Homogeneous modeling of ammoxidation chemistry: nitrile formation using a soluble analogue of MoO_3

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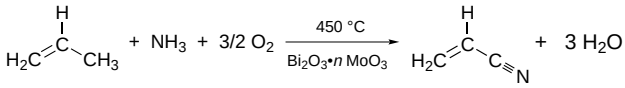
The reaction of the soluble MoO_3 analogue $[Mo_6O_{19}]^{2-}$ with $Ph_3P{=}NCH_2Ph$ replicates key features of heterogeneous ammoxidation chemistry by producing moderate yields of PhC≡N through the proposed intermediacy of the benzylimido hexamolybdate complex $[Mo_6O_{18}(NCH_2Ph)]^{2-}$.

The SOHIO/BP process for the heterogeneous oxidation of propene by O_2 in the presence of ammonia to yield acrylonitrile (*i.e.*, the 'ammoxidation' of propene) constitutes the largest volume example of an allylic oxidation in commercial practice.[1] A minimalistic representation of this remarkable transformation is provided in Scheme 1. It is now well established that the bismuth oxide component of the catalyst serves to abstract a hydrogen atom from propene, affording an allyl radical;[2] subsequent C–N bond formation and redox events occur at sites within the MoO_3 component.[3] Drawing on the extensive studies of Grasselli and Burrington,[4] key nitrogenous surface species proposed to be involved in this chemistry include imido {Mo≡NH}, allylamido {Mo=NHCH$_2$CH=CH$_2$}, allylimido {Mo≡NCH$_2$CH=CH$_2$}, and allylideneamido {Mo=N=CHCH=CH$_2$} fragments. Several groups have reproduced aspects of the proposed transformations in studies of various mononuclear systems.[5–7]



Scheme 1

In order to further refine these homogenous analogues of proposed ammoxidation events we sought to transfer this chemistry into a coordination environment which more closely resembles that provided by bulk MoO_3. As shown in Fig. 1, the soluble hexamolybdate cluster $[Mo_6O_{19}]^{2-}$ possesses an MoO_6 coordination sphere[8] which is conspicuously similar to that within MoO_3.[9] Realizing that a large number of organoimido-substituted hexamolybdates recently have been accessed through reactions of $[Mo_6O_{19}]^{2-}$ with various imido delivery reagents,[10] this structural correspondence suggested to us that

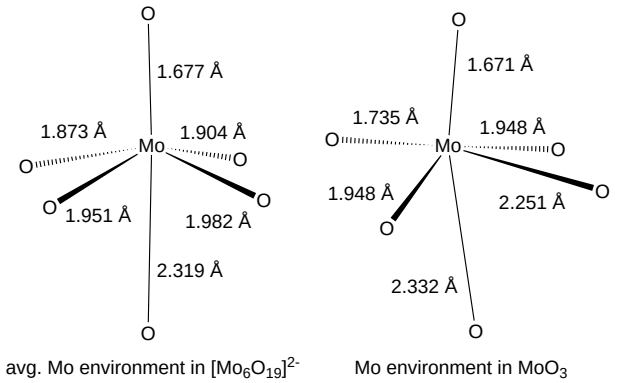


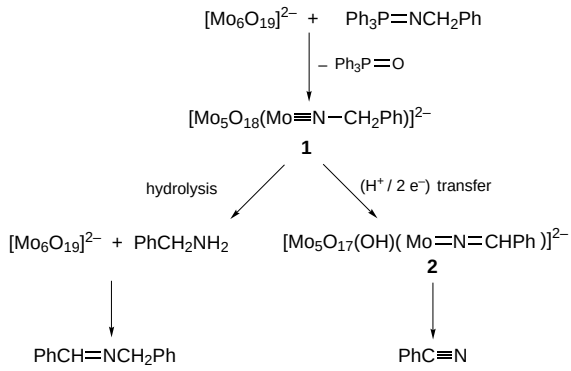
Fig. 1 Comparison of the Mo environments in $[Mo_6O_{19}]^{2-}$[8] and in MoO_3[9]

allylimido- and benzylimido-hexamolybdates would provide the closest approximation yet available of purported ammoxidation surface species. We now report that the reaction of $[Mo_6O_{19}]^{2-}$ with the benzylimido delivery reagent $Ph_3P{=}NCH_2Ph$ affords benzonitrile in moderate yield (37%) thus replicating essential features of heterogeneous ammoxidation chemistry through the proposed intermediacy of an unstable benzylimido hexamolybdate system $[NBu_4]_2[Mo_6O_{18}(NCH_2Ph)]$, **1**.

The addition of 1.47 mmol of $Ph_3P{=}NCH_2Ph$ to an equimolar amount of $[NBu_4]_2[Mo_6O_{19}]$ in 30 ml MeCN at room temp. produces a brown coloration within 1 min of mixing. After this solution was heated at 82 °C under N_2 for 72 h, analysis by GC–MS techniques revealed the presence of benzonitrile (0.54 mmol, 37%) and *N*-benzylidenebenzylamine (0.25 mmol, 34%) along with quantitative production of triphenylphosphine oxide. Using an identical protocol, the thermolysis of $Ph_3P{=}NCH_2Ph$ in the absence of hexamolybdate produced only a trace of benzonitrile (0.009 mmol, 0.6%) and a modest amount of triphenylphosphine oxide (0.17 mmol, 11.7%); importantly, the latter product signals the presence of residual water in the acetonitrile solvent. ^{1}H NMR monitoring throughout the reaction between $Ph_3P{=}NCH_2Ph$ and $[Mo_6O_{19}]^{2-}$ provided only broad and uninformative spectra, inferring the presence of paramagnetic species. In confirmation, aliquots withdrawn from the reaction solution were analyzed by EPR spectroscopy as frozen glasses and gave spectra identical to that published for the brown trianion $[Mo_6O_{19}]^{3-}$.[11]

In order to test whether $PhCH{=}NCH_2Ph$ is an intermediate in the formation of benzonitrile, a MeCN solution containing equimolar quantities of the imine and the hexamolybdate was treated and analyzed as above. No reaction occurred, suggesting that the imine is formed on a reaction pathway different from that leading to benzonitrile. Benzyl amine was suspected as the imine precursor since various polyoxometalates are known to effect this transformation.[12] Accordingly, the reaction of 1.47 mmol amounts of $PhCH_2NH_2$ and $[Mo_6O_{19}]^{2-}$ in MeCN was performed as described above and produced a brown solution immediately; subsequent GC–MS analysis revealed the production of $PhCH{=}NCH_2Ph$ (0.37 mmol, 46%) and only minor amounts of PhCN (0.029 mmol, 1.8%). It is important to note that the 0.25 mmol of $PhCH{=}NCH_2Ph$ produced in the reaction between $Ph_3P{=}NCH_2Ph$ and $[Mo_6O_{19}]^{2-}$ requires far more benzyl amine (0.50 mmol) than can be accounted for by hydrolytic decomposition of $Ph_3P{=}NCH_2Ph$ alone (0.17 mmol); this discrepancy can be accommodated by the reasonable assumption that the reaction between $Ph_3P{=}NCH_2Ph$ and $[Mo_6O_{19}]^{2-}$ affords an intermediate which is more sensitive than $Ph_3P{=}NCH_2Ph$ toward hydrolytic release of $PhCH_2NH_2$.

Since an initial redox reaction between $Ph_3P{=}CH_2Ph$ and the hexamolybdate is unlikely,† and given the demonstrations of forming complexes $[Mo_6O_{18}(NR)]^{2-}$ in reactions between the hexamolybdate and $Ph_3P{=}NR$ reagents,[10a,d] we propose that our observations are best accommodated by formation of an unstable benzylimido hexamolybdate $[Mo_6O_{18}(NCH_2Ph)]^{2-}$, **1**, which undergoes two modes of decomposition. In accord with observations on related d^0 benzylimido[13,14] (and allylimido[6]) complexes, **1** should be extremely moisture sensitive



Scheme 2 Proposed decomposition pathways for **1**

and its hydrolysis (to produce benzyl amine and hexamolybdate) will initiate the reaction sequence leading to $PhCH{=}NCH_2Ph$ (Scheme 1).

The conversion $\{[Ph–CH_2–N]^{2-} \rightarrow Ph–C{\equiv}N\}$ requires the formal export of 2 H^+ and 4 e^-. Precedent suggests that the α-CH_2 hydrogens within **1** should be acidic[6,13,14] while the oxo sites within **1** will display enhanced basicity[10b,g] as a result of the effective electron donation provided by the benzylimido ligand. These combined attributes suggest that the decomposition of **1** to produce benzonitrile is triggered by initial H^+ migration, probably in a pairwise[10g] fashion; an accompanying 2 e^- reduction of its hexamolybdate cage will produce a reduced benzylideneamido dianion **2** (Scheme 2).[6,13] While further reduction of **2** is improbable, several species in the reaction solution should be capable of oxidizing **2** {the most potent of which is $[Mo_6O_{19}]^{2-}$}. Such an oxidation would increase the acidity of the remaining methine hydrogen atom, facilitating a second H^+–2 e^- transfer process, allowing the release of benzonitrile. Efforts are underway to isolate complexes analogous to **1** and **2**.

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Footnotes and References

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† *p*-$CH_3C_6H_4N{=}PPh_3$ (E_{pa} = 0.74 V *vs.* SCE) is easier to oxidize than is $PhCH_2N{=}PPh_3$ (E_{pa} = 1.06 V *vs.* SCE), yet the former reacts with $[Mo_6O_{19}]^{2-}$ to give only metathesis without electron transfer.[10a]

1 R. K Grasselli, in *Heterogenous Catalysis*, ed. B. L. Shapiro, Texas A&M University Press, College Station, TX, 1984, p. 182.
2 J. D. Burrington, C. T. Kartisek and R. K. Grasselli, *J. Org. Chem.*, 1981, **46**, 1877; W. Martin and J. H. Lunsford, *J. Am. Chem. Soc.*, 1981, **103**, 3728.
3 J. Haber and B. Grzybowska, *J. Catal.*, 1973, **28**, 489; B. Grzybowska, J. Haber and J. Janas, *J. Catal.*, 1977, **49**, 150; J. D. Burrington and R. K. Grasselli, *J. Catal.*, 1979, **59**, 79; J. D. Burrington, C. T. Kartisek and R. K. Grasselli, *J. Catal.* 1983, **81**, 489.
4 R. K. Grasselli and J. D. Burrington, *Ind. Eng. Chem. Prod. Res. Dev.*, 1984, **23**, 394 and references therein.
5 D. M.-T. Chan and W. A. Nugent, *Inorg. Chem.*, 1985, **24**, 1422.
6 E. A. Maatta and Y. Du, *J. Am. Chem. Soc.*, 1988, **110**, 8249.
7 J. Belgacem, J. Kress and J. A. Osborn, *J. Mol. Catal.*, 1994, **86**, 267.
8 H. R. Allcock, E. C. Bissell and E. T. Shawl, *Inorg. Chem.*, 1973, **12**, 2963.
9 L. Kihlborg, *Ark. Kemi*, 1963, **21**, 357.
10 (*a*) Y. Du, A. L. Rheingold and E. A. Maatta, *J. Am. Chem. Soc.*, 1992, **114**, 345; (*b*) J. B. Strong, R. Ostrander, A. L. Rheingold and E. A. Maatta, *J. Am. Chem. Soc.*, 1994, **116**, 3601; (*c*) R. J. Errington, C. Lax, D. G. Richards, W. Clegg and K. A. Fraser, in *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity*, ed. M. T. Pope and A. Müller, Kluwer, Dordrecht, 1994, p. 105; (*d*) A. Proust, R. Thouvenot, M. Chaussade, F. Robert and P. Gouzerh, *Inorg. Chim. Acta*, 1994, **224**, 81; (*e*) W. Clegg, R. J. Errington, K. A. Fraser, S. A. Holmes and A. Schäfer, *J. Chem. Soc., Chem. Commun.*, 1995, 455; (*f*) J. L. Stark, A. L. Rheingold and E. A. Maatta, *J. Chem. Soc., Chem. Commun.*, 1995, 1165; (*g*) J. L. Stark, V. G. Young, Jr. and E. A. Maatta, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2547.
11 M. Che, M. Fournier and J. P. Launay, *J. Chem. Phys.*, 1979, **71**, 1954.
12 R. Neumann and M. Lissel, *J. Org. Chem.*, 1991, **56**, 5707; K. Nakayama, M. Hamamoto, Y. Nishiyama, and Y. Ishii, *Chem. Lett.*, 1993, 1699.
13 Y. Du, A. L. Rheingold and E. A. Maatta, *J. Chem. Soc., Chem. Commun.*, 1994, 2163.
14 Y. Du, Ph.D. Thesis, Kansas State University 1992.

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