

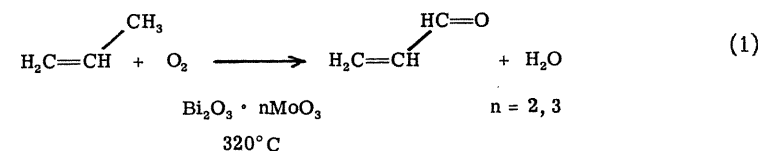
## Active Sites on Molybdate Surfaces, Mechanistic Considerations for Selective Oxidation, and Ammoxidation of Propene

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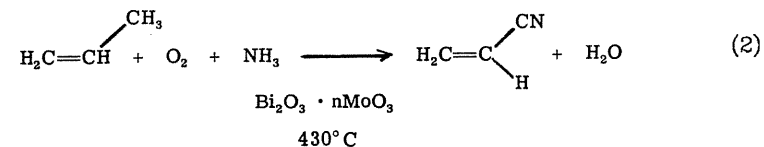
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Molybdates involving various metal additives play a dominant role in such industrially important catalytic processes as selective oxidation (propene to acrolein) and ammoxidation (propene to acrylonitrile); however, the details of the reaction mechanism and of the surface sites responsible are yet quite uncertain. In order to establish the thermochemistry and detailed mechanistic steps involved with such reactions, we have performed *ab initio* quantum chemical calculations [generalized valence bond (GVB) and configuration interaction (CI)]. These studies indicate a special importance of multiple surface dioxo Mo sites (possessing two Mo-O double bonds and hence spectator oxo groups) arranged together so as to provide the means for promoting the sequence of transformations.

Various catalysts based on molybdates have been used both for *selective oxidation of propene to acrolein*



and *ammoxidation of propene to acrylonitrile*,



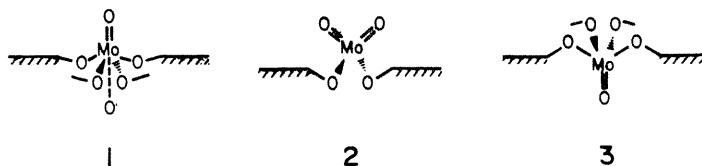
Numerous experimental studies have provided mechanistic information about these catalytic reactions; however, there are as yet many uncertainties concerning the character of the active site and its relation to the details of the mechanism. In this paper we will use the results of *ab initio*

quantum chemical calculations [generalized valence bond (GVB) and configuration interaction (CI)] to help analyze the details of the reaction mechanisms and the relation of various reaction steps to specific surface sites.

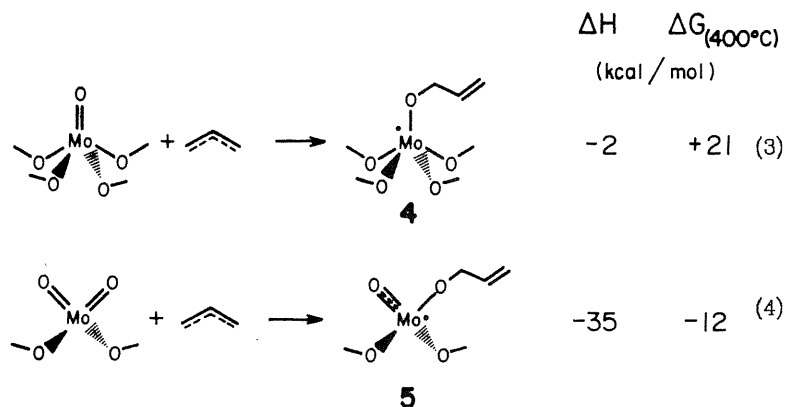
In the following sections we discuss the principle of spectator oxo promotion that we find to play a crucial role in promoting particular reaction steps; we then examine the details of selective oxidation; and, finally, we outline preliminary results on ammoxidation.

### Spectator Oxo Effects

Molybdates lead to bulk structures involving either octahedral or tetrahedral coordination of oxygens about each Mo. On various surfaces, the most stable configurations for such molybdates are likely to be

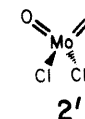


where **1** and **3** correspond to bulk octahedral sites and **2** to bulk tetrahedral sites. Here there are four (**1**) and (**3**) or two (**2**) single bonds to oxygen atoms that have a single bond to another Mo center, and one (**1**) and (**3**) or two (**2**) double bonds to oxygens that are not bonded to other Mo atoms. Typically the M-O single bond lengths are  $\sim 1.95$  Å and the Mo-O double bond lengths are 1.67 to 1.73 Å. In addition, the octahedral site **1** would have a sixth oxygen neighbor at 2.2 to 2.4 Å (**1**). All three surface structures are formally  $\text{Mo}^{\text{VI}}$  and all involve Mo-O double bonds. However, we find that these species lead to extremely different chemistry. Thus, in selective oxidation of propene, a critical step is trapping of an allyl radical at an Mo=O bond. However, we find that only for species **2** is this process strongly exothermic.



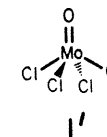
This remarkable difference arises from the spectator oxo effect (2,3), as discussed below.

Figure 1 shows the bonding for **2'**



as a model of **2**. Here we see that each Mo=O bond has the form of a covalent double bond involving spin pairing of two singly-occupied Mo d orbitals and two singly-occupied O p orbitals. Denoting the Mo=O axis as z and the  $\text{MoO}_2$  plane as yz, the Mo-O sigma bond involves Mo  $d_{z^2}$  and O  $p_z$  orbitals, while the Mo-O pi bond involves Mo  $d_{xz}$  and O  $p_x$  orbitals. Two such double bonds require four electrons in four orthogonal Mo d orbitals. On the other hand, the two Mo-Cl bonds (modeling single bonds to bridging oxygens in molybdates) involve a large amount of ionic character with some 5s-5p character on the Mo. Thus the  $\text{Mo}^{\text{VI}}$  center in **2** should be best visualized in terms of ionic bonds to the two bridging oxygens, while the Mo=O bonds should be considered as covalent double bonds. The requirement of two singly-occupied d orbitals for each Mo=O bond leads to an O=Mo=O angle of  $106^\circ$  (the  $\pi$  bonds would prefer  $90^\circ$ ; the  $\sigma$  bonds,  $125^\circ$ ) (**3**). In addition to the two singly-occupied p orbitals involved in the Mo=O bond, each oxygen has four valence electrons in two nonbonding orbitals (mixture of O 2s and O 2p<sub>y</sub>).

The bonding is quite different when there is only one double bond, as indicated in Figure 2 (the orbitals are for **1'**)



where each Cl models the bridging oxygens of **1**). Here there are *two* pi bonds between Mo and O. Thus the Mo has a total of four ionic bonds to the four Cl, two singly-occupied  $d\pi$  orbitals ( $d_{xz}$  and  $d_{yz}$  if the Mo=O axis is z) used in the two Mo=O pi bonds and an empty  $d_{z^2}$  orbital. The two Mo=O pi bonds require two singly-occupied p $\pi$  orbitals on the oxygen ( $p_x$  and  $p_y$ ), leaving four electrons in the O 2s and O 2p<sub>z</sub> orbitals. With two electrons in O 2p<sub>z</sub> and none in Mo  $d_{z^2}$ , we obtain a Lewis base-Lewis acid bond in the sigma system, leading to a net bond involving six electrons (four from oxygen and two from Mo). [As indicated in Figure 2, there is some charge transfer from Mo to O in the  $\pi$  bonds and from O to Mo in the  $\sigma$  bond, but the net description remains a *six-electron* bond.] The result is a partial triple bond or a **super double bond** that is much stronger than the double bond of **2**. Why can't species **2** make two such super double bonds? The requirement is *two* singly-occupied metal pi orbitals ( $\pi_x$  and  $\pi_y$ ) for *each* super double bond so that there are just not enough Mo pi orbitals to go around (analogous to the difference between O=C=O with two *double* bonds and C=O with a partial triple bond about twice as strong).

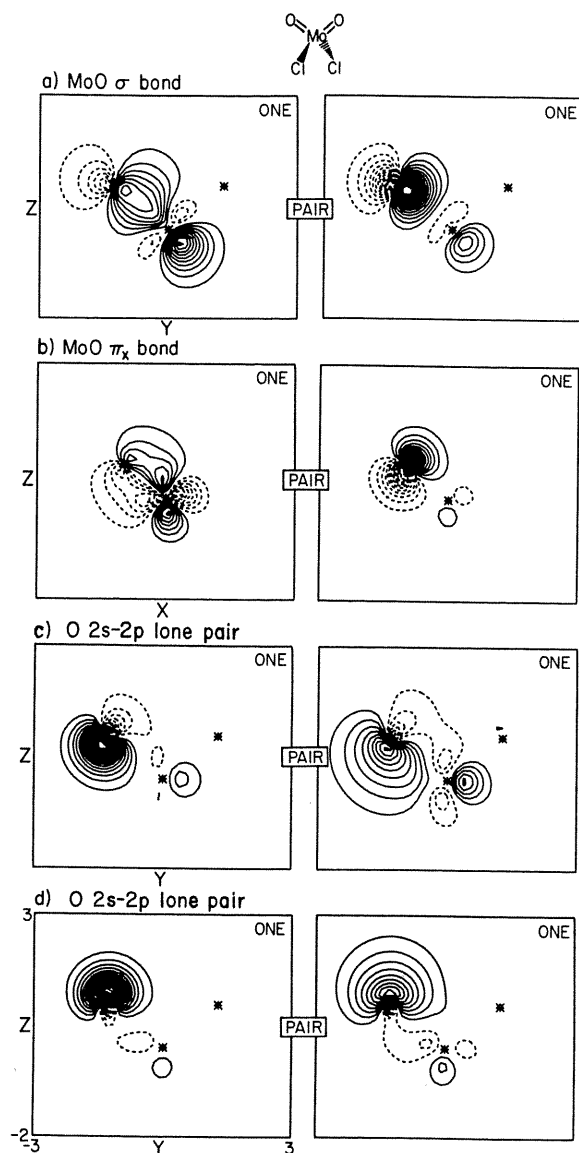


Figure 1. GVB orbitals for the four electron pairs involving the left Mo=O double in species 2. Dotted contours indicate negative amplitude. Increments between contours are 0.050 a.u.; the zero contour is not shown.

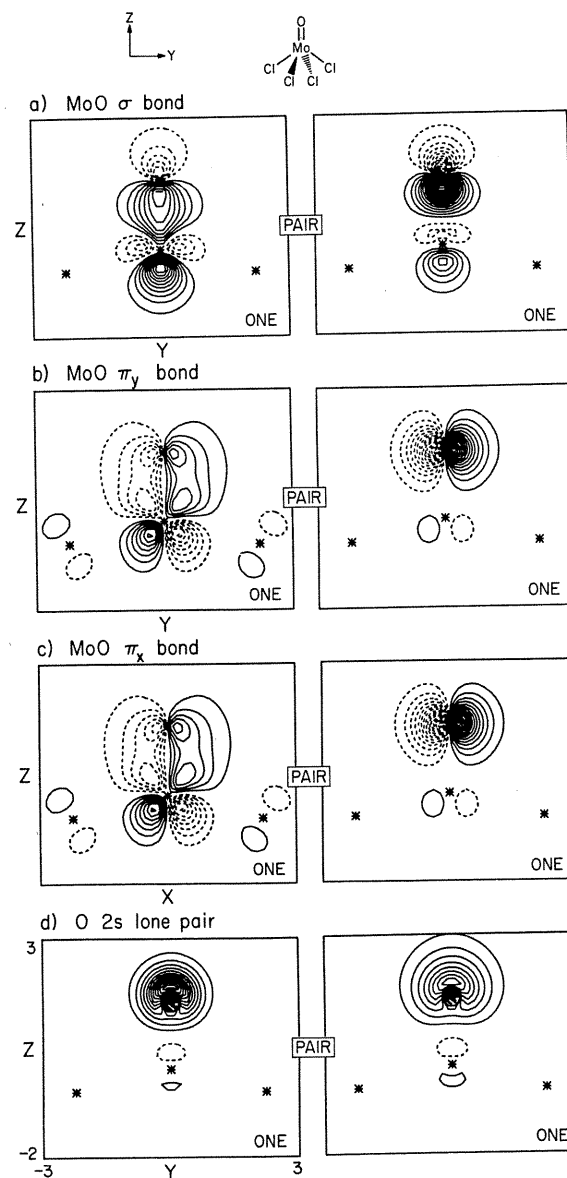
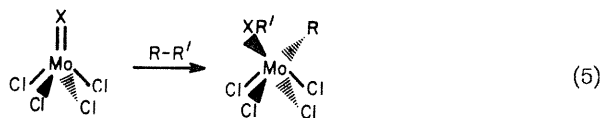


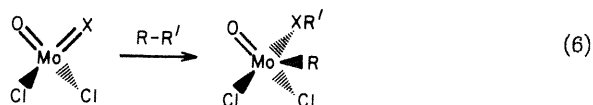
Figure 2. GVB orbitals for the four electron pairs involving the Mo=O super double bond for species 1. (Same plotting conventions as in Figure 1.)

Based on the above arguments, we expect reaction (4) to be much more favorable than reaction (3) because (3) involves attack on a stronger bond. However, there is a *second* equally important factor involved in the difference in reaction enthalpies for (3) and (4). The extra Mo=O bond of **2** would appear to be a spectator to reaction (4), but in fact it helps *promote* the reaction. The reason is that in the product, **5**, this spectator group is free to utilize two Mo d $\pi$  orbitals to form a super double bond, whereas in the reactant, **2**, the second Mo=O bond (the one involved directly in the reaction) requires one of these d $\pi$  orbitals. Thus the spectator Mo=O bond changes from a double bond to a super double bond when the allyl reacts with the *other* Mo=O bond. The net result then is that reaction (4) is more favored than (3) by 33 kcal.

This spectator oxo promotion is a general effect, so that considering

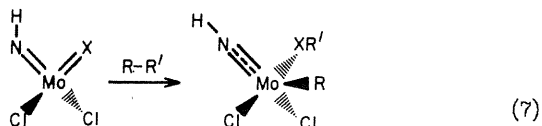


versus



the spectator oxo group promotes reaction at the adjacent double-bonded group in (6) by  $\approx 33$  kcal with respect to (5).

We find a similar but smaller spectator effect of  $\approx 16$  kcal for imido groups, promoting reactions such as



Thus, as shown in Figure 3, **6** has a (bent) Mo=NH double bond involving two singly-occupied N p orbitals (both perpendicular to the NH bond) paired up to form a sigma bond and a pi bond to the Mo (utilizing an Mo d $\pi$  orbital and an Mo d $\sigma$  orbital). Here the N 2s lone pair is not involved in bonding. However, for **7**, the Mo=NH bond is linear, leading to two Mo-N pi bonds. There is also a Lewis base-Lewis acid sigma bond between N and Mo; however, in this case it involves the N 2s pair (the N 2p $_z$  orbital being involved in the NH bond) rather than the pz pair as for O. The result is an Mo-NH super double bond about half as super as the Mo=O super double bond.

In the next section we will use this concept of the *spectator effect* in examining likely pathways for selective oxidation of propene to acrolein.

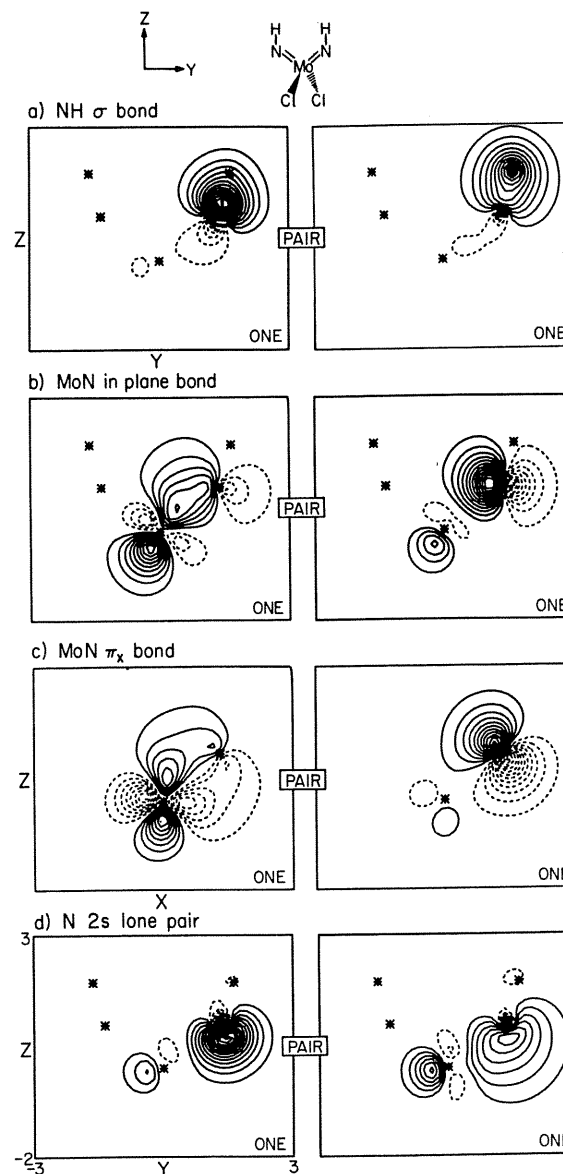
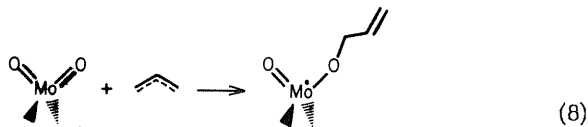


Figure 3. The GVB orbitals for the four electron pairs in the right Mo=NH bond of species **5**. (Same plotting conventions as in Figure 1.)

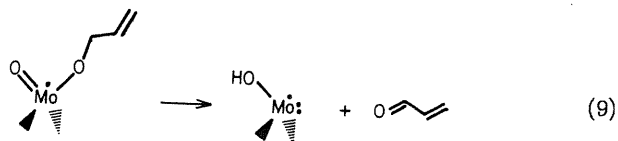
### Mechanistic Studies on Selective Oxidation

For selective oxidation (1) and ammoxidation (2) of propene by bismuth molybdates,

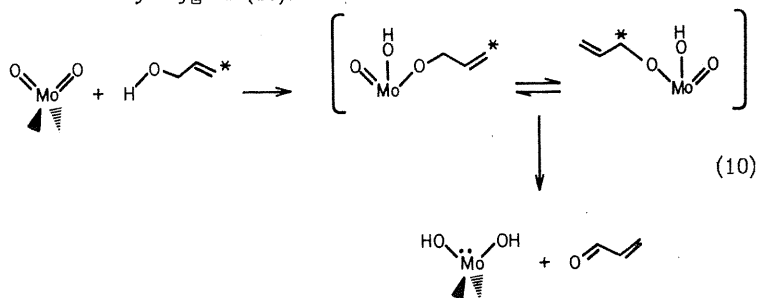
- i) it has been well established that the rate-determining step is allyl hydrogen abstraction to yield allyl radical (4,5),
- ii) it is generally acknowledged that the Bi oxide site is involved in this initial step since  $\text{Bi}_2\text{O}_3$  will abstract the H but does not do oxidation, while  $\text{MoO}_3$  will do oxidation of allyl but is ineffective at allyl H abstraction (6-9), and
- iii) Grasselli, Burrington, and co-workers (9) have proposed a detailed mechanism involving trapping of the allyl radical from (i) at a dioxo Mo site



followed by  $\beta$ -hydride elimination to form acrolein



As additional evidence for the role of the dioxo site, they carried out experiments using labeled allyl alcohol (rather than propene) that could be most simply interpreted in terms of reaction at a dioxo site followed by interchange of allyl between spectator oxo and alkoxy oxygens (10).



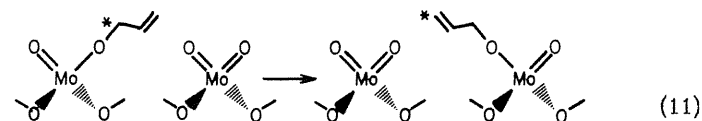
In order to explore further the details of these mechanisms, we calculated the energetics for some of the reaction steps.

Concerning trapping of an allyl at a surface molybdate site, we find that the process for the dioxo unit (4) is quite favorable, whereas the

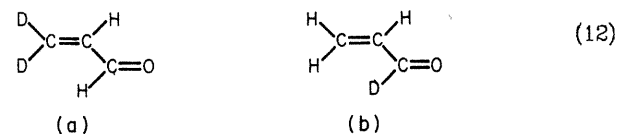
process for the monoxo unit (3) is less favorable. This results from the spectator oxo stabilization present in the dioxo unit and agrees with the basic tenet (8) of the Grasselli-Burrington mechanism. However, one-center steps such as (9) for propene and (10) for allyl alcohol involving reaction *with* the spectator oxo group are unfavorable. For example, the step in (9) is endothermic by  $\sim 45$  kcal and the step in (10) is endothermic by  $\sim 25$  kcal. As a result, we were led to the idea that the *collections of adjacent dioxo units* are critical to the selective oxidation process. \* This idea is illustrated in Figure 4 where step b corresponds to (8). Rather than the one-center process (10), we propose that the  $\beta$ -hydride abstraction is by an adjacent dioxo unit as in Figure 4c. The stabilization due to the spectator oxo group of the second center is critical in keeping the free energy charge negative.

The first question to ask concerning the mechanism in Figure 4 is whether the crystal structure is compatible with adjacent surface dioxo units. Figure 5 shows the (010) surface of  $\alpha\text{-Bi}_2(\text{MoO}_4)_3$  [corresponding to the parent Scheelite structure,  $\text{CaWO}_4$ ] (11). Here we see that there are adjacent dioxo centers along the crystal surface.

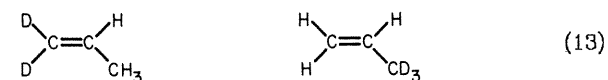
With these adjacent dioxo units, we would expect allyl transfer steps such as



to be facile. This should lead to equilibration of the C1 and C3 carbons and hence a fixed ratio of



regardless of whether the starting propene is



or whether the starting allyl alcohol is

\* This conclusion is buttressed by recent results that were reported after the original theoretical analysis and submission of our paper (11).

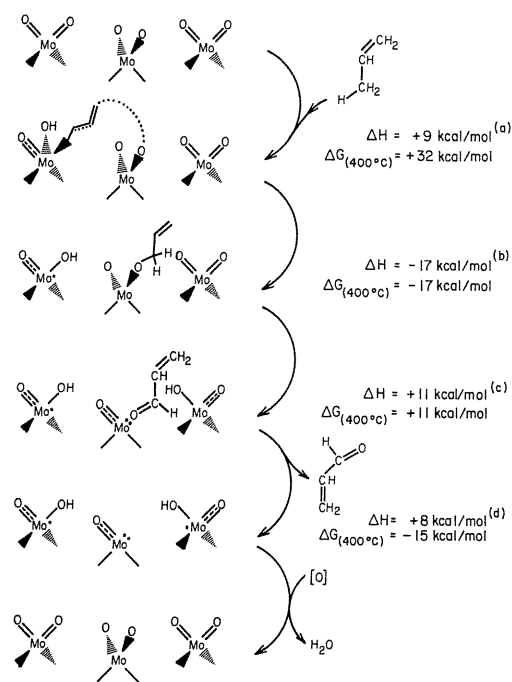


Figure 4. The multiple dioxo mechanism for selective oxidation.

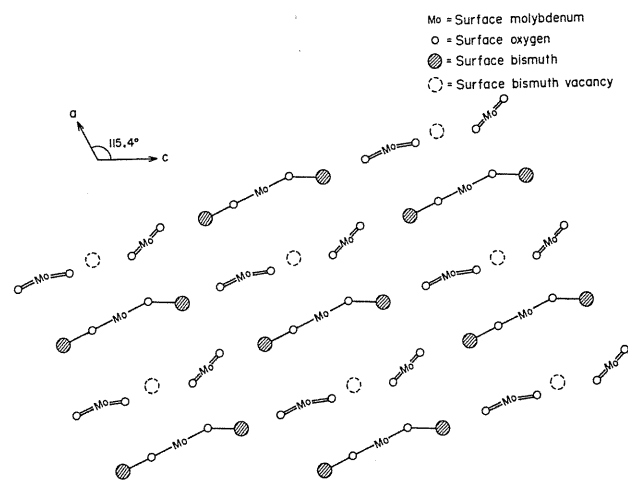
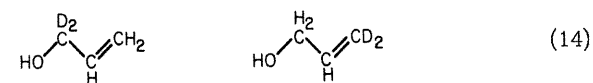


Figure 5. The (010) surface of  $\alpha\text{-Bi}_2(\text{MoO}_4)_3$  [corresponding to the (001) surface of the parent Scheelite structure,  $\text{CaWO}_4$ ].



This is consistent with abundant experimental evidence (Grasselli *et al.*) (9) that the ratio of products (12a) to (12b) is 70% to 30%, independent of starting material in (13) or (14).

It is important to note that  $\alpha\text{-Bi}_2(\text{MoO}_4)_3$  has this active site with adjacent Mo dioxo groups. Such sites do *not* exist in the parent Scheelite structure (8) ( $\text{CaWO}_4$ ), but with Bi, two adjacent Ca sites out of each six are vacant (indicated by dotted circles in Figure 5), leading to the special active site.

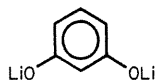
The availability of several adjacent Mo dioxo units suggests the possibility of step (a) in Figure 4 in activating the propene. It is generally accepted that this activation occurs on a Bi site since  $\text{MoO}_3$  is not effective in abstracting the allyl hydrogen. However, Bi is *essential* to the existence of the chain of Mo dioxo units in Figure 5, and hence it is possible that the activation is actually by a Mo dioxo unit that exists because of the Bi-induced vacancies and not actually on a Bi oxide site. These ideas are consistent with the fact that allyl iodide is readily converted to acrolein over *bismuth-free*  $\text{MoO}_3$ , while the conversion of propene to acrolein over  $\text{MoO}_3$  is inactive ( $\sim 2\%$  yield) (7). The C-I bond strength as in  $\text{C}_3\text{H}_5\text{I}$  is 43.5 kcal/mol, whereas the C-H bond strength as in  $\text{C}_3\text{H}_6$  is 87.5 kcal/mol (7). Therefore it may be postulated that an important differential factor in the breaking of the C-H bond of propene may be the extra stabilization needed that is provided by the Bi-induced configuration of Mo dioxo sites. This is supportive of the idea of nonadditivity of the active sites of the two separate oxides,  $\text{Bi}_2\text{O}_3$  and  $\text{MoO}_3$ , and the requirement for active sites of Bi, Mo, and O to act together (as a unit) for the conversion of propylene to acrolein (8).

The isotope studies (*vide supra*) have been used to establish that a  $\pi$ -allyl species is initially formed and, indeed, scrambling may occur at this stage (9). This may well be the case, and we cannot address the issue of  $\sigma$ -allyl versus  $\pi$ -allyl directly since we have not yet studied  $\pi$ -allyl complexes. However, the formation of  $\pi$ -allyl is *not required* in our mechanism. Equilibration via steps as in (12) involving only  $\sigma$ -allyls as stable species are mechanistically equivalent to  $\pi$ -allyl. [The energy estimates of Figure 4 do *not* include any special stabilization due to Bi.]

In Figure 4 we quote current estimates of the reaction enthalpies for the various steps in our mechanism. There are numerous uncertainties here (12), and with the present uncertainties we certainly cannot say that the mechanism is confirmed. However, each step is approximately thermoneutral and hence the scheme is certainly energetically plausible. Assuming an energy barrier of 10 kcal for the reverse of step (a), Figure 4, leads to allyl H-abstraction as the rate-determining step, in agreement with experiment (the estimated  $E_{\text{act}} = 19$  kcal would be close to the experimental value of  $E_{\text{act}} = 22$  kcal).

Summarizing, we agree with Grasselli *et al.* (9) that Mo dioxo units are essential in selective oxidation; however, we find that single dioxo units cannot complete the reaction. We propose that selective oxidation requires a collection of at least three adjacent dioxo units to enter into three potentially endothermic reaction steps, facilitating the desired

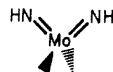
reaction. Indeed, we find for  $\text{Bi}_2(\text{MoO}_4)_3$  that the dioxo units should be ideal for carrying out the sequence of steps involved in selective oxidation. Using this idea that multiple dioxo sites are required, one might be able to develop strategies for promoter additives and for preparative techniques based on enhancing the probability of such sites. Perhaps the role of such sites could be tested using bidentate or multidentate ligands, e.g.,



that would bond only to specific configurations.

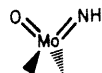
### Ammoxidation

In mechanistic studies of ammoxidation by Bi-molybdates, Grasselli *et al.* (9) have suggested a critical role of bis-imido sites,

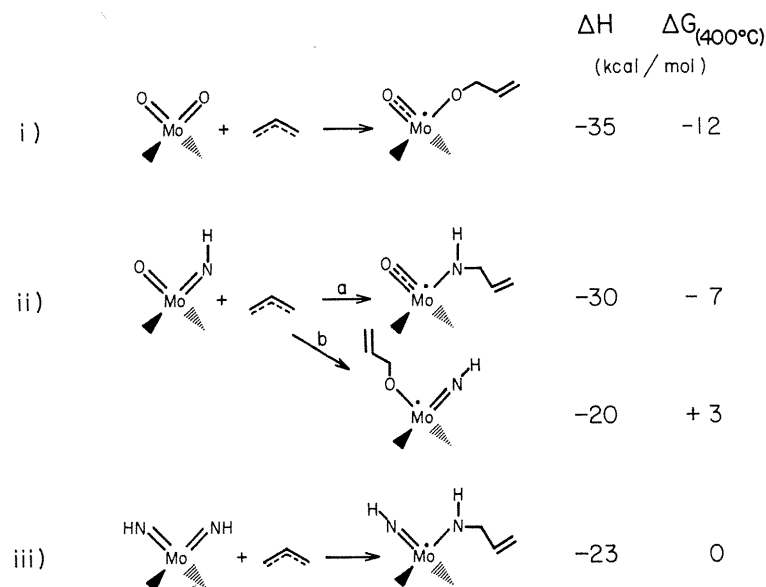


Indeed, assuming an active site analogous to that in Figure 5 but with oxo groups replaced by imido groups leads to a scheme analogous to Figure 4, where spectator imido groups play the role of spectator oxo groups in steps (a), (b), and (c) of Figure 4.

At intermediate  $\text{NH}_3$  pressures, oxo-imido species



are probably present on the surface. Because of the difference between spectator-oxo and spectator-imido effects, reaction at the N is greatly favored over reaction at the oxygen. Thus, for allyl trapping by N,  $\Delta H = -30$  kcal, whereas for allyl trapping by O,  $\Delta H = -20$  kcal [see (ii)a, (ii)b]. Thus, in thermodynamic equilibrium, only reaction at the N would be observed. Kinetic data of Grasselli *et al.* (10) have been interpreted to indicate that allylic N insertion is approximately three times *faster* than allylic O insertion, i.e.,  $\frac{K(\text{acrylonitrile})}{K(\text{acrolein})} \sim 3$ . Comparing the theory with experiment suggests kinetic control with an activation energy of  $\Delta H^\ddagger = 0$  for (ii)a and  $\Delta H^\ddagger \approx 2$  kcal for (ii)b. We are currently in the process of examining the energetics for various possible catalytic sequences involved in ammoxidation.



### Acknowledgments

We would like to thank Bob Grasselli, Jim Burrington, and Keith Hall for spirited discussions of various aspects of chemistry on molybdates. We also gratefully acknowledge partial support of this work from the Department of Energy (under a contract with the Jet Propulsion Laboratory) and the Donors of the Petroleum Research Fund of the American Chemical Society. One of the authors (JNA) wishes to acknowledge support in the form of a fellowship from the Fannie and John Hertz Foundation. This chapter is Contribution No. 7101 from the Arthur Amos Noyes Laboratory of Chemical Physics.

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RECEIVED October 4, 1984

Reprinted from ACS SYMPOSIUM SERIES NO. 279

*Solid State Chemistry in Catalysis*

Robert K. Grasselli and James F. Brazdil, Editors

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