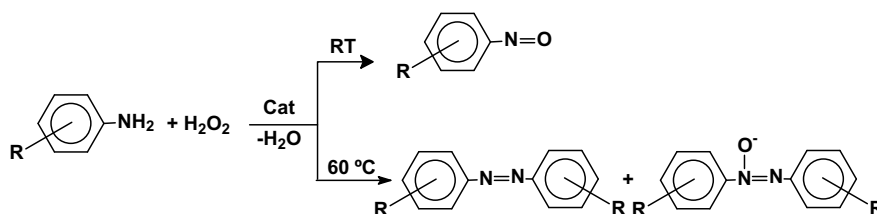
Table 1
Aniline oxidation in various solvents[a]

	Solvent	Conv. (%)	Selectivity (%)			TON[b]
			Nitroso	Azo	Azoxy	
1	t-BuOH	97	97	2	1	470
2	MeOH	95	90	7	3	428
3	CH_2Cl_2	96	80	14	6	384
4	CCl_4	97	84	11	5	407
5	Toluene	84	83	12	5	349
6	CH_3CN	72	90	7	3	324

[a] Reaction conditions: PhNH$_2$ 0.01 mol; 30% H$_2O_2$ 0.02 mol, solvent 10 g, catalyst **1** 0.02 mmol; time 12 h; temp. rt.
[b] TON for nitroso derivative = moles of nitroso product formed per mole of catalyst.

in t-BuOH at rt (Table 1, entry 1) to form single phase system with aqueous oxidant and organic substrates and product. Very high aniline conversion (97%) and excellent selectivity for nitroso benzene (97%) were obtained. When other solvents were tested for the same reaction, alcohols were found to be better with high conversion and selectivity for the nitroso compound. In the case of the chlorinated solvents, the conversion was high, however, the selectivity for the nitroso product decreased to 80% and 84%, respectively (entries 3 and 4).

Comparatively lower conversions were obtained in the case of toluene and acetonitrile as a solvent (Table 1, entries 5 and 6). In all the cases, the turnover number (TON) for the nitroso compound was very high (up to 470) compared to the TON reported previously using W and Mo based coordination polymers (TON < 10),[18] [Mo(O$_2$)(O)(H$_2$O)(hmpa)] (TON ~ 9)[17] or Mo(O)$_2$(acac)$_2$ (TON < 10).[16] This shows the high efficiency of catalyst **1** for selective aniline oxidation.

The influence of temperature on aniline conversion and product selectivity was also examined (Table 2). When the reaction temperature was increased gradually from rt to 100 °C, the rate of the reaction increased and the product distribution changed significantly. The reaction was complete in 12 h at rt (entry 1), whereas at 100 °C it was complete in only 4 h (entry 5); however, the selectivity for the nitroso compound was maximum (97%) at rt which decreased to only 8% at 100 °C. At higher temperatures azo and azoxy compounds were formed as major products compared to nitroso derivative. Formation of the nitro product was also observed at high temperatures.

Considering the good conversion and highest selectivity for aniline oxidation in t-butanol at rt, catalyst **1** was tested

Scheme 2. Oxidation of primary aromatic amines.

Table 2
Effect of temperature on aniline oxidation[a]

	Temperature (°C)	Time (h)	Conv. (%)	Selectivity (%)			
				Nitroso	Azo	Azoxy	Nitro
1	rt	12	97	97	2	1	0
2	40	10	99	80	14	6	0
3	60	6	99	56	18	21	5
4	80	4	99	24	25	43	8
5	100	4	99	8	30	47	15

[a] Reaction conditions: aniline 0.01 mol; 30% H_2O_2 0.02 mol; *t*-BuOH 10 g; catalyst **1** 0.02 mmol.

for the oxidation of a variety of substituted aromatic amines under these conditions and the results are summarized in Table 3. Amongst the substrates tested, the best results were obtained in the case of *p*-methylaniline with 100% conversion and 99% selectivity for the nitroso compound at rt. High conversions and selectivity for nitroso compounds were obtained for activated and electron rich anilines (entries 2 and 4); however, the conversion decreased for sterically hindered 2,6-dimethylaniline though with very high selectivity (99%) for the nitroso product. Halogenated anilines (entries 9–12) were oxidized successfully with a high conversion and a very high selectivity for the nitroso compound. In the case of hydroxyanilines the conversion decreased slightly but the selectivity remained very high (98%) (entries 7 and 8). In the case of all amines tested, very high selectivity for nitroso compound was obtained. The TON for nitroso compound in all the cases is high with the maximum TON of 495 for *p*-methylaniline which is much higher than that reported previously with different molybdenum/tungsten-based catalysts (<10).[16–18]

It is interesting to note that *p*-nitroaniline was also oxidized successfully using catalyst **1**. The conversion as well as selectivity for *p*-nitroaniline oxidation did not decrease significantly compared to aniline. In earlier reports, when

Mo/W-based coordination polymers were used for *p*-nitroaniline oxidation, the yield dropped drastically from 82% for aniline to 20% for *p*-nitroaniline.[18] Similar drastic reduction in yield was reported for [Mo(O$_2$)(O)(H$_2$O)(hmpa)] (77% for aniline and 10% for *p*-nitroaniline).[17] When Mo(O)$_2$(acac)$_2$ was used as a catalyst no catalytic activity was observed with anilines with electron withdrawing substituents on the aromatic ring compared to a 77% yield for aniline using the same catalyst.[16] In the present case, the conversion was marginally decreased from 97% for aniline to 85% for *p*-nitroaniline with almost similar selectivity for nitroso compound (97% for aniline and 95% for *p*-nitroaniline).

These results show that molybdenum acetylide complex **1** is a very efficient catalyst for the oxidation of variety of primary aromatic amines with excellent selectivity for the nitroso compound. It tolerates electron rich as well as electron withdrawing substituents on aromatic ring demonstrating the wider applicability of this catalyst for selective oxidation of primary aromatic amines to nitroso derivatives.

Molybdenum acetylide complex CpMo(CO)$_3$(C≡CPh) was used for the first time for the selective oxidation of primary aromatic amines to nitroso derivatives with very high conversion and selectivity for the nitroso compounds. In situ generated oxo-peroxo molybdenum acetylide complex proved to be the catalytically active species. A variety of substituted anilines were successfully oxidized to the corresponding nitroso compounds under very mild conditions with very high TON.

Table 3
Oxidation of various amines[a]

	Anilines, substituents=	Conv. (%)	Selectivity (%)				TON[b]
			Nitroso	Azo	Azoxy	Nitro	
1	—	97	97	2	1	0	470
2	*p*-Me	100	99	1	0	0	495
3	2,6-Dimethyl	75	99	1	0	0	371
4	*p*-OCH$_3$	83	97	2	1	0	403
5	*o*-Phenylene diamine	77	98	1	1	0	371
6	*p*-Phenylene diamine	84	99	1	0	0	416
7	*o*-OH	73	98	1	1	0	358
8	*p*-OH	75	98	1	1	0	368
9	*o*-Cl	60	96	2	2	0	288
10	*m*-Cl	72	99	0	1	0	356
11	*o*-F	79	79	8	11	2	312
12	*m*-F	70	74	10	14	2	259
13	*p*-NO$_2$	85	95	2	1	2	404
14	Benzyl amine	80	75	12	7	6	300

[a] Reaction conditions: amine 0.01 mol; oxidant 30% H_2O_2 0.02 mol; solvent *t*-BuOH 10 gm; catalyst **1** 0.02 mmol; temperature rt, time 12 h.
[b] TON for nitroso derivative = moles of nitroso product formed per mole of catalyst.

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20. Bruce, M. I.; Humphrey, M. G.; Matisons, J. G.; Roy, S. K.; Swincer, A. G. *Aust. J. Chem.* **1984**, *37*, 1955; A mixture of CpMo(CO)$_3$Cl (2.0 g, 0.0071 mol), (H–C≡CPh) (1.05 g, 0.010 mol) and a catalytic amount of CuI (5 mg) was stirred at room temperature in diethylamine (50 mL) for 15 min. The solvent was removed in vacuum, and the residue was purified by column chromatography on silica gel using hexane/dichloromethane 80:20 v/v mixture as a solvent system. Yield of CpMo(CO)$_3$(–C≡CPh) = 1.5 g, 68.1% based on CpMo(CO)$_3$Cl. The compound was confirmed using FTIR spectroscopy. $v_{(CO)}$, 1940, 2031 cm^{-1}; $v_{(C≡C)}$, 2102 cm^{-1}. NMR in CDCl$_3$: δ (^{1}H); 5.5 (s, 5H, Cp), 7.15–7.38 (m. 5H, Ph); δ (^{13}C); 92.93 Cp, 87.85, 126.01, 127.0, 129.39, 130.8, 130.87 (C≡CPh); 222.4, 238.78 (CO).
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22. The liquid-phase catalytic oxidation of amines: A 50 mL two neck round bottom flask was charged with amine (0.01 mol), 30% hydrogen peroxide (0.02 mol), 10 g solvent and catalyst **1** (0.02 mmol). The reaction mixture was stirred at rt for 12 h until the completion of the reaction. The reaction was monitored using GC (Agilent 6890 Gas Chromatograph equipped with a HP-5 dimethyl polysiloxane, 60 m length, 0.25 mm internal diameter, 0.25 μm film thickness) column with flame ionization detector. Products were confirmed using GC–MS (Model GC Agilent 6890N with HP5 MS 30 m capillary column, MS Agilent 5973 Network MSD) and GC–IR (Perkin Elmer Spectrum 2001, column DB-1, 25 m length, 0.32 mm internal diameter).