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Review

The role of bismuth in the SOHIO process

Tracy A. Hanna*

Department of Chemistry, Texas Christian University, Box 298860, Fort Worth, TX 76129, USA

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Contents

Abstract

The Standard Oil of Ohio Company (SOHIO) process is the oxidation/ammoxidation of propene over bismuth/molybdate catalysts. Studies in the heterogeneous systems show that bismuth is involved in the rate-determining hydrogen abstraction from propene in both cases, and may be involved in later steps of the process as well. Model studies support the intervention of bismuth(III) in the rate-determining step and molybdenum(VI) in later steps. Few model studies with bismuth-containing compounds have been reported.

Keywords: Bismuth; SOHIO process; Homogeneous model systems; Molybdenum; Oxidation catalysis; Ammoxidation catalysis

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* Tel.: +1-817-257-6197; fax: +1-817-257-5851.
E-mail address: t.hanna@tcu.edu (T.A. Hanna).

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1. Introduction

The coordination chemistry of bismuth has applications in areas including medicine [1], materials synthesis, organic synthesis, and catalysis. In the field of catalysis, one of the most important processes involving bismuth is Standard Oil of Ohio Company (SOHIO) oxidation/ammoxidation [2]. This review will provide an overview of the SOHIO process, and describe what is known about the role of bismuth in SOHIO oxidation and ammoxidation catalysis. The goal is not to update the field since the last review, but rather to examine the evidence for the exact role (or lack thereof) of bismuth in each mechanistic step.

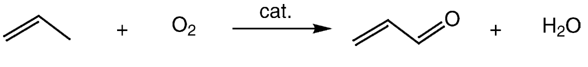
Section 2 will delineate the homogeneous model systems that have been described to date. Although immense research effort has been devoted to mechanistic studies of the heterogeneous system, the chemistry of homogeneous model compounds is relatively limited.

This article will focus on bismuth molybdenum oxides that utilize propene as a substrate. Although these bicomponent systems are no longer used in industry, an understanding of their chemistry is very applicable to current catalysis. Present industrial catalysts are generally multicomponent systems rather than pure Bi/Mo oxides, however it has been shown that the surface layer of these systems is made up of Bi/Mo oxides, and that the active sites comprise these two metals [3].

There is also significant interest in catalysis for the oxidation/ammoxidation of propane rather than propene. Bismuth molybdates, among other catalysts, are used for propane ammoxidation, which is of significant current industrial interest [4,5]. Although the mechanism is necessarily more complex than that of propene ammoxidation, the dehydrogenation step is believed to occur in the gas phase to form propene [5] which is then oxidized/ammoxidized on the Bi/Mo catalyst. Bismuth molybdate catalysts must therefore be optimized for new reaction conditions in order to be suitable for propane ammoxidation.

1.1. The SOHIO process: overview

The SOHIO process is the selective oxidation (reaction (1)) and ammoxidation (reaction (2)) of propylene to make acrolein and acrylonitrile, used in industry on large scales. In 2000, the worldwide demand of acrylonitrile alone was estimated at 5,000,000 tons per year [6].



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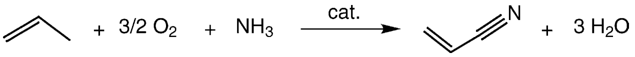


(2)

The predominant commercial processes for acrylonitrile and acrolein production use multicomponent catalysts based on $Bi_2O_3 \cdot MoO_3$ catalysts developed by SOHIO workers in 1959–1962 [7,8], where incorporation of other metal additives has increased yield and selectivity. Bismuth is known to be necessary to both the rate-determining and later steps of the catalytic cycle.

Commercial interest has driven a good deal of fundamental investigation into the mechanism of the SOHIO process, usually using simple bismuth molybdate compositions rather than the more complex catalysts used industrially [2,9–11]. Although many of the intimate details remain obscure, certain aspects of acrolein and acrylonitrile formation are well-accepted [2].

For acrolein, the overall process is believed to comprise the following steps:

1. Coordination of propene to the catalyst.
2. Activation of the propene at a bismuth site to form a π-allylic species (slow).
3. C–O bond formation.
4. A second hydrogen abstraction to form acrolein and a reduced site.
5. Reoxidation of the active site by oxygen migration from bulk catalyst.

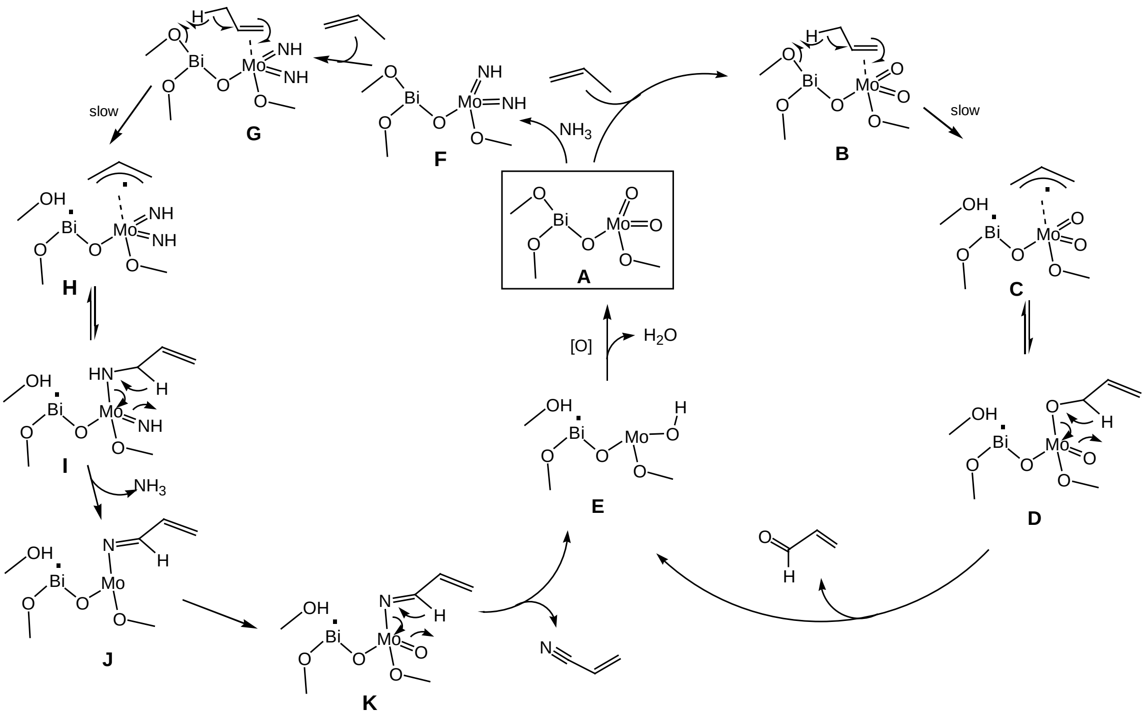
For acrylonitrile, the process is believed to be similar, but with initial NH_3 absorption and/or substitution for a terminal Mo=O moiety, and subsequent C–N bond formation rather than C–O bond formation. The preeminent mechanistic theory was proposed by Grasselli (Scheme 1) [2,12].

Several reviews of the SOHIO process have been published [2,9–11,13,14].

1.2. Experimental uncertainties

There has been an impressive amount of research on the mechanism of the SOHIO process over the past 40 years, yet the exact mechanistic details remain controversial. Though many ingenious studies have been carried out, there are many obstacles to the complete elucidation of the heterogeneous chemistry. Below are some reasons for the difficulty of determining mechanistic details in the “real” systems.

1. As in all heterogeneous catalysts, the surface has many types of sites and exactly which one(s) is/are active is difficult to ascertain.
2. Catalyst performance is highly dependent on pretreatment, exact reaction conditions, method of fabrication, structural type, purity, etc. [3]. Not only performance, but also mechanism may differ depending on reaction conditions. Grasselli for example proposed two different mechanisms for high and low feed partial pressures [15,16]. Different articles often describe results that are hard to compare because of such variables.
3. Directly conflicting results are sometimes found in literature, for example the ^{18}O segregation into Bi or Mo sites reported by Otsubo and co-workers [17] and contradicted by Keulks and Matsuzaki [18] or the same [19] or different [20] amounts of ^{18}O incorporation in acrolein



Scheme 1. Grasselli's proposed mechanism for the SOHIO process [2,12].

and CO_2 produced from propene oxidation. Raman spectra taken before and after $^{18}O_2$ reoxidation of γ-bismuth molybate after propene reduction show three different trends in three different articles [21–23].

4. Conclusions are often made on the basis of change in activity or selectivity when a variable is changed. However, it is not always safe to assume that such an experiment can define the role of that variable in an otherwise unchanged mechanism. For example, reduced molybdenum oxide can be reoxidized by O_2 gas, so one may be tempted to conclude that the bismuth molybdates are reoxidized at molybdenum sites. However, bismuth oxide can also be reoxidized by O_2 gas; it is therefore not clear which type of reoxidation mechanism applies to the bimetallic oxide.
5. The "real" catalysts currently used are multi-component, including Bi, Mo, Fe, Ce, etc. The mechanism in these systems cannot be identical to that of simpler Bi molybdates, though it is certainly related [3]. Exactly what is in common and what is different cannot be determined with literature extant today.
6. In general experiments are ingenious and lend support to various mechanisms, but almost all provide circumstantial evidence. There appears to be a limit to the information that can be obtained. The hey-day of experimentation on heterogeneous systems lasted into the late 1980's. After that period the frequency of publications decreased, while homogeneous model systems began to appear in the literature. Molybdenum-containing model systems predominated for the remainder of the decade, and only in recent years have bismuth-containing model systems been reported.

2. Role of bismuth in the SOHIO process

The presence of bismuth in the multicomponent catalyst is vital. Grasselli stated, in a recent review of ammoxidation, "without Bi, all of the other elements mentioned above, taken separately or together, are incapable of catalyzing the ammoxidation reaction" [2]. The role(s) of bismuth has been variously described over the years. The sections below will describe the evidence for bismuth's participation in various steps of the SOHIO process.

2.1. Propene coordination

Grasselli and co-workers generally describe the initial step as propene coordination to a molybdenum site (structure **B**, Scheme 1). In the Bi/Mo catalysts, the rates for propylene oxidation decrease in the order multicomponent $> Bi_2O_3 \cdot 2MoO_3 \sim Bi_2O_3 \cdot 3MoO_3 > Bi_2O_3 \cdot MoO_3 > MoO_3 \sim Bi_2O_3$ [24]. Grasselli and coworkers explain this result as a balance between the number of Mo chemisorption sites and Bi H-abstraction sites [24,25]. Also, at 320 °C the addition of ammonia to a propylene/O_2 feed produces a drastic decrease in activity, though at 430 °C there is no effect. Grasselli et al. suggest this is due to ammonia coordination to unsaturated Mo sites, blocking propene coordination. At high temperature they propose that the coordination either is reversible, or else ammonia reacts to form terminal imido groups, no longer blocking absorption sites [26].

Haber and Grzybowska showed that the reduction of bismuth molybdates with propene had no correlation with molybdenum coordination (four-coordinate or six-coordinate) [27] and therefore suggested that propene is absorbed on bismuth sites. However, Matsuura reported that propene absorption on Bi_2O_3 is very weak, compared to propene absorption on MoO_3 and $BiMoO_6$, which are similar [28]. Likewise, the Grasselli group found that the formation of 1,5-hexadiene is very low over Bi_2O_3 under conditions for which propylene is activated over bismuth molybdate, and argued that the absence of Mo absorption sites on the bismuth oxide is responsible for the low activity [24].

Overall, the evidence for initial coordination at a molybdenum site is stronger than that for coordination at a bismuth site, and this view is generally accepted.

2.2. *Propene activation*

It is generally agreed that propene activation occurs at a bismuth site, and that this is the rate-determining step of the SOHIO process at temperatures above 400 °C [29]. Details of this step include

1. the nature of the species formed from C–H bond cleavage;
2. the site of hydrogen abstraction (bridging versus terminal oxygen, Mo–O–Bi versus Bi–O–Bi);
3. the oxidation state of the bismuth before and after propene activation.

The last two will be discussed together.

2.2.1. *The nature of the species formed from C–H bond cleavage*

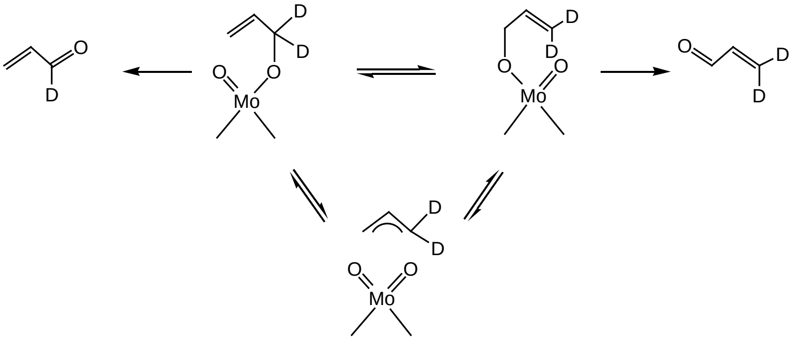
This point has received a great deal of study. The intermediate organic species is believed to be symmetric. The distribution of deuterium between the two end carbons in acrolein [29], and later isotope studies by Sachtler showing that ^{14}C substitution on one end of the starting propene led to ^{14}C incorporation on both ends of the product acrolein [30] were both taken to indicate the intermediacy of a symmetric allyl species after hydrogen abstraction. Later work demonstrated an additional facile isomerization pathway elsewhere in the catalytic cycle, Scheme 2 (compare structure **D** from Scheme 1), that also leads to equivalence of the terminal carbon centers [31].

Numerous studies have been undertaken to determine the nature of the charge on the allyl intermediate. Sachtler found that the C–H bond in butene is broken more easily at a secondary C atom than on a primary C atom, and suggested a positive or zero charge on the allyl complex [30]. Grasselli and co-workers later attempted to determine the charge density of the allyl group without the complication of steric differences by examining the effect of *para*-phenyl substituents on the oxidation of allylbenzenes. The resulting data were compared with the rate effects observed in benzyl radical-forming azo decomposition. Based on agreement in trend for three of the four points, the authors concluded that the allyl complex has radical-like character [32,33].

A more convincing indication of the radical character of the allyl intermediate is based on the reactivity of bismuth oxide. Bi_2O_3 will not oxidize propene to acrolein without Mo present, but rather forms 1,5-hexadiene, the expected product of allyl radical dimerization [34,35]. No oxidation is observed if MoO_3 is exposed to propene under similar conditions. If, however, bismuth oxide is placed upstream of MoO_3 in a flow reactor, not only are gas-phase allyl radicals detectably produced by the Bi_2O_3 [36], they are absorbed by the MoO_3, and a very small amount of acrolein is produced [37]. The acrolein produced is sufficiently small that Martir and Lunsford conclude that “the conversion of allyl radicals to acrolein is not particularly efficient over MoO_3. Thus, it appears that the functions of the two oxides are not additive and that active sites consisting of Bi, Mo, and O are responsible for oxidation of propylene to acrolein” [37].

2.2.2. *The site and oxidation states during hydrogen abstraction*

2.2.2.1. Bi or Mo site. Many experimental results confirm that the initial hydrogen abstraction occurs at a bismuth site. The experiments described above provide evidence for the



Scheme 2. Acrolein isomerization pathway [31].

location of the hydrogen abstraction at a bismuth center, as well as for the radical nature of the intermediate. Additionally, acrolein is produced if either allyl iodide [38], allyl alcohol [31], or 3,3′-azopropene [24] is passed over MoO_3 at high temperature. All these cases demonstrate that if the propene activation step can be bypassed, MoO_3 is capable of continuing the oxidation process, albeit with lower activity and selectivity than bismuth molybdate. However, without bismuth the propene activation generally does not occur.

The direct role of bismuth in the dehydrogenation was also demonstrated by Haber and co-workers, who supported isolated bismuth ions at the surface of MoO_3 and showed that, for low bismuth coverage, the yield of acrolein increased proportionally to the number of supported Bi^{3+} ions. At higher surface coverages the acrolein yield attained a constant value [39].

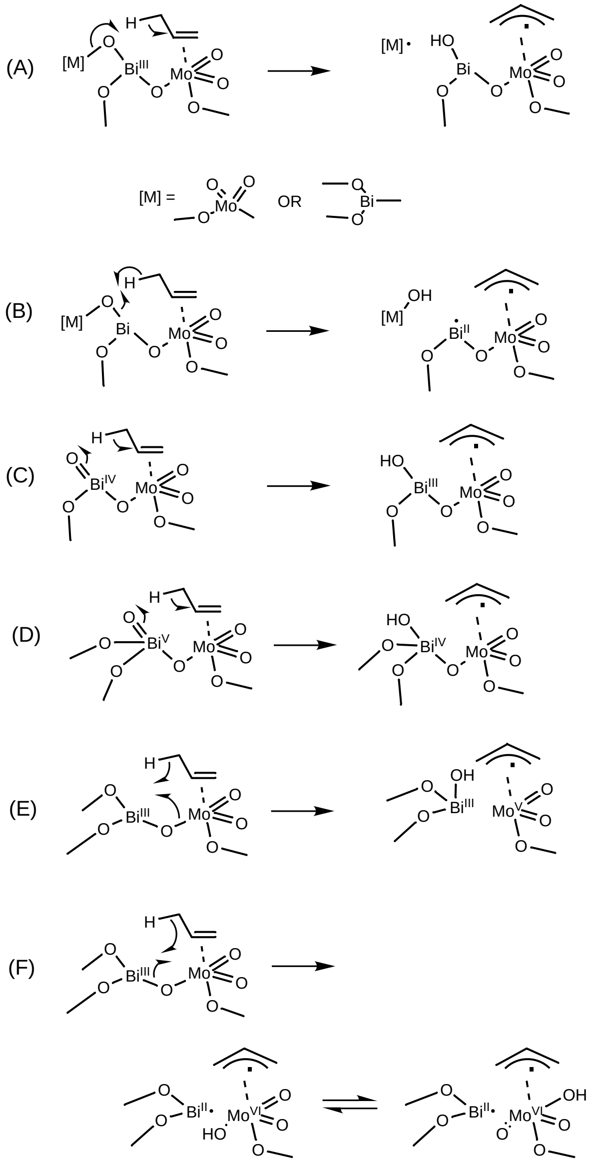
Sleight stated that “bismuth is not significantly or directly involved in the” allyl formation, based on studies of oxides with the scheelite structure, which show that defects without bismuth can still cause isomerization and low levels of oxidation [40]. This view, however, has not been accepted.

2.2.2.2. Possible mechanisms. The oxygen involved in hydrogen abstraction may be terminal or bridging, and if bridging, may be Bi–O–Bi or Bi–O–Mo. The oxidation state of the two metals both before and after the first hydrogen abstraction is also controversial. Based on proposed mechanisms found in literature, Scheme 3 shows six possible mechanistic pathways. To facilitate comparison, the product of allyl activation is drawn as an allyl radical absorbed on a Mo site in all cases.

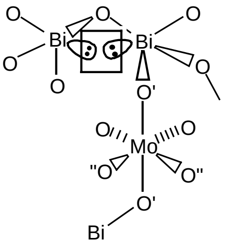
Grasselli has also drawn an expanded picture of the active site (Fig. 1), which includes a Bi–O–Bi moiety [12,13,22]. Mechanisms (A), (B), (D), and (F) of Scheme 3 utilize a bridging oxygen for H abstraction as suggested in Fig. 1.

2.2.2.3. Evidence for and against different mechanisms. Some experimental evidence does not distinguish between these mechanisms, such as the increase in activity with increased number of cation vacancy sites. DeRossi et al. have suggested that cation vacancies associated with bismuth [40] are involved in the hydrogen abstraction, possibly by favoring and stabilizing the formation of a hydroxyl group at the surface of the catalyst [41]. Brazdil et al. pointed out that cation vacancies lead to higher order Mo–O bonds, and improve lattice O diffusion [42]. These arguments would be consistent with any of the mechanisms shown in Scheme 3.

Goddard and co-workers’ theoretical study favors the intervention of terminal bismuth oxo groups ((C) and (D) of Scheme 3) [43,44]. They suggest that since Bi_2O_3 is known to chemisorb O_2 dissociatively [45], that in the catalyst the O_2 reacts with surface Bi sites to create a very small amount of Bi(V), which then abstracts hydrogen ((D), Scheme 3) [43]. Their $E_{a,calc} = 36.9$ kcal/mol for Bi(III) → Bi(V) versus 41.6 for Bi(III) → Bi(II). An earlier theoretical study [46] also suggests that Bi in Bi_2O_3 has the ability to adsorb



Scheme 3. Possible mechanisms for propene activation.



O' = Oxygen responsible for H-abstraction
O" = Oxygen associated with Mo; responsible for oxygen insertion into the allylic intermediate
□ = Proposed center for O_2 reduction and dissociative chemisorption

Fig. 1. Grasselli diagram of proposed active site [12,13,22]

oxygen with donation of electrons from its 6p band. Anderson cites experimental evidence that ^{18}O exchange on Bi_2O_3 has an activation energy of 38 kcal/mol (close to Goddard's calculated value for Bi(III) → Bi(V)). ^{18}O exchange on $Bi_2(MoO_4)_3$, though, was found to have an activation energy of 67 kcal/mol. Anderson et al. attribute this to the presence of Mo causing oxygen to bind more strongly [46]. Anderson et al. in a later article concluded that the oxidation state of Bi is uncertain [47].

The suggestion that gaseous O_2 reacts with surface bismuth to form the active site [43,44] is clearly untenable, as the rate-determining hydrogen abstraction step is zero order in oxygen [11]. Also, Di Cosimo et al. have shown that propylene can be oxidatively dehydrodimerized over a Bi/La oxide ion-conductive catalyst under conditions such that a catalyst disk separates a feed of propylene in helium from air. The surface of the disk exposed to propylene was reoxidized by oxide ion conduction from air exposed to the other side of the disk, improving product selectivity [45]. Under this experimental protocol the proposed Bi(V)=O groups formed by oxygen absorption would be on the far side of the disk that is not exposed to propylene—and this system would therefore not be capable of activating propylene. On the other hand, Goddard et al. also suggest that Bi(V) centers may be formed via lattice O migration [43,44], which would not contradict the above experimental evidence.

The requirement for Bi(V) centers, even formed via lattice migration, seems excessive in non-catalytic systems. The conversion of propylene to acrolein was initially in the 40–50% range over Bi/Mo catalysts in the absence of oxygen [48]. If activation occurs only at Bi(V) centers then most of these high oxidation state centers must be generated by lattice oxygen diffusion from catalysts that are already partially reduced, which is unlikely.

Pathways (A), (C), (D), (E), and (F) of Scheme 3 all describe the oxidation state of bismuth as III or higher throughout the catalytic cycle. This is consistent with the fact that reduced bismuth has not been directly observed during Bi/Mo catalysis, though it has been observed after reduction. Bi(III) must therefore be reduced, but that is not necessarily the major pathway during catalysis. Bi(V) or Bi(IV) centers have not been observed even in the fully oxidized catalyst.

X-ray diffraction of Bi_2O_3 catalysts after reaction with propylene showed lines due to Bi_2O_3 and bismuth metal only. Reoxidation with air caused the disappearance of the lines associated with bismuth metal [34,35]. Bismuth metal was only observed in bismuth molybdate catalysts, however, after extended reduction; after short periods of reduction an unknown phase with a chemical composition close to $2Bi_2O_3 \cdot MoO_3$ was observed by powder diffraction [48].

Later experiments by Keulks and co-workers with X-ray diffraction and auger spectroscopy show Bi^0 and Mo(IV) after 6% reduction. Reoxidation at 200 °C led to Mo(VI) + Bi^{n+} ($n = 1$ or 2), while continued reoxidation at 600 °C formed Bi(III) [49] These results indicate that the Bi^{n+} state is energetically accessible. Indeed, Peacock proposed the involvement of Bi(II) in the redox cycle ((B) or (F), Scheme 3) but could not determine its presence or absence by ESR due to the lack of known bismuth(II) ESR activity for comparison [50].

Overall, experiments with the heterogeneous systems have been unable to distinguish between the various possible mechanisms illustrated in Scheme 3.

2.3. *Later steps*

The primary role of bismuth in the SOHIO process appears to be the propene activation described above, but it has also been shown to be important in later steps. However, the role of bismuth in later steps is not well defined. When allyl iodide [38], allyl alcohol [31], 3,3′-azopropene [24], or gas-phase allyl radicals [37] were passed over MoO_3 at high temperature acrolein was formed, but with lower yield and selectivity than that observed in the bismuth molybdate system [37]. This can be interpreted in two ways; although these allyl sources can form acrolein over MoO_3, they are not the selective intermediates formed during propene oxidation [16,24,25], or the bismuth is involved in later steps as well as in the rate-determining step [11,37]. There is other support for bismuth being involved in later steps, as shown below.

2.3.1. *C–O bond formation (σ-allyl intermediate)*

Kinetic and isotope labeling experiments indicate that second H abstraction must either occur after reversible C–O bond formation or before irreversible C–O bond formation; Grasselli and co-workers contend the former [31]. Microwave spectroscopy supports the presence of a dynamic σ-allyl/π-allyl intermediate [20,51].

Grasselli's mechanism (Scheme 1) shows the O insertion of a Mo terminal oxo group into the allyl intermediate to make the σ-allyl complex. It would be consistent to expect the source of the acrolein oxygen to be the same terminal oxo group. In 1988, however, Nugent and Mayer wrote that it was not yet established that the terminal oxo groups on Mo are the ultimate nucleophiles [9]. There are several reasons for this doubt.

Otsubo and co-workers made ^{18}O-labeled acrolein using Bi/Mo catalysts with Bi bound ^{18}O. This provides evidence that the oxygen inserted into acrolein was at least partially associated with Bi polyhedra [17]. Keulks and Matsuzaki, on the other hand, reported conflicting results with similar experiments and stated that the Otsubo/Miura evidence is incorrect [18].

Moro-oka and co-workers also did some ^{18}O labeling studies; though they did not tie an ^{18}O to a specific metal, they demonstrated that the type of lattice oxygen used for dehydrogenation is different from the type used for oxygen incorporation, by prereducing the catalyst with either propene (oxidation and dehydrogenation) or butene (dehydrogenation only), reoxidizing with $^{18}O_2$, then following the incorporation of ^{18}O into acrolein formed over these pretreated catalysts [52]. This suggested that more than one type of lattice O is involved in propene oxidation, consistent with Otsubo's work [17] and Miura's A and B-site theory [53,54]. If it is assumed that a terminal Bi–O or Bi–O–Mo oxygen is involved in the hydrogen abstraction step, then by process of elimination one may implicate a Mo-bound oxygen in the oxygen insertion.

Raman experiments by Grasselli's group indicated that the spectra after propene versus butene reduction and $^{18}O_2$ reoxidation were different [22], consistent with Ueda's results. Ono and Ogata [23] and Hoefs and co-workers [21], in contrast, found that catalysts undergoing these treatments gave essentially the same Raman spectra. Unfortunately, bismuth–oxygen bands were overlapping and obscured [22,55], making it impossible to observe Raman shifts in that region.

Thus, uncertainty remains regarding the question of whether the acrolein oxygen originates from a Bi- or Mo-bound oxygen of the active site.

2.3.2. C–N bond formation

Like C–O insertion, it is not fully established that a terminal molybdenum imido group is the source of acrylonitrile nitrogen [9]. Although Scheme 1 shows a parallel mechanism for O- and N-insertion from terminal Mo=Q groups (Q: N or O), one key difference between these reactions is the source of the heteroatom. Unlike the lattice diffusion of oxygen to insert into acrolein, the nitrogen is believed to originate from absorption of gaseous ammonia onto the active site.

Matsuura suggests that NH_3 is dissociatively absorbed on bismuth oxide sites [28] based on competitive absorption experiments on Bi/Mo catalysts. This may be followed by migration to molybdenum, or formation of a Bi–N–Mo bond. Grasselli, however, describes the reaction of ammonia with terminal Mo=O groups to form terminal Mo=NH groups. Little experimental evidence is available regarding this question.

2.3.3. Second hydrogen abstraction

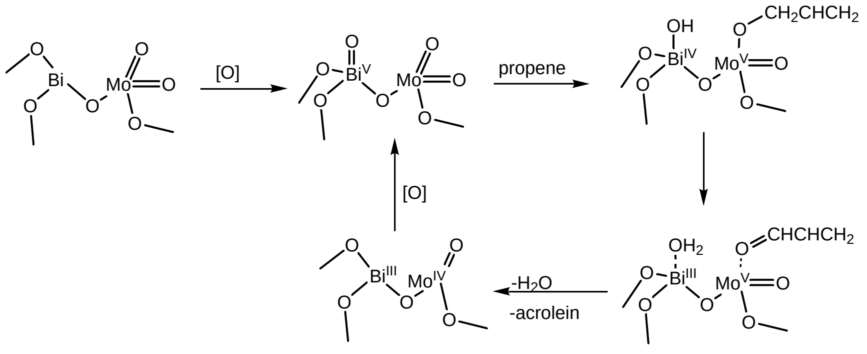
The second hydrogen abstraction may occur either at a bismuth or molybdenum site. In the reaction of allyl alcohol with five catalysts of differing compositions, the order of decreasing activity and decreasing conversion followed the order multicomponent catalyst > $Bi_2O_3 \cdot MoO_3$ > $Bi_2O_3 \cdot 3MoO_3$ > MoO_3 > Bi_2O_3. The authors concluded that the successive introduction of bismuth into the molybdate esters formed during the oxidation facilitates the second hydrogen abstraction ((D) → (E), Scheme 1) to form acrolein [31]. This enhancement, according to Grasselli, is either by abstraction of hydrogen via Bi–O bonds or by providing a low-energy sink of overlapping Bi 6p/Mo 4d orbitals for the electron transfer after hydrogen abstraction by Mo oxygens [31,56].

Bismuth enhancement was also seen in the selective oxidation of allylbenzene in which the cinnemaldehyde selectivity increased in the order $MoO_3 < Bi_2Mo_3O_{12} < Bi_2MoO_6$ [25,33]. Grasselli and co-workers also describe this as an example of the role of bismuth in accelerating the 1,4-hydrogen shift in acrolein formation [33].

Goddard and Jang proposed an interesting mechanism of Bi(IV) being the site of the second hydrogen abstraction (Scheme 4). In combination with their proposed first H-abstraction step (**D**, Scheme 3), this would be consistent with Haber's work showing that each bismuth ion could activate only one propene molecule in an 0.6 s pulse [39]. This work implies that the bismuth site involved in the second hydrogen abstraction must be the same bismuth site as that involved in the first hydrogen abstraction.

2.3.4. Oxygen transport (lattice mobility)

Most investigators agree that an important role of bismuth is to promote oxygen mobility in the lattice. Bismuth oxides are often excellent oxide ion conductors [57]. Grasselli cites the importance of bismuth oxide (Bi_2O_2) channels for optimal oxygen transport in bismuth molybdates [2]. Sleight writes that "the primary role of bismuth is to enable rapid replenishment of the depleted active site with oxygen." This is based on studies that show rapid reoxidation of bimuth-containing catalysts compared to those without bismuth [40]. The relative rates of reoxidation of the molybdate catalysts by O_2 decrease in the order $BiMoO_6 > Bi_2Mo_2O_9 > Bi_2Mo_3O_{12} > Bi_3FeMo_2O_{12}$ > multicomponent systems, suggesting the importance of bismuth in lattice mobility [25].



Scheme 4. Gossard's proposed mechanism for product-forming steps [43,44].

Giordani et al. suggested that bismuth's role is to keep the Mo in the Mo(VI) state responsible for acrolein formation, arguing that byproduct formation occurs on lower oxidation state Mo centers (consistent with previous results that acrolein selectivity is inversely proportional to Mo(V) concentration [58]) [59]. Peacock and others did ESR experiments on bismuth molybdate catalysts and found that Mo(V) signals decreased over time with propene alone [60], and were not seen when oxygen was present, presumably due to effective oxygen transport. Without sufficient bulk catalyst, surface oxidation is not maintained [58,61].

2.3.5. *Reoxidation of catalyst (oxygen absorption)*

2.3.5.1. Reoxidation at molybdenum? Otsubo's work indicated that Bi-related oxygens [62] arrived via diffusion from MoO_2 reoxidation sites [17] (consistent with theoretical calculations by Ruckenstein and Dadyburjor [63]).

2.3.5.2. Reoxidation at bismuth? Sleight describes bismuth as an important absorption site for oxygen based on kinetic results [40]. Grasselli and co-workers reasoned that dioxygen dissociation and reduction occurs at the high electron density region generated by the orbitals of the two lone electron pairs of Bi–O–Bi sites (see Fig. 1) [2,22]. Calculations by Anderson et al. support this view [46].

2.3.5.3. Reoxidation at Bi–O–Mo? Ono and co-workers indicate that Mo tetrahedra where Bi cations are present are more active than those without Bi present, based on Raman spectroscopic studies with ^{18}O tracer [20,23,64]. When using gaseous $^{18}O_2$ for propene oxidation over bismuth molybdates, they found very little ^{18}O incorporation into terminal Mo oxo groups but significant exchange into Mo–O–Bi bridging positions. They conclude that the terminal Mo oxygens are inactive [20], but the Mo–O–Bi bridging oxygen sites are most active as reoxidation sites.

2.3.5.4. Multiple sites? Experiments that show reoxidation of butene-reduced catalyst giving different results from the reoxidation of propene-reduced catalyst may indicate that reoxidation sites are different for the two cases. Glaeser et al. studies show differences between reoxidation kinetics after different types of reduction. They conclude that diffusion is rate-controlling rather than absorption and dissociation of O_2, since "this would lead to identical reoxidation kinetics regardless of reductant" [22]. That however assumes that reoxidation sites are identical in both cases, which may not be true. Molybdenum oxides can be reoxidized after reduction, and so can bismuth oxides; there is not necessarily just one available pathway for Mo/Bi reoxidation.

2.4. *Role of bismuth in heterogenous mechanism; summary*

When the evidence is examined in detail, a surprising number of questions remain concerning the detailed role of bismuth in propene oxidation/ammoxidation. Bismuth is definitely involved in the initial hydrogen abstraction step, but the type of oxygen involved and the metal oxidation states have not been established. Initial propene absorption is most likely on molybdenum, but oxygen insertion and the second hydrogen abstraction may involve either or both metal sites. Bismuth is believed to facilitate oxygen transport through the bulk catalyst, but the absorption site for that oxygen also remains controversial.

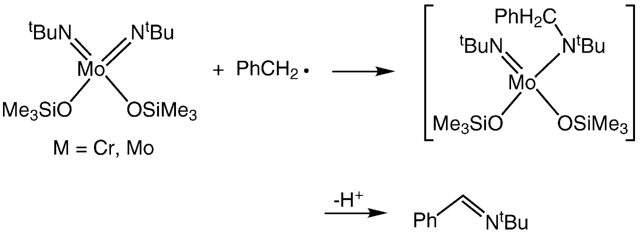
Considering the difficulties of obtaining exact information on the heterogeneous systems, however, a very large amount of knowledge has been gained. Model studies described below have also added to the knowledge of mechanistic possibilities, and support certain proposed pathways in the heterogeneous system. Scheme 1 takes both in situ and model studies (below) into account, and has served as an excellent working mechanism. Commercial systems have been optimized to a very high degree.

Nonetheless, studies of the mechanism of propene oxidation and ammoxidation remain of interest for several reasons. Partial oxidation chemistry is not limited to one system, but the learnings gained from one system may potentially lead to improvements in others. For example, the current interest in propane oxidation leads to a desire for the optimization of Bi/Mo catalysts for new operating conditions. Also, an understanding of the capabilities of these heterogeneous and the homogeneous materials can lead to new types of catalytic processes. As eloquently stated by Osborn et al. "the results of surface studies are a source of ideas for the molecular chemists in the construction of new molecules, the development of new reactions and, hopefully, the discovery of new catalysts" [65].

3. Model studies

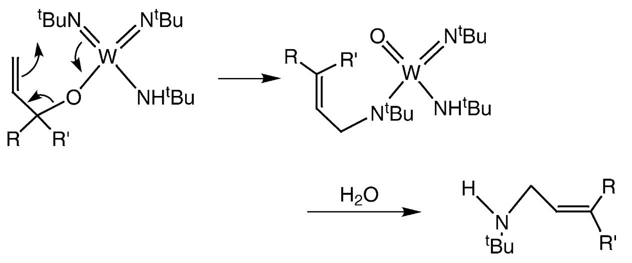
3.1. *Molybdenum/tungsten models*

Chan and co-workers have shown that the addition of benzyl radical to Cr and Mo imido complexes (Eq. (3)) forms benzylidene-*tert*-butylamine [66,67]. These reactions are analogous to the trapping and oxidation of allyl radical observed on MoO_3.

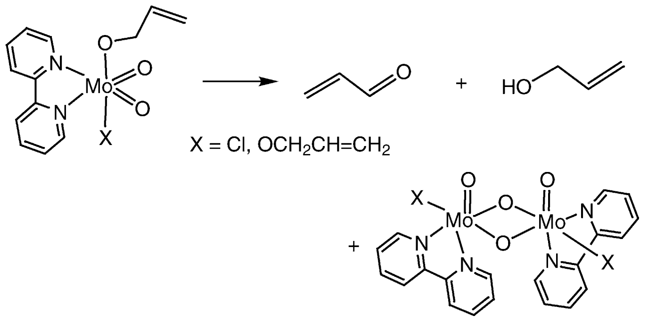


(3)

They also reported the migration of an allyl group from an oxo to an imido nitrogen atom (Eq. (4)), though product distributions indicated that a competing pathway also exists (possibly migration between imido groups [65]) [67]. Osborn and co-workers reported allyl migration between oxo ligands in Mo dioxo diallyloxides, and determined a relative allylic migratory order using a series of Mo(VI) oxo and organoimido complexes [65,68]. These results both support the isomerization pathway shown in Scheme 2.

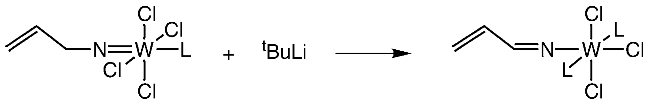


(4)



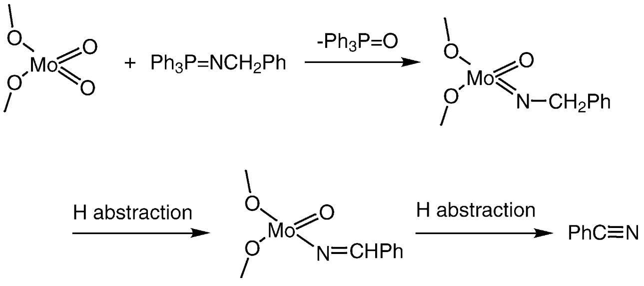
(5)

A 1,4-H shift to Mo=O or Mo=NR from an allyloxo or allylimido group formed acrolein in Osborn model complexes (Eq. (5)), support for occurrence of the second H-abstraction step at a molybdenum site in the heterogeneous process [65,69]. Both hydrogen abstraction and allyl migration are accelerated by electron deficiency and coordinative unsaturation at the Mo(VI) center. Osborn and co-workers thoroughly reviewed the Mo model chemistry reported as of 1994 [65].



(6)

Maatta and co-workers described the synthesis and reactivity of Mo and W allylimido complexes in the +6 and +5 oxidation states [70,71]. They found that an allylimido ligand can undergo deprotonation with concomitant 2e-transfer to the metal, illustrated in Eq. (6), affording an allylideneamido ligand similar to those in structures **J** and **K** (Scheme 1) in the Grasselli ammoxidation mechanism [72].



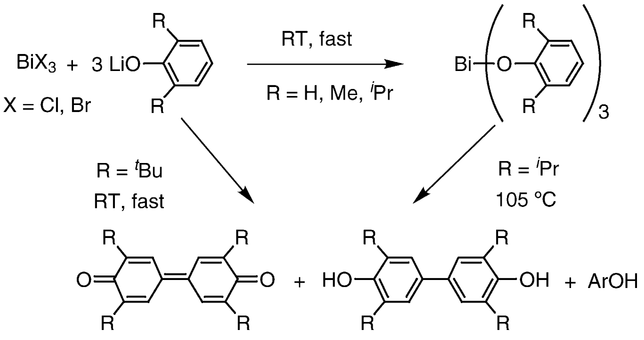
(7)

The Maatta [73,74] and Proust [75] groups have also developed polyoxomolybdate cluster imido compounds in order to study model systems even more similar to the heterogeneous catalyst. Maatta's hexamolybdate cluster produced benzonitrile from $Ph_3P{=}NCH_2Ph$ via the proposed pathway in Eq. (7) [74]. This result supports the plausibility of both the second and third hydrogen abstraction steps at a molybdenum site to form acrylonitrile.

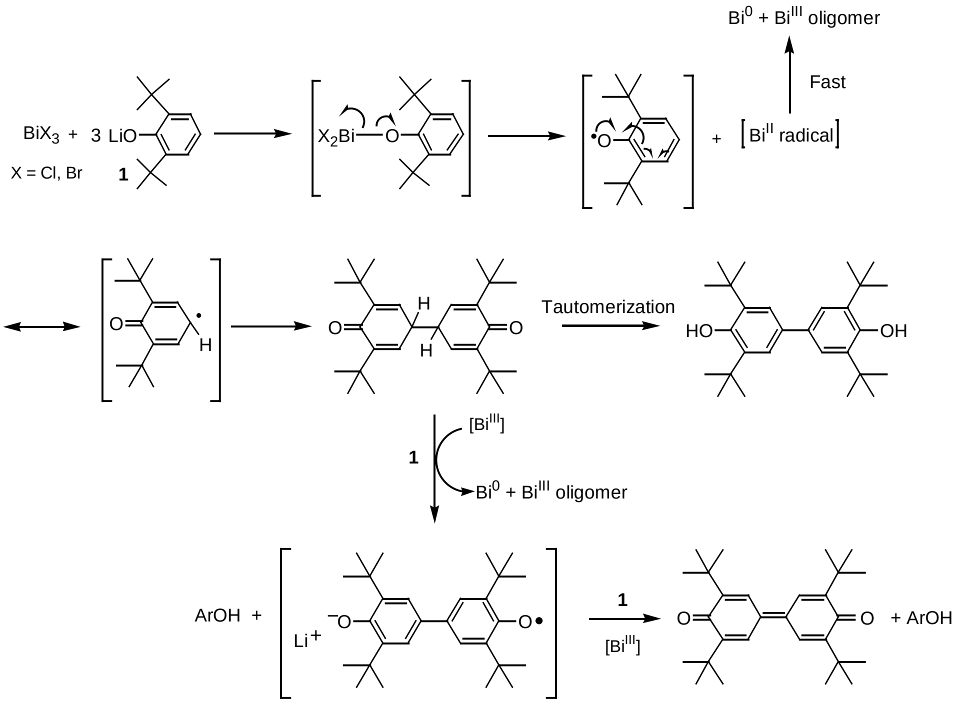
In summary, models of the molybdenum site have given support for the ability of terminal Mo(VI) oxo and imido groups to perform C–O/C–N bond formation, allylic migration, and hydrogen abstraction from σ-allyloxy and allylimido intermediates. These studies generally support Grasselli's version (Scheme 1) of the SOHIO mechanism.

3.2. Bismuth models

Significantly less work has been done to model the role of bismuth in the heterogeneous catalyst. Rademann and co-workers reported that propene will reduce mass-selected bismuth oxide clusters with no terminal oxo groups [76]. The organic product was not identified. The implication that bridging oxygen atoms can participate in propene oxidation supports rate-determining steps (A), (B), (E), or (F) (Scheme 3). Later work by Rademann demonstrated the reactivity of $Bi_4O_6^+$ clusters with oxygen and ethylene, pointing out that the cluster has a reactive radical center on a bridging O atom [77]. A theoretical study of similar systems concluded that these bismuth clusters might be able to oxidize ethane in the presence of O_2 but not in its absence. Calculations on propene were not described, however the authors stated that the energetics for propene would be similar [78].

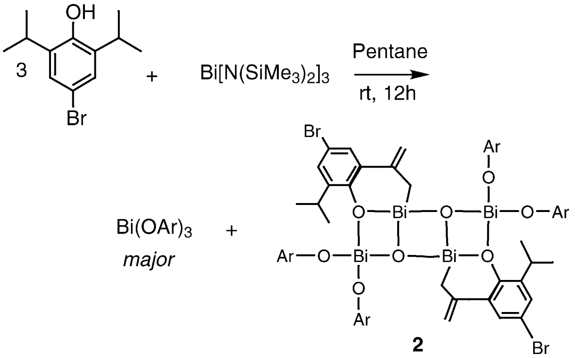


(8)



Scheme 5. Mechanism of ligand oxidation in bismuth model system [79].

We recently described the first molecular bismuth model system with reactivity similar to the SOHIO process [79]. Eq. (8) describes our homogeneous bismuth aryloxide system. The mechanism of the oxidation is shown in Scheme 5. The reactions shown in Eq. (8) represent the first experimental support for the proposal that the fundamental step in SOHIO propylene activation involves Bi(III)–O bond homolysis to form Bi(II) [2] (Versions (**B**) or (**F**), Scheme 3; there has been no previous experimental support for this fundamental step in any system. This model system is easily accessed and modified, thus it opens the door to further investigations of this basic reaction type and the nature of the bismuth(II) radical [79].



(9)

We have recently found that the complex $Bi(OAr)_3$ where $Ar = 2,6\text{-}{}^{i}Pr\text{-}4\text{-}BrC_6H_2$ led to C–H activation of the ligand to form an organometallic ladder Bi complex **2** (Eq. (9)) [80]. In addition to an illustration of C–H activation using Bi(III), this may also be the first example of trapping a Bi(II) radical {Bi=O}.

Compound **2** is the product of intramolecular C–H activation of the ^{i}Pr group of the aryloxide ligand. This important recent result strengthens the connection between the SOHIO process and this model system, as Bi(III) has activated allylic H atoms similar to those activated in propene in the SOHIO rate-determining step. Further studies will be necessary to provide evidence concerning the mechanism of this hydrogen abstraction.

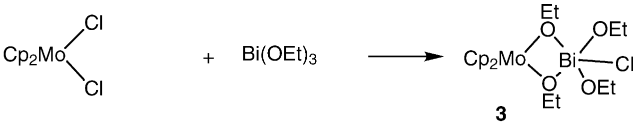
In summary, model studies by both Rademann et al. and Hanna et al. support the pathways (B) or (F) of Scheme 3 for propene activation by demonstrating

1. the accessibility of Bi(II);
2. the ability of Bi–O–Bi groups to be reduced by propene; and
3. the ability of Bi(III) to cause C–H activation of a propene-like moiety.

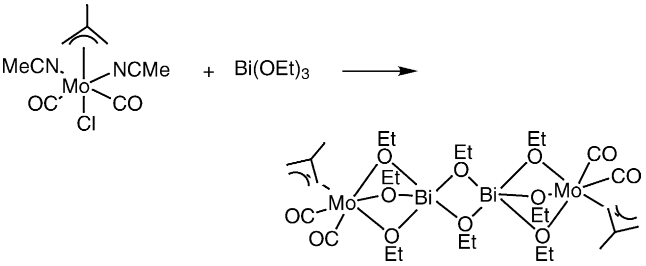
3.3. Bismuth/molybdenum models

Only reactivity models have been discussed in previous sections, but no homogeneous Mo/Bi systems have been described that model SOHIO reactivity. Accordingly, the few homogeneous Bi/Mo oxides and alkoxides that have been reported as structural models are presented in this section.

The first soluble bismuth molybdate was reported by Klemperer in 1980 [81]. Their complex $[{}^{t}Bu_4N]_2[Ph_3Bi(MoO_4)_2] \cdot 3H_2O$ contains Bi(V) and Mo(VI) centers. Villanneau et al. recently reported the structure of a second high oxidation state Bi/Mo compound $[{}^{t}Bu_4N][Bi\{Mo_5O_{13}(OMe)_4(NO)\}_2] \cdot 3MeOH$, which contains Bi(III) and Mo(VI). Both contain Mo–O–Bi bridges, but their reactivity has not been reported [82].

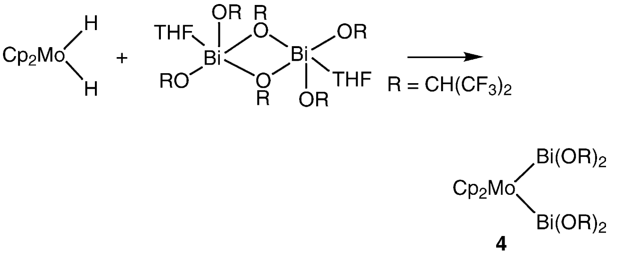


(10)

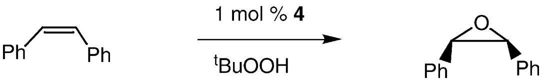


(11)

Limberg and co-workers have recently described a series of Mo/Bi complexes containing Bi(III) and Mo(IV), with bridging alkoxy groups [83–86]. They first reported compound **3**, with a molybdocene dialkoxide moiety bridged to a bismuth alkoxide by a Lewis acid/base interaction with the molybdenum alkoxy groups [83]. Their next model complexes included Mo-bound allyl groups, but the molybdenum centers are in a lower oxidation state (Eq. (11)) [84].



(12)



(13)

In an attempt to prepare a precursor for a Mo–O–Bi bridged compound, Limberg reported a Mo/Bi alkoxide with direct Mo(IV)–Bi(III) bonds (Eq. (12)) [85]. Although they were unable to isolate the corresponding Mo–O–Bi bridged compound, Limberg et al. did demonstrate catalytic epoxidation of stilbene using **4**. They suggest that the epoxidation occurs via the intermediacy of a transient complex with active Mo–O–Bi bridges [85].

Overall, though few soluble Bi/Mo compounds exist, recent activity provides hope that bimetallic reactivity models will be developed in the near future.

4. Conclusion

Homogeneous model systems have illustrated the ability of both Mo and Bi complexes to perform many of the fundamental transformations proposed to intervene in the SOHIO process. Of course, chemistry of molecular models cannot be considered as proof of any mechanistic steps in the heterogeneous system.

Bismuth is clearly vital to the SOHIO process, but it can be seen that the details of its chemistry remain unclear. Bismuth is known to play a role in rate-determining hydrogen abstraction, and may intervene in oxygen insertion, later hydrogen abstraction steps, and reoxidation as well. The description of the chemistry of bismuth-containing model complexes will lead both to an improved understanding of its role in the SOHIO process and to new and interesting homogeneous patterns of reactivity.

Acknowledgements

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