Probing the catalytic oxidation of alcohols *via* an anionic dimolybdate centre using multistage mass spectrometry

Tom Waters, Richard A. J. O'Hair* and Anthony G. Wedd

School of Chemistry, University of Melbourne, Parkville, Victoria 3052, Australia.
E-mail: r.ohair@chemistry.unimelb.edu.au

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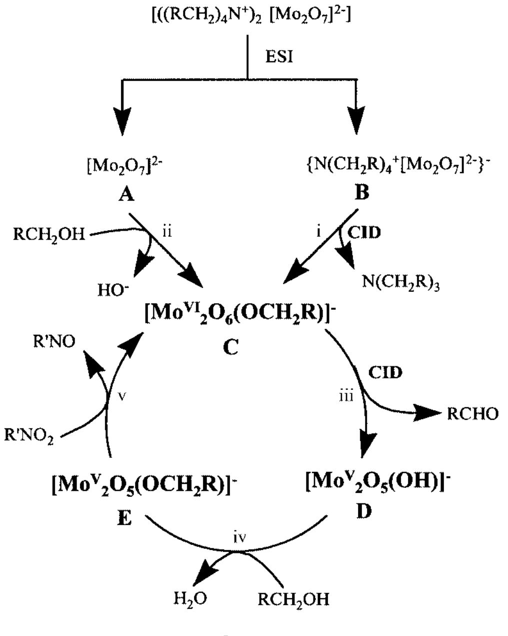
Multistage mass spectrometry experiments in a quadrupole ion trap combined with isotope labelling have revealed a novel gas phase catalytic cycle for the oxidation of alcohols *via* an anionic dimolybdate centre.

We report the catalytic oxidation of alcohols in the gas phase using a dimolybdate anion as the active species. The nature of each step in the catalytic cycle can be probed through (i) multistage mass spectrometry experiments using a modified quadrupole ion trap mass spectrometer[1] and (ii) isotope substitution experiments which involve labelling of neutral reagents and the dimolybdate centre.

Complex reactivity of alcohols in the gas phase has been observed for highly unsaturated transition metal ionic species,[2,3] including oxo–molybdenum cations.[2] In contrast, the present study demonstrates 'simple' modes of reactivity with an oxo–molybdenum anion which allow catalytic behaviour. The observation by multistage mass spectrometry of true gas phase oxidation catalysed by transition metal ions remains rare.[4] In addition, the present system may shed light on the industrial oxidation of methanol to formaldehyde as catalysed by amorphous solid state molybdate catalysts.[5] A detailed molecular understanding of the mechanisms of this process remains elusive.[6]

Quaternary ammonium salts of the dimolybdate anion in MeCN can be transferred to the gas phase *via* electrospray ionisation.[7] The main species observed are the dianion, $[Mo_2O_7]^{2-}$ **A** and the ion pair, $\{N(CH_2R)_4{}^+[Mo_2O_7]^{2-}\}^-$ **B**.[8] Both these species can act as precursors of $[Mo_2O_6(OCH_2R)]^-$ **C** which catalyses the oxygen atom transfer reaction (1) (Scheme 1; R = alkyl, R′ = aryl, alkyl):

$$RCH_2OH + R'NO_2 \rightarrow RCHO + H_2O + R'NO \qquad (1)$$



Scheme 1

Collision induced dissociation (CID) of **B** initiates an ion pair S_N2 reaction,[9] resulting in loss of trialkylamine and O-alkylation of **A** to form an alkylated dimolybdate species, **C** (Scheme 1(i)). Note that: (i) this is the first report of an ion pair S_N2 reaction involving an inorganic dianion and a tetraalkylammonium cation (*cf.* ref. 10) and (ii) thermolysis of trialkyloxonium salts of $[PMo_{12}O_{40}]^{3-}$ in the condensed phase also results in S_N2 O-alkylation.[11]

Gas phase ion–molecule reactions of **A**with various alcohols also yields **C**.[12] Labelling studies with $CH_3{}^{18}OH$ clearly reveal that this is not an S_N2 reaction (Fig. 1(a)). Rather, deprotonation of alcohol by a terminal oxo ligand[13] is followed by displacement of the resultant hydroxo ligand by the alkoxy anion (Scheme 1(ii), Table 1).

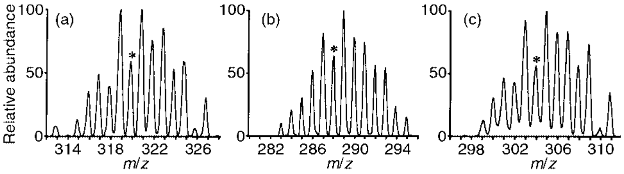


Fig. 1 Expansion of the isotope patterns for key product ions from gas phase reactions involving ^{18}O labelling experiments. The central peak of lower intensity in the isotope pattern is denoted by an asterisk, and is used to evaluate the outcome of the reaction. The numbering of the species and reactions is as according to Scheme 1. (a) shows that the product ion **C** from reaction (ii) is $[Mo_2O_6(^{18}OMe)]^-$; (b) shows that $[Mo_2O_6(^{18}OMe)]^-$ loses $CH_2{}^{18}O$ in reaction (iii), with concomitant formation of the product ion **D** $[Mo^V{}_2O_5(OH)]^-$; (c) shows that the product ion **E** from reaction (iv) is $[Mo^V{}_2O_5(^{18}OMe)]^-$.

CID of the alkylated dimolybdate species **C** results in reductive elimination of the alkoxo ligand as the aldehyde (Scheme 1(iii)). This corresponds to the formal redox half reaction: $RCH_2O^- \rightarrow RCHO + H^+ + 2e^-$. In the complementary half reaction, the dimolybdate(VI) centre is reduced by 2e⁻ and protonated to form $[Mo^V{}_2O_5(OH)]^-$ **D**. Labelling studies indicate that the oxygen from the alkoxo ligand is lost in this step (*i.e.* $CH_2{}^{18}O$ is lost; Fig. 1(b), Table 1).

The cycle is continued when **D** rapidly reacts with alcohol to form $[Mo^V{}_2O_5(OCH_2R)]^-$ **E** (Scheme 1(iv)). Once again the labelling studies reveal that this is not an S_N2 reaction (Fig. 1(c)), but rather a gas phase esterification reaction.

To complete the cycle, **E** is oxidised *via* an oxygen atom transfer to regenerate **C** (Scheme 1(v)). This reaction requires the presence of a second neutral reagent (along with alcohol) in the ion trap. To date we have used *m*-fluoronitrobenzene and nitromethane (*i.e.* $R'NO_2$ where R′ is Me or *m*-C_6H_4F) as oxygen atom donors.[14] Injection of $R'NO_2$ in the absence of alcohol indicates that oxygen atom transfer to **D** is also possible. This pathway does not compete with reaction (v) in Scheme 1 in the presence of alcohol owing to the fast rate of esterification.[15]

The present system raises questions about the mechanism(s) involved in the industrial oxidation of alcohols as catalysed by solid state molybdate catalysts.[5,6] In particular, can a related cycle (*cf.* reactions (iii)–(v) of Scheme 1) be applied to the layer compound $Mo_2O_5(OMe)_2$, proposed as a model heterogeneous

Table 1 Ionic products from reactions of $[Mo_2O_7]^{2-}$ **A** and $\{NBu_4^+[Mo_2O_7]^{2-}\}^-$ **B** under multistage mass spectrometry conditions

	m/z of ionic products from reaction sequence:[a,b]				
Alcohol	**A**	$\xrightarrow[\text{reaction (ii)}]{\text{MS}^2}$ **C**	$\xrightarrow[\text{reaction (iii)}]{\text{MS}^3}$ **D**	$\xrightarrow[\text{reaction (iv)}]{\text{MS}^4}$ **E**	$\xrightarrow[\text{reaction (v)}]{\text{MS}^5}$ **C**
CH_3OH	151.5	318	288	302	318
CH_3OD[c]	151.5	318	288	302	318
CD_3OD[d]	151.5	321	289	305	321
$CH_3{}^{18}OH$[e]	151.5	320	288	304	320
EtOH	151.5	332	288	316	332
Pr^nOH	151.5	346	288	330	346
	B	$\xrightarrow[\text{reaction (i)}]{\text{MS}^2}$ **C**	$\xrightarrow[\text{reaction (iii)}]{\text{MS}^3}$ **D**	$\xrightarrow[\text{reaction (iv)}]{\text{MS}^4}$ **E**	$\xrightarrow[\text{reaction (v)}]{\text{MS}^5}$ **C**
CH_3OH	546	360	288	302	318
CH_3OD	546	360	288	302	318
CD_3OD	546	360	288	305	321
$CH_3{}^{18}OH$	546	360	288	304	320
EtOH	546	360	288	316	332
Pr^nOH	546	360	288	330	346

[a] *m/z* refers to the central peak of lower intensity in the isotope pattern. [b] Refer to Scheme 1 for labelling of ionic species. [c] A sample from Cambridge Isotope Laboratories (99% D). [d] A sample from Cambridge Isotope Laboratories (99.9% D). [e] A sample from Isotec (95%^{18}O).

catalyst?[6] Given its layer structure features alternating *trans*-$Mo^{VI}O(OMe)$ centres separated by bridging oxo ligands, a simple mechanism can be devised for the oxidation of MeOH to H_2CO involving two Mo^{VI} sites on adjacent layers. This accommodates the fact that O_2 transfers two O atoms (eqn. (2)), rather than the single O atom from $R'NO_2$ (eqn. (1))

$$2\ \text{MeOH} + O_2 \rightarrow 2\ CH_2O + H_2O \qquad (2)$$

Further gas phase work is underway to examine (i) whether larger polyoxoanions also catalyse the oxidation of alcohols; (ii) the behaviour of other oxygen atom transfer reagents (*e.g.* O_2); (iii) models of oxo–molybdenum and –tungsten enzymes which catalyse oxygen atom transfer reactions.[16]

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Notes and references

1 *Practical Aspects of Ion Trap Mass Spectrometry*, ed. R. E. March and J. F. J. Todd, CRC Press, Boca Raton, FL, 1995: (*a*) vol. 1 *Fundamentals of Ion Trap Mass Spectrometry*; (*b*) vol. 2 *Ion Trap Instrumentation*. The operation of the modified instrument has been described previously: G. E. Reid, R. J. Simpson and R. A. J. O'Hair, *Int. J. Mass Spectrom.*, 1999, **190**/**191**, 209.

2 E. F. Fialko, A. V. Kikhtenko and V. B. Goncharov, *Organometallics*, 1998, **17**, 25.

3 I. K. Gregor and R. C. Gregor, *J. Organomet. Chem.*, 1995, **486**, 109 and references cited therein.

4 For FTICR studies on catalytic oxidation of (*a*) olefins, see: D. Stockigt and H. Schwarz, *Liebigs. Ann.*, 1995, 429; (*b*) CO, see: E. F. Fialko, A. V. Kikhtenko, V. B. Goncharov and K. I. Zamaraev, *Catal. Lett.*, 1996, **41**, 7.

5 H. R. Gerberich, A. L. Stautzenberger and W. C. Hopkins, *Formaldehyde*, in *Kirk-Othmer Encyclopedia of Chemical Technology*, ed. M. Grayson and D. Eckroth, Wiley, New York, 3rd edn., 1980, vol. 11, pp. 231–250.

6 E. M. McCarron, R. L. Harlow, Z. G. Li, C. Suto and Y. Yuen, *J. Solid State Chem.*, 1998, **136**, 247 and references therein.

7 Electrospray solutions were made to 0.1 g mL^{-1} in MeCN. Typical ESI conditions: Sheath gas flow rate 50 (arbitrary units), auxilliary gas flow rate 0 (arbitrary units), spray voltage 3 kV, capillary temp. 100 °C, capillary voltage –5 V, tube lens offset –5 V.

8 For previous studies on ESI/MS of polyoxoanions, see: T.-C. Lau, J. Wang, R. Guevremont and K. W. M. Siu, *J. Chem. Soc., Chem. Commun.*, 1995, 877.

9 We have also observed gas phase S_N2 reactions of **A** with neutral reagents such as MeI and Me_3SiCl.

10 S. Gronert and J. Azebu, *Org. Lett.*, 1999, **1**, 503.

11 W. H. Knoth and R. D. Farlee, *Inorg. Chem.*, 1984, **23**, 4765.

12 A range of molybdenum alkoxides $[Mo_2O_6(OCH_2R)]^-$ **C** where R = H, Me, Et or Pr^n can be 'synthesised' using reactions (i) and (ii) of Scheme 1. We have also discovered an alternative gas phase synthesis, involving a gas phase ion–molecule 'transesterification' reaction whereby one alkoxo ligand is replaced by another. Unfortunately the related *tert*-butoxide $[Mo_2O_6(OBu^t)]^-$ is unavailable presently owing to the poor volatility of Bu^tOH.

13 We have also synthesised a dimolybdate centre in which the six terminal oxo ligands are labelled with ^{18}O (for related O isotope labelling studies of polyoxoanions, see: G. D. Hinch, D. E. Wycoff and R. K. Murmann, *Polyhedron*, 1986, **5**, 487). Upon reaction of labelled **A** with $CH_3{}^{16}OH$ a mass increase of 13 Da was observed (*cf.* 15 Da with unlabelled **A**) indicating loss of a terminal oxo ligand with $^{18}OH^-$.

14 For a review on related oxygen atom transfer reactions, see: R. H.Holm and J. P. Donahue, *Polyhedron*, 1993, **12**, 571.

15 Neutral reagents were injected at a flow rate of 3 μL min^{-1} at a split of 1:5000 in the ratio RCH_2OH: $R'NO_2$ = 4:1. At these conditions, reaction of $[Mo^V{}_2O_5(OH)]^-$ with EtOH and *m*-$FC_6H_4NO_2$ results in the formation of $[Mo^V{}_2O_5(OEt)]^-$ (*m/z* 316, from esterification) at the almost complete exclusion of $[Mo^{VI}{}_2O_6(OH)]^-$ (*m/z* 304, from oxidation). This confirms oxygen atom addition to $[Mo^V{}_2O_5(OH)]^-$ does not compete with esterification. All MS^n experiments were carried out using a *Q* value of 0.25. Ion-molecule reactions times were typically: reaction (ii) = 5 s; reaction (iv) = 20 ms; reaction (v) = 200 ms. Typical CID reactions were carried out for 30 ms using the following activation amplitudes: reaction (i) = 0.75 V; reaction (iii) = 0.65 V.

16 C. G. Young and A. G. Wedd, *Chem. Commun.*, 1997, 1251.

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