Molybdenum-Allyloxo and -Allylamido Complexes as Models for the Catalytic Surface Intermediates of the Oxidation of Propene to Acrolein and Acrylonitrile

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Molybdenum(VI)-allyloxo and -allylamido complexes with oxo or imido ancillary ligands are synthesized and shown to decompose under mild conditions to acrolein and allylideneamine, respectively, with dimeric Mo^{V} compounds as the other products; the analogies between these results and those proposed for the mechanism of the oxidation and ammoxidation of propene are discussed.

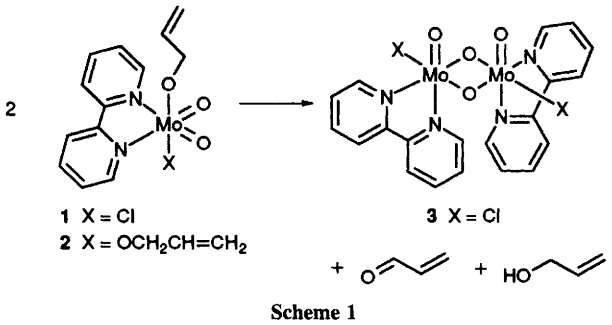
The oxidation of propene to acrolein [eqn. (1)] and the ammoxidation of propene to acrylonitrile [eqn. (2)] using heterogeneous mixed oxide catalysts have found important industrial applications such as in the SOHIO process.[1,2]

$$CH_2{=}CHMe + O_2 \xrightarrow[300\text{–}450\,^{\circ}C]{Bi_2O_3/MoO_3} CH_2{=}CHCHO + H_2O \quad (1)$$

$$CH_2{=}CHMe + NH_3 + 3/2\,O_2 \xrightarrow[400\text{–}460\,^{\circ}C]{Bi_2O_3/MoO_3} CH_2{=}CHCN + 3\,H_2O \quad (2)$$

Compelling evidence for the mechanism of these reactions has been obtained[3] from careful kinetic, isotopic labelling and chemical probe studies. In the absence of the direct characterization of the surface intermediates, further understanding of the catalytic chemistry involved may, however, be substantiated by studies on related, well-defined molecular systems. Modelling of certain of the reaction steps has already been carried out.[4,5] We present here high oxidation state molybdenum-allyloxo and -allylamido complexes and the formation of organic products therefrom, which may be considered as mimicking the purported surface intermediates and the so-called second allylic hydrogen abstraction steps[3] of the heterogeneous processes.

By reacting MoO_2Cl_2 with $LiOCH_2CH{=}CH_2$ (1 or 2 equiv.) in $MeCN/Et_2O$ at −30 °C, followed by filtration of LiCl and addition of bipyridyl (bipy) (1 equiv.), the complexes $[MoO_2(OCH_2CH{=}CH_2)X(bipy)]$ [X = Cl **1**, $OCH_2CH{=}CH_2$



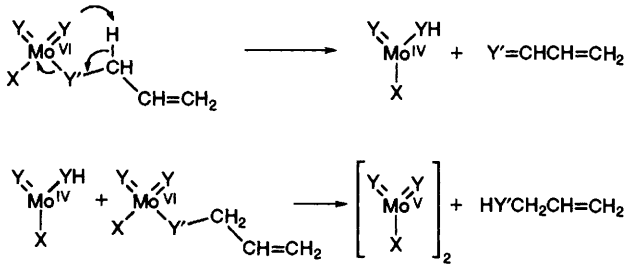
Scheme 1

2†] can be separated in high yield as white powders after the appropriate work up. Their NMR spectra‡ are in accord with an octahedral structure (Scheme 1), previously observed in related compounds.[6,7] The acetonitrile adducts $[MoO_2(OCH_2CH{=}CH_2)X(MeCN)_2]$ formed before addition of bipy were too unstable at room temp. to be fully characterized. The decomposition of the bipy adducts at 65 °C in CD_3CN, followed by ^1H NMR (Fig. 1) and GC, showed the conversion of **1** into acrolein (*ca.* 0.5 equiv.), allyl alcohol (*ca.* 0.5 equiv.) and a brown precipitate identified by elemental analysis and X-ray diffraction[8] as being essentially pure $[Mo^{V}O_2Cl(bipy)]_2$[9] (**3**,† 90% yield, Scheme 1).

For **2**, the corresponding process is slower and less clean, producing allyl alcohol (*ca.* 0.8 equiv.) and acrolein (*ca.* 0.4 equiv.) along with a mixture of organometallic products. With pyridine as solvent the Mo^{V}-allyloxo compound $[MoO_2(OCH_2CH{=}CH_2)Py]_4$ **4** was obtained albeit in low yield (10%), and characterized crystallographically.[8] Further observations on these reactions show that: (*i*) the initial rate of decomposition in CD_3CN shows an essentially first-order dependence on the concentration of **2**. The addition of an excess of bipy (4 equiv.) reduces this rate by a factor of two indicating that dissociation of bipy is probably involved and that the tetracoordinated species thus obtained is more susceptible to decomposition than the parent octahedral complex. (*ii*) The relative order of the initial rates of decomposition is: $[MoO_2(OCH_2CH{=}CH_2)Cl(CD_3CN)_2]$ > $[MoO_2(OCH_2CH{=}CH_2)_2(CD_3CN)_2]$ > $[MoO_2(OCH_2CH{=}CH_2)Cl(bipy)]$ **1** > $[MoO_2(OCH_2CH{=}CH_2)_2(bipy)]$ **2**. We see that chloro-allyloxo complexes such as **1**, despite forming stronger octahedral adducts, decompose more rapidly than the corresponding bis allyloxo compounds such as **2**. This suggests that the redox reaction is also favoured by electron deficiency at the metal centre, consistent with greater stabilization of the Mo^{VI} centre by the presence of the additional stronger π-donor allyloxo ligand.

The analogous bis imido complex $[Mo(NBu^t)_2(OCH_2CH{=}CH_2)Cl(bipy)]$ **5**†‡ is obtained similarly as a yellow powder from $[Mo(NBu^t)_2Cl_2]$[10] in Et_2O at 25 °C, but readily loses its bipy ligand in solution. $[Mo(NBu^t)_2(OCH_2CH{=}CH_2)_2]$ **6** and $[Mo(NBu^t)_2(OCH_2CH{=}CMe_2)_2]$ **7**† were also synthesised‡ and do not form stable bipy (or MeCN) adducts. Complexes **5–7** are much more stable than the corresponding bis oxo species **1**, **2**, needing one day to decompose at 65 °C in CD_3CN. The presence of the strongly σ and π-donating NBu^t ligands clearly impedes the oxidation of the allyloxo ligands by the Mo^{VI} centre. The only organic products detected are the allylideneamines $Bu^tN{=}CHCH{=}CH_2$ or $Bu^tN{=}CHCH{=}CMe_2$ (0.6 equiv.). We propose that, as for the bis oxo compounds, formation of acrolein (or prenal) and Mo^{IV} occurs in a first stage, but the product aldehyde reacts rapidly with an imido ligand of **5–7** to yield the allylideneamine and the oxo-imido Mo^{VI} analogue.[11] Indeed, it was shown in separate experiments that acrolein reacts rapidly even at room temp. with **5–7** to give allylideneamine. Further, **5–7** give rise to an increasing rate of decomposition with time, which is consistent with such an additional process leading to an oxo-imido Mo^{VI} intermediate which decomposes more rapidly than the parent bis imido Mo^{VI} complex. Allyl migration from the oxygen of an allyloxo ligand to the nitrogen of an imido ligand to form an allylamido complex[4a] seems excluded here, although such [3,3]sigmatropic shifts have been established in other complexes of this type.[12] Indeed the non-rearranged allylideneamine $Bu^tN{=}CHCH{=}CMe_2$ is obtained from **7**. Allyl alcohol also reacts with the imido ligands[13] in **5–7**, which explains its unexpected absence as organic product as well as the formation of a mixture of unidentified inorganic complexes obtained in these cases.

The analogous allylamido complexes $\{Mo(NR)_2[N(Ph)CH_2CH{=}CH_2]_2\}$ (R = Bu^t **8**,† Ph **9**‡) can be obtained from $Mo(NR)_2Cl_2$ and $LiN(Ph)CH_2CH{=}CH_2$ (2 equiv.) in Et_2O at −30 °C, and recrystallised from pentane to give yellow needles **8** or a brown solid **9**. These are in turn even more stable than **5–7**, total decomposition of **8** in CD_3CN being only achieved after 3 days at 80 °C. The formation of $PhN{=}CHCH{=}CH_2$ and $HPhNCH_2CH{=}CH_2$, taken with the faster decomposition of the more electron deficient **9** (1 day at 80 °C) relative to **8**, would seem to indicate that the oxidation mechanisms involved for the allylamido and allyloxo complexes are very similar.



Scheme 2

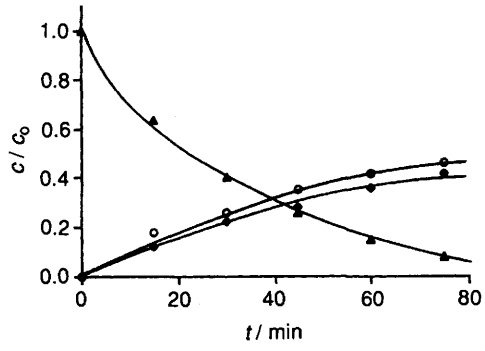


Fig. 1 Conversion of $MoO_2(OCH_2CH{=}CH_2)Cl(bipy)$ **1** into acrolein (◆) and allyl alcohol (○) in $CDCl_3$ ($c = 5 \times 10^{-2}$ mol dm^{-3}) at 65 °C

† Satisfactory analysis has been obtained.

‡ *Spectral data*: ^1H NMR at 200 MHz, δ relative to $SiMe_4$, multiplicity, relative intensity, coupling constant and assignment,[a] in CD_2Cl_2,[b] in $CDCl_3$,[c] in CD_3CN.

1[a]: 9.44 (d, 2H, bipy); 8.42 (d, 2H, bipy); 8.27 (t, 2H, bipy); 7.80 (t, 2H, bipy); 5.55 (m, 1H, $^3J_{HbHa}$ 6, $^3J_{HbHc}$ 11, $^3J_{HbHt}$ 16 Hz, $=CH_b-$); 4.68 (d, 1H, $^3J_{HtHb}$ 16 Hz, $=CH_cH_t$); 4.66 (d, 1H, $^3J_{HcHb}$ 11 Hz, $=CH_cH_t$); 4.36 (d, 2H, $^3J_{HaHb}$ 6 Hz, $-CH_{a2}-$).

2[b]: 9.50 (d, 2H, bipy); 8.46 (d, 2H, bipy); 8.28 (t, 2H, bipy); 7.80 (t, 2H, bipy); 5.55 (m, 1H, $^3J_{HbHa}$ 6, $^3J_{HbHc}$ 10.5, $^3J_{HbHt}$ 17.5 Hz, $=CH_b-$); 4.78 (d, 1H, $^3J_{HcHb}$ 10.5 Hz, $=CH_cH_t$); 4.75 (d, 1H, $^3J_{HtHb}$ 17.5 Hz, $=CH_cH_t$); 4.58 (d, 2H, $^3J_{HaHb}$ 6 Hz, $-CH_{a2}-$).

5[a]: 9.46 (d, 2H, bipy); 8.42 (d, 2H, bipy); 8.21 (t, 2H, bipy); 7.74 (t, 2H, bipy); 5.59 (m, 1H, $=CH-$); 4.75 (d, 1H, $=CH_2$); 4.68 (d, 1H, $=CH_2$); 4.46 (d, 2H, $-CH_2-$); 1.60 (s, 18H, CMe_3).

6[c]: 6.00 (m, 1H, $=CH-$); 5.24 (d, 1H, $=CH_2$); 5.05 (d, 1H, $=CH_2$); 4.74 (d, 2H, $-CH_2-$); 1.41 (s, 9H, CMe_3).

7[b]: 5.48 (t, 2H, $=CH-$); 4.74 (d, 4H, $-CH_2-$); 1.67, 1.57 (2s, 12H, $=CMe_2$); 1.39 (s, 18H, CMe_3).

8[c]: 7.21 (m, 4H, Ph); 6.86 (m, 1H, Ph); 6.02 (m, 1H, $^3J_{HbHa}$ 6, $^3J_{HbHc}$ 10.5, $^3J_{HbHt}$ 17.5 Hz, $=CH_b-$); 5.25 (d, 1H, $^3J_{HtHb}$ 17.5 Hz, $=CH_cH_t$); 5.15 (d, 1H, $^3J_{HcHb}$ 10.5 Hz, $=CH_cH_t$); 4.96 (d, 2H, $^3J_{HaHb}$ 6 Hz, $-CH_{a2}-$); 1.28 (s, 9H, CMe_3).

9[c]: 7.02 (d, 2H, Ar); 6.90 (t, 1H, Ar); 5.40 (t, 1H, $^3J_{HH}$ 9 Hz, $=CH-$); 4.42 (d, 2H, $^3J_{HH}$ 9 Hz, $-CH_2-$); 2.42 [s, 6H, $CH_3(Ar)$]; 1.60, 1.28 (2s, 6H, $=CMe_2$); 1.02 (s, 9H, CMe_3).

These observations are consistent with a single mechanism for the decomposition of these three types of complexes (Scheme 2), ignoring the bipy decoordination/recoordination steps involved for **1**, **2** and **5**. In a first intramolecular rate-determining step[14] a 1,4 H-shift occurs to Mo=O (or Mo=NR)[15] with formation of acrolein or allylideneamine and a Mo^{IV} species in an overall two-electron process. We favour transfer to Y (O or NR) rather than to X since H transfer to chloride in **1** seems most improbable. The 1,4-H shift occurs more easily from allyloxo than from allylamido ligands, and transfer to Mo=O is favoured over Mo=NR. The oxo is preferred over imido as a spectator ligand for this transfer. This models the catalytic surface mechanism which involves an identical step although a $Mo^{V} \rightarrow Mo^{III}$ redox couple was implicated in this case. The ligand effects on reactivity appear to correlate well with the catalytic results,[3] both heterogeneous and homogeneous processes being more facile with an oxygen-rich ligand environment (*i.e.* the presence of oxo and allyloxo groups) than with nitrogenated ligands.

The second step of Scheme 2 involves the intermolecular reaction of the reactive Mo^{IV} intermediate with the initial Mo^{VI} complex to yield a dimeric Mo^{V} compound and liberate allyl alcohol or allylamine.

These model studies also suggest new mechanistic proposals, although care must be taken in the extrapolation of solution results to surface chemistry given the enormous difference in reaction conditions. In particular, the formation of allylideneamines, either by the reaction of initially produced acrolein with imido ligands, or by the direct dehydrogenation of allylamido ligands, suggests that these molecules may be formed as intermediates in the ammoxidation of propene. From our results the acrolein/allylideneamine route would appear to be the most favourable, the allylideneammonia $HN{=}CHCH{=}CH_2$ being expected to interact further with the catalytic surface to yield allylideneamido species,[5] which would undergo further hydrogen abstraction leading to acrylonitrile. We are currently investigating such possibilities.

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