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Aspects of Selective Oxidation and Ammoxidation Mechanisms over Bismuth Molybdate Catalysts

4. Allyl Amine as a Probe for Nitrogen Insertion

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The catalytic oxidation and ammoxidation of allyl amine has been investigated at 400°C over MoO_3, Bi_2MoO_6, and $Bi_2Mo_3O_{12}$. Acrylonitrile and propionitrile account for 85% of the observed products, with smaller amounts of acetonitrile, propylene, diallyl amine, and CO_2. Acrolein is also formed in small amounts when water is added. The oxidation of 1,1-d_2-allyl amine over $Bi_2MoO_3O_{12}$ at 400°C gave a 90 : 10 d_0 : α-d-acrylonitrile mixture, and a 74 : 21 : 5 d_0 : α-d : d_2-propionitrile mixture, with a 93 : 1 : 6 mixture of 1,1-d_2 : 1-d_1 : d_0 recovered allyl amine. The corresponding values for ammoxidation of 1,1-d_2-allyl amine are 95 : 5, 96 : 4 : 0, and 88 : 8 : 4. The presence of ammonia increases selectivity to propionitrile at the expense of acrylonitrile. From these results, a mechanism evolves in which the initial σ-N-allyl complex produces tautomerization products faster than it forms the π-allyl complex. These results further substantiate a mechanism involving fast π–σ interconversion for selective propylene oxidation and ammoxidation to acrolein and acrylonitrile, respectively.

INTRODUCTION

The mechanism of selective oxidation and ammoxidation of propylene over heterogeneous catalysts has been the topic of several recent papers (*1–3*). The nature of the fast N-incorporation step in the ammoxidation reaction, which is difficult to study, has received relatively little attention. Studies of the ammoxidation of allyl alcohol (*2*) have suggested that equilibrating *O*- and *N*-allylic species could account for the scrambling of deuterium label and the resulting acrylonitrile/acrolein product distribution.

This work is aimed at by-passing the rate-determining allylic hydrogen abstraction step in ammoxidation by generation of the *N*-allylic intermediate *in situ* using 1,1-d_2-allyl amine as the precursor. A study of the product distribution and position of the deuterium label has been performed to provide a test for *N* to *O* allylic migration, as well as for the subsequent formation of a σ-allylic intermediate via C–N bond cleavage in the initial π–N allylic species.

EXPERIMENTAL

General. All experiments were performed in the absence of gaseous oxygen by the pulse method using He carrier gas, the microreactor/gas chromatograph system, and NMR, mass spectra, and GC instrumentation described previously (*2*).

Unsupported, fixed-bed (20–35 mesh) MoO_3 (0.7 m^2/g), Bi_2MoO_6 (1.8 m^2/g), and $Bi_2Mo_3O_{12}$ (1.9 m^2/g) catalysts were prepared by the methods described previously (*2*). Experimental parameters are listed in Tables 1–4. *Allyl amine-1,1-d_2* was prepared by $LiAlD_4$ reduction of the Diels–Alder adduct of acrylonitrile and anthracene, followed by retro-Diels–Alder pyrolysis (*4*); NMR ($CDCl_3$), δ(multiplicity, assignment): 0.9 (triplet, NH_2), 4.75–5.05 (multiplet, $=CH_2$); 5.77 (quartet, $=CH-$), $-CH_2-$ signal (2.7); integration was con-

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sistent with a 95% 1,1-d_2 : 2% 3,3-d_2 : 3% 1-d-allyl amine mixture.

Using the pulse microreactor/GC apparatus previously described (*1*), a feed mixture of allyl amine in benzene or in H_2O was vaporized into a He stream or a He stream containing a pulse of gaseous ammonia (molar ratio allyl amine : NH_3 = 1.0 : 4.5) before passing through a microreactor packed with 3 cm^3 of catalyst, 5.8 sec contact time.

Oxidation and ammoxidation of allyl amine-1,1d₂. Position and distribution of deuterium in acrylonitrile and recovered allyl amine was determined by proton NMR and GC/mass spectral analysis of the *N*-allyl-*N*-(2-cyanoethyl) amine/allyl amine mixture formed after preparative GC isolation of the allyl amine/acrylonitrile mixture. Propionitrile, isolated by GC, was also analyzed by mass spectral and proton NMR analysis.

RESULTS

1. Oxidation and Ammoxidation of Allyl Amine

The major products over MoO_3, Bi_2MoO_6, and $Bi_2Mo_3O_{12}$ at 400°C are acrylonitrile and propionitrile, with smaller amounts of acetonitrile, propylene, diallyl amine, and CO_2 (Table 1). Conversion and distribution of products were similar for the three oxides. The product distribution for reaction without (oxidation) and with ammonia (ammoxidation) present are similar, except for an increase in propionitrile, acetonitrile, and diallyl amine selectivities for the latter at the expense of acrylonitrile selectivity. For both reactions under these conditions (400°C, 6 sec contact time, feed = 3.6 μl of 5.8 *M* allyl amine in benzene or H_2O), only traces of acrolein are found. However, when the concentration of water is increased (2.9 *M* allyl amine) for oxidation under the same conditions, acrolein is found in ~8% (MoO_3) and ~4% ($Bi_2Mo_3O_{12}$) yields at the expense of acetonitrile, consistent with the results of previous studies (*2*). At 460°C, Cathala and Germain (*5*) observed a 93% selectivity to acrylonitrile from allyl amine over a Bi–Mo–O/SiO_2 catalyst at short contact times. Acrolein, CO, and CO_2 were also observed at higher conversions.

2. Oxidation and Ammoxidation of Allyl Amine-1,1-d₂

Since the products analyzed account for only 20–40% of the starting allyl amine, a direct comparison of the relative rates of

TABLE 1

Oxidation and Ammoxidation of Allyl Amine (Benzene Diluent) over Bi/Mo/O Catalysts at 400°C[a]

Product or conversion	Percentage selectivity or conversion					
	MoO_3		$Bi_2Mo_3O_{12}$		Bi_2MoO_6	
	Ox.	Ammox.	Ox.	Ammox.	Ox.	Ammox.
Allyl amine conversion to products[b]	32.6	40.3	21.7	32.1	27.3	41.5
Selectivity to						
Acrylonitrile	41.4	27.0	50.6	30.8	42.1	23.2
Propionitrile	46.1	54.7	34.6	50.6	44.3	60.4
Acetonitrile	4.3	9.9	6.0	10.6	3.7	7.7
Diallyl amine	0.0	2.7	0.0	3.1	0.0	2.4
Propylene	6.1	4.5	6.0	3.7	4.8	4.8
CO_2	2.1	1.2	2.8	1.2	5.1	1.4

[a] 3.0 cm^3 catalyst, 5.8 sec contact time, 3.6 μl of 5.8 *M* allyl amine in benzene.

[b] Σ observed product percentage yields.

reaction for 1,1-d_2 and d_0 is not possible. This low material balance is probably due to strong chemisorption of allyl amine on Bronsted acid sites, present in all these oxides (*2*). This explanation is consistent with the higher observed material balances for the reaction in the presence of ammonia (ammoxidation, Table 1). However, the lower selectivity to acrylonitrile in favor of propionitrile in the oxidation of 1,1-d_2-allyl amine (Table 2) indicates breaking of the allylic CD(H) bond in the product controlling step for acrylonitrile formation.

The total product distribution for the oxidation and ammoxidation of 1,1-d_2-allyl amine using both benzene and H_2O as diluents (Table 3) shows that water has a more pronounced effect in the oxidation vs the ammoxidation reaction. For oxidation, propionitrile yield is drastically reduced upon addition of water with higher selectivities to the remaining products, while for ammoxidation water has less of an effect on product distribution.

The distribution of deuterium label in acrylonitrile and recovered allyl amine for oxidation (Table 4) and ammoxidation (Table 5) shows that mainly formation of d_0-acrylonitrile occurs, with no allyl amine isomerization (no D in the 3-position) but some H–D exchange. Thus, the major path to acrylonitrile occurs without formation of an allylic intermediate, i.e., the C–N bond remains intact. While propionitrile formed in ammoxidation (benzene diluent) is also almost entirely d_0, a substantial amount of α-d-propionitrile is formed for oxidation (21%, Table 4) and for ammoxidation in the presence of water (15%, Table 5).

TABLE 2

Conversion of 1,1-d_2- and d_0-Allyl Amine to Acrylonitrile and Propionitrile at 400°C over $Bi_2Mo_3O_{12}$ (Benzene Diluent)[a]

	Percentage yield or selectivity			
	Oxidation		Ammoxidation	
	d_0	1,1-d_2	d_0	1,1-d_2
Acrylonitrile (AN) yield	11.0	7.5	9.9	6.0
Propionitrile (PN) yield	7.5	10.9	16.2	13.5
AN selectivity	50.6	32.6	30.8	23.5
PN selectivity	34.6	47.8	50.6	52.9
Diallyl amine selectivity	0.0	10.1	3.1	9.4

[a] Conditions listed in Table 1.

TABLE 3

Oxidation and Ammoxidation of 1,1-d_2-Allyl Amine over $Bi_2Mo_3O_{12}$ at 400°C[a]

Product or conversion[b]	Percentage conversion or selectivity			
	Oxidation		Ammoxidation	
	Benzene	H_2O	Benzene	H_2O[c]
Allyl amine conversion to products[d]	23.1	13.9	25.5	16.2
Selectivity to				
Acrylonitrile	32.6	36.6	23.5	17.9
Propionitrile	47.8	31.7	52.9	50.7
Acetonitrile	4.3	10.1	11.8	19.7
Diallyl amine	10.1	13.7	9.4	8.0
Propylene	5.2	7.9	2.4	3.7

[a] Conditions listed in Table 1, using 3.6 μl of 5.8 *M* allyl amine in benzene or water.

[b] CO_2 not analyzed.

[c] 4.0 μl of a 5.0 *M* 1,1-d_2-allyl amine/9.9 *M* NH_3 solution injected.

[d] Σ observed product yields.

DISCUSSION

The observed results for the reaction of allyl amine over molybdate catalysts at 400°C can be summarized as follows:

(1) Acrylonitrile, propionitrile, and smaller amounts of acetonitrile, propylene, diallyl amine and CO_2 are formed in similar selectivities for MoO_3, $Bi_2Mo_3O_{12}$, and Bi_2MoO_6 (Table 1).

(2) The presence of ammonia increases selectivity to propionitrile, at the expense of acrylonitrile selectivity (Table 1).

(3) The presence of water produces a reduction in propionitrile selectivity in oxida-

TABLE 4

Distribution of Deuterated Products (%) in Oxidation of 1,1-d_2-Allyl Amine[a] at 400°C in Benzene[b]

Product	d_2		d_1		d_0
	—CD_2—	CD_2═CH—	—CHD—	CH_2═CD—	
Allyl amine	93	0	1	0	6
Acrylonitrile	—	0	—	10	90
Propionitrile	5	—	21	—	74

[a] 95% 1,1-d_2 : 2% 3.3-d_2 : 3% 1-d mixture; numbers corrected for 100% 1,1-d_2.

[b] Conditions in Table 1; analysis by NMR and mass spectroscopy.

tion, while in ammoxidation, propionitrile selectivity is insensitive to the presence of water (Table 3).

(4) Ammoxidation of 1,1-d_2-allyl amine (injected from benzene solution) results in d_0-acrylonitrile and d_0-propionitrile almost exclusively (95 and 96%, respectively). The deuterated products are entirely d_1 with deuterium present at the vinyl methylene position of acrylonitrile, but at the α-methylene position of propionitrile. Recovered allyl amine is unisomerized (88% 1,1-d_2, no d at the 3-position), but H–D exchange occurs (8% 1-d_1, 4% d_0). In the presence of added water, substantial d incorporation into the α position of propionitrile (15% α-d) occurs (Table 5).

(5) Oxidation of 1,1-d_2-allyl amine (injected from benzene solution) produces less d_0-acrylonitrile (90% d_0) and d_0-propionitrile (74% d_0) than in ammoxidation. Recovered allyl amine is mainly 1,1-d_2 (93%), with no deuterium in the 3-position, as in ammoxidation; H–D exchange also occurs (1% 1-d, 6% d_0). The deuterium in both acrylonitrile and propionitrile is at the α-positions (Table 4).

(6) Propionitrile and diallyl amine selectivities increase in the oxidation and ammoxidation of allyl amine at the expense of acrylonitrile selectivity upon deuteration of the allyl amine in the 1-position (Table 2).

These results can be explained based on the mechanism shown in Scheme 1. The observed products (blocked off) are consistent with formation of an initial σ–N allyl molybdate species (**1**) on active site **9** which undergoes nearly irreversible tautomerization to form the stable species **2** faster than C–N cleavage to form a π-allylic species. Formation of d_0-acrylonitrile from **2** occurs by dehydration to give **3** and subsequent allylic deuterium abstraction to give precursor **4**, which undergoes a second deuterium abstraction to give d_0 acrylonitrile. Intramolecular H–D exchange at the vinyl

TABLE 5

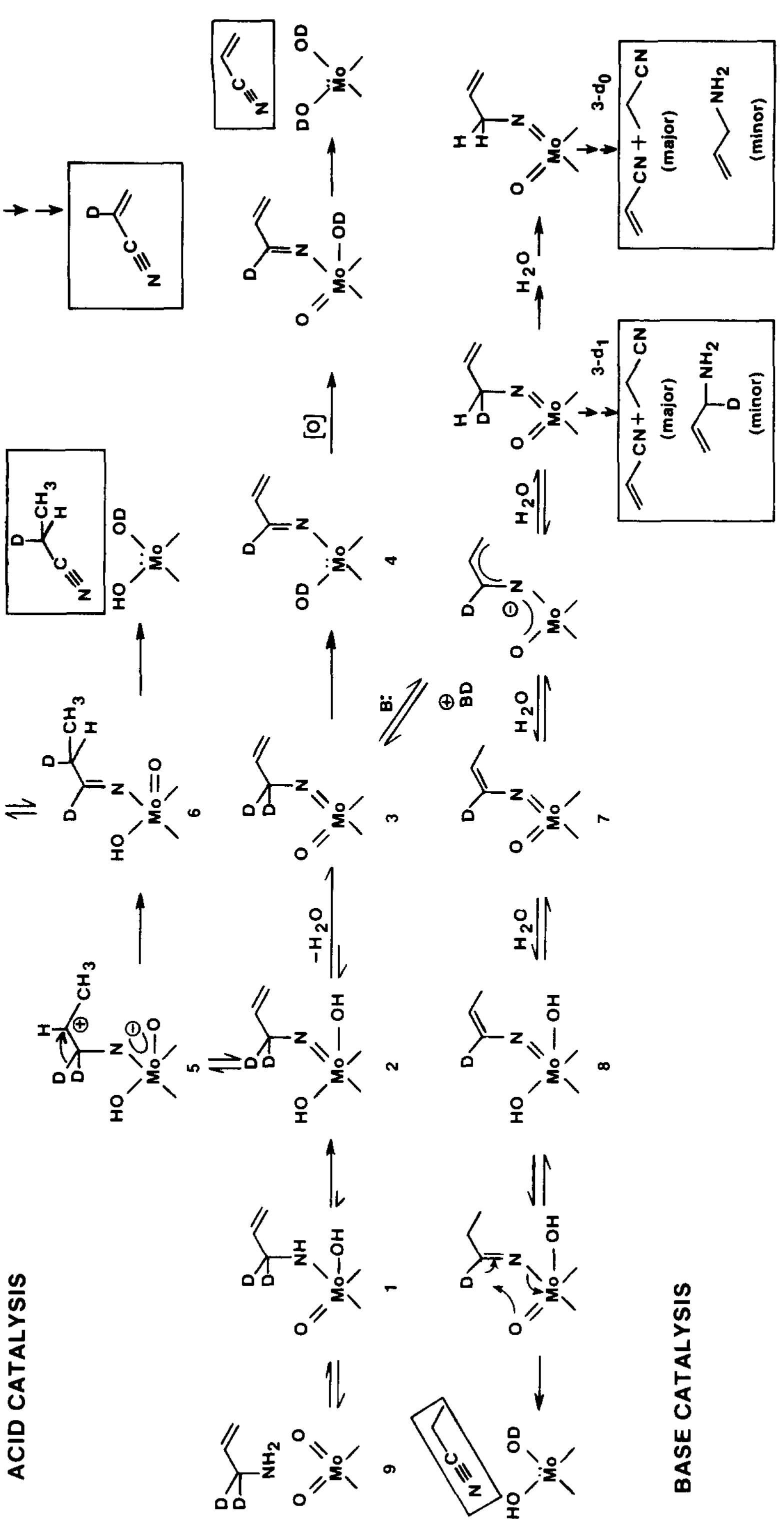
Distribution of Deuterated Products (%) in Ammoxidation of 1,1-d_2-Allyl Amine[a] at 400°C in Benzene[b]

Product	d_2		d_1		d_0
	—CD_2—	CD_2═CH—	—CHD—	CHD═CH—	
Allyl amine	88	0	8	0	4
Acrylonitrile	—	0	—	5	95
Propionitrile[c]	0 (1)	—	4 (15)	—	96 (84)

[a] See footnote a, Table 4.

[b] See footnote a, Table 3.

[c] Numbers in parentheses for ammoxidation using H_2O instead of benzene as injected solvent.



SCHEME 1. Reaction of allyl amine with molybdate catalysts.

methylene position of intermediate **4** would result in the small amount of the observed 3-D acrylonitrile (5%) in ammoxidation of 1,1-d_2-allyl amine. Acid catalyzed exchange of –O–D giving –O–H in **4** prohibits this exchange in the oxidation experiments. The formation of acrolein at a higher concentration of water in the injected solution (2.9 *M* allyl amine), also observed in a previous study (*2*), results from the hydrolysis of the imine intermediate **4**.

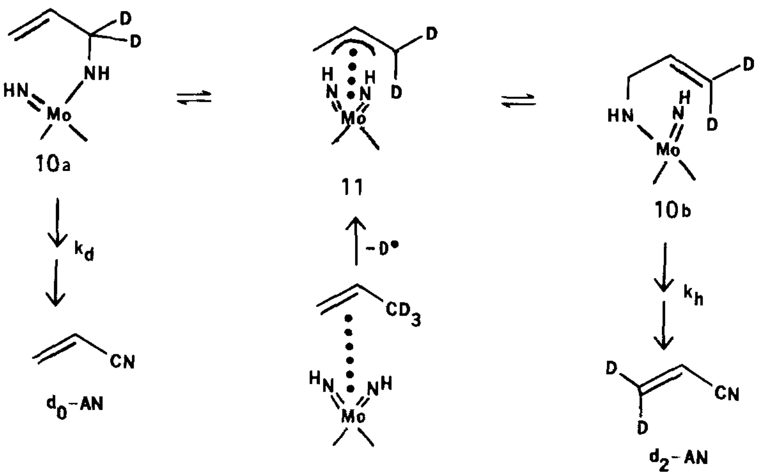
Propionitrile formation occurs both by a facile d_0-forming base-catalyzed route and a slower 1-*d*-forming acid catalyzed path. The allyl amine itself can function as catalyst in the more facile base-catalyzed route, which is enhanced by ammonia and inhibited by water. The amine base abstracts an allylic D + from **3** to form anion **7**, which on reprotonation at the terminal position produces **8**. Rehydration, tautomerization, and a second D-abstraction results in d_0-propionitrile. Propionitrile formation via a similar allyl amine-to-imine double bond migration involving allyl-anionic species has been reported for the reaction of allyl amine over basic oxide catalysts (*6*).

The small amount of H–D exchange in isolated allyl amine can be explained based on the intermediate **7**. Protonation of **7** at the α position produces an α-*d*, form of **3**, (**3**-d_1) which would be in equilibrium with a small amount of a **1**-d_1 analogue and thus α-d_1 allyl amine. Repetition of this process gives d_0-allyl amine via **3**-d_0 (Scheme 1).

In the slow acid-catalyzed route, which occurs in oxidation and in the presence of water, intramolecular protonation at the terminal methylene position produces zwitterion **5**, which can undergo 1,2-D shift to produce the more stable neutral species **6**. Deprotonation followed by D-abstraction analogous to the base-catalyzed route produces 1-*d*-propionitrile. The observed incorporation of deuterium into the methyl group of propionitrile in the presence of D_2O supports this mechanism. Alternatively **6** could undergo 1,5-H shift and double bond migration to form **2**-1,2-d_2 and subsequently **3**-1,2-d_2 on dehydration, which would, by the mechanism via **4** described above lead to α-*d*-acrylonitrile, as is observed in the absence of ammonia (10% α-*d*, Table 4). When ammonia is present, this acid-catalyzed route is suppressed and the acrylonitrile and propionitrile that form are almost exclusively d_0 (95, 96%, respectively, Table 5).

In this scheme, deuteration of allyl amine in the allylic position should cause selectivity to propionitrile to increase with respect to acrylonitrile in the oxidation reaction, since D abstraction is required in the conversion of **3** to **4** (acrylonitrile path) while formation of **5** from **2** (propionitrile path) requires no C–D bond breaking. Thus a higher selectivity to propionitrile is observed for oxidation of 1,1-d_2 than for d_0-allyl amine (34.6 vs 47.8%, respectively, Table 2). For ammoxidation in the absence of water, only a slight selectivity increase is observed (50.6 vs 52.9%, Table 2) since propionitrile (d_0) forms mainly by the base-catalyzed route (**3** → **7**), which requires C–D bond breaking. Selectivity to diallyl amine, a product which requires no C–D bond breaking at all, is also increased on deuteration in the allylic position, as expected. Similar selectivity increases have also been observed for catalytic oxidation of propylene to propylene oxides upon deuteration of the olefin (*7*).

From the results of this study, it is apparent that the allylic intermediate formed in the ammoxidation of propylene is not accessible from allyl amine. This is evident from a comparison of the isotopic distribution of acrylonitrile produced from 3,3,3-d_3-propylene ammoxidation [$d_2 : d_0 = 60:40$, $k_H/k_D = 2.1$ (430°C)] with that of 1,1-d_2-allyl amine oxidation or ammoxidation from this study (90–95% d_0). The 60:40 distribution in the former reaction results from a rapid interconversion of σ-allylic species **10a** and **10b** via π-allyl complex **11** (Scheme 2). Reversible C–N bond formation is expected here, since the interconversion of **10a** and



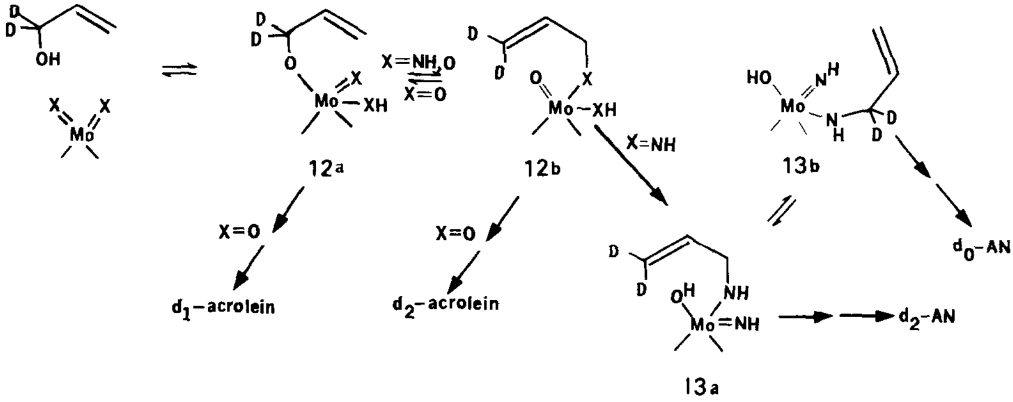
SCHEME 2. Ammoxidation of propylene-3,3,3-d_3 with molybdate catalysts (AN = acrylonitrile).

10b (the acrylonitrile precursors) is energetically a degenerate rearrangement. For the allyl amine oxidation intermediate **1** (Scheme 1), essentially irreversible tautomerization to **2** occurs in preference to formation of **3** via C–N cleavage. This path via **2** leads ultimately to d_0-acrylonitrile (Scheme 1).

The catalytic oxidation or ammoxidation of allyl amine is also unlike these reactions of allyl alcohol in which extensive isomerization occurs via the equilibration of allylic intermediates **12a** and **12b**, and **13a** and **13b** (Scheme 3).

These differences can again be explained by the nearly irreversible tautomerization of **1** to **2**. Such tautomerization is not possible for **12a** (X = O, oxidation), while for **12b** (X = NH), irreversible tautomerization forms the more sterically favored **13a** rather than a Mo=N-allyl species analogous to **2**.

The formation of **1** rather than **13b** or **12b** (X = NH) results from 1,1-d_2-allyl amine ammoxidation since allyl amine can effectively compete with ammonia for terminal Mo=O Lewis acid sites. In the reaction of allyl alcohol, which is a much weaker base than ammonia, fast formation of Mo=NH double bonds prior to alcohol chemisorption occurs, resulting in formation of **12a**. By the same reasoning, in the ammoxidation of propylene, which is an even weaker base, allylic intermediate **11** forms, which contains terminal Mo=NH double bonds.



SCHEME 3. Ammoxidation of 1,1-d_2-allyl alcohol with molybdate catalysts (AN = acrylonitrile).

Thus, while N to N allyl migration in propylene ammoxidation, and O to N allyl migration in allyl alcohol ammoxidation occur, the original allylic C–N bond is not broken in the catalytic oxidation or ammoxidation of allyl amine to acrylonitrile, due to essentially irreversible tautomerization and subsequent dehydration of the initially formed σ-*N*-allyl molybdate.

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