JOURNAL OF CATALYSIS 59, 314–316 (1979)

# LETTERS TO THE EDITORS

## On the Mechanism of Ammoxidation of Propylene to Acrylonitrile

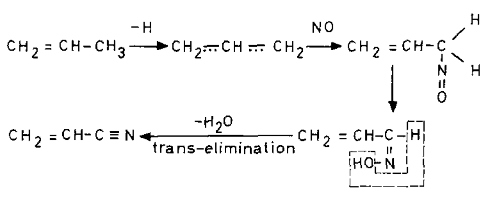
In the ammoxidation of propylene (with $NH_3$ and air) to acrylonitrile, the NO formed from the oxidation of $NH_3$ may be postulated as a common intermediate. How this NO reacts further with the allyl species will of course depend on the specific nature of the catalyst used, the conversion level, and other reaction conditions. The direct reaction of NO itself with propylene for the synthesis of acrylonitrile has been studied recently by Zidan *et al.* (*1*, *2*) on $NiO/Al_2O_3$ and $NiO/SiO_2–Al_2O_3$ catalysts (at low conversions of propylene). The mechanism suggested by them consists of the reduction of the catalyst by propylene with formation of allyl and further dehydrogenated species, which then form acrylonitrile with atomic nitrogen released by the dissociation of NO. The catalyst is reoxidized by NO. The formation of acetonitrile is attributed to the oxidation of acrylonitrile over a fresh or barely reduced catalyst, and that of $CO_2$ to the oxidation of acrolein.

In the case of the more extensively studied (*3*) Bi–Mo–O-type catalysts, most widely used in the commercial process for acrylonitrile, operating at 430 to 480°C at high conversions and high selectivities and with acetonitrile and hydrogen cyanide as important and valuable by-products in addition to acetyldehyde, formaldehyde, $CO_2$, and water, an alternative mechanism involving NO as an intermediate is the following.

The late Professor R. J. Kokes once suggested (*4*) that though an adsorbed allyl species is the common intermediate in both the oxidation and ammoxidation of propylene, a peroxide linkage is formed in the former case (*5*), while a direct addition of NO (formed from oxidation of $NH_3$) to the allyl radical is important in the ammoxidation of propylene. This is quite in agreement with earlier observations (*6–8*) that (1) an adsorbed allyl intermediate is common to both acrolein and acrylonitrile, and (2) most of the acrylonitrile is formed directly from propylene and *not* via acrolein. The idea of NO as an intermediate in the ammoxidation of propylene is strengthened by the following points: (a) Concentrations of 1–2% NO are occasionally found in the products during laboratory testing in a fluidized bed of commercial Bi–Mo–O/$SiO_2$-type catalysts for the acrylonitrile process; (b) direct combination of propylene and NO can yield acrylonitrile as now reported by Zidan *et al.* (*1*, *2*) and as claimed earlier in the patent literature; and (c) among molybdates, bismuth molybdate has the highest activity for the oxidation of $NH_3$ (cf. Trifirò and Pasquon (*9*)).

The mechanism proposed by Kokes is shown below.

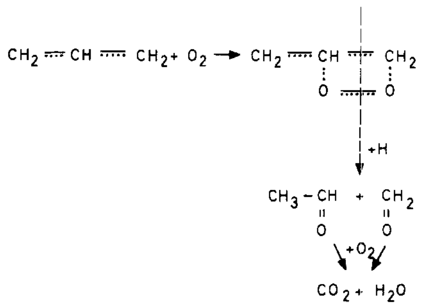
$$2NH_3 + 2\tfrac{1}{2}O_2 \rightarrow 2NO + 3H_2O$$



0021-9517/79/110314-03$02.00/0

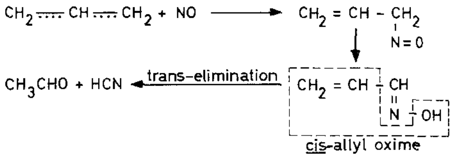
Kokes did not explain how his mechanism accounts for the formation of acetaldehyde, formaldehyde, acetonitrile, and HCN during the oxidation/ammoxidation of propylene. However, it is possible to make a reasonable extrapolation from his basic ideas and forward the following tentative reaction mechanisms for the formation of the above-mentioned by-products in the commercial acrylonitrile process. The starting point for all cases is the (generally accepted) adsorbed allyl intermediate.

(a) *Formation of* $CH_3CHO$ *and* $CH_2O$.

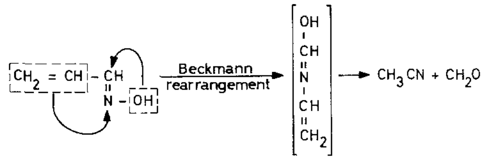


(b) *Formation of* $CH_3CHO$ *and HCN.* Here one has to recall that oximes can exhibit geometrical isomerism around the C=N bond and hence can exist either in the *cis* (*syn*) or in the *trans* (*anti*) form. Of these two, the *trans* form is the thermodynamically more favored one (*10*).

Acetaldehyde and HCN are formed when *cis*-allyl oxime undergoes a *trans* elimination.



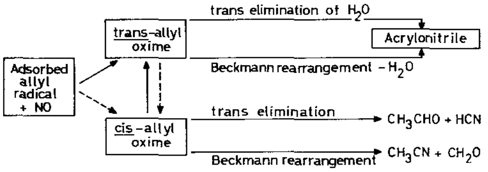
(c) *Formation of* $CH_3CN$ *and* $CH_2O$. If the *cis*-allyl oxime, however, undergoes a Beckmann rearrangement, instead of a *trans* elimination, then $CH_3CN$ and $CH_2O$ are obtained.



Beckmann rearrangement usually takes place only in the presence of an acidic medium or acidic catalyst. $MoO_3$ itself is not very acidic but $SiO_2$–$MoO_3$ is strongly acidic, liberating iodine from KI. Hence the commercial bismuth–molybdate/silica catalyst may be acidic enough to cause Beckmann rearrangement of *cis*-allyl oxime at 430 to 480°C.

It may be noted here that if the *trans*-allyl oxime undergoes Beckmann rearrangement, the product will be acrylamide, which would readily dehydrate at the reaction temperature to give acrylonitrile. Thus *the stabler and thermodynamically favored trans oxime yields only acrylonitrile as the product through both reaction routes, trans elimination and Beckmann rearrangement.*

The above schemes can be summarized as follows.



It is also significant that some of the patents on ammoxidation catalysts (*11*) mention the addition of alkali (up to 0.1% as $K_2O$) to the catalyst. This may perhaps be to neutralize the excess acidity of the catalyst and thus reduce the Beckmann rearrangement of the *cis*-allyl oxime and hence the formation of acetonitrile. Reduced acetonitrile yield is indeed one of the major claims for the superiority of such multicomponent molybdate catalysts.

Thus the postulate of NO as an intermediate in the ammoxidation of propylene is not only in agreement with the direct synthesis of acrylonitrile from propylene and NO, as reported by Zidan *et al.* (*1*, *2*), but also gives an explanation for the formation of the important by-products of the reaction at high conversions and selectivities as in the commercial acrylonitrile process.

The generality of such reactions of NO is also noticeable in the very recent work of Voorhoeve *et al.* (*12*) on the formation of compounds with the C≡N bond, like HCN and $NH_4OCN$, during the reduction of NO with CO and $H_2$, as may occur in catalytic treatment of automobile exhaust gases.

## ACKNOWLEDGMENTS

This work originated from a personal discussion with the late Professor R. J. Kokes at the Johns Hopkins University in July 1971. The critical comments of Professors W. M. H. Sachtler, S. J. Teichner, and J. E. Germain on the draft manuscript are gratefully acknowledged.

*Note added in proof.* A direct proof for the formation of allyl oximes from NO and allyl species over nickel catalysts has just been provided from homogeneous catalysis: Clement *et al.* (*13*) have found that an allyl-nickel complex can react with NO at low temperatures to give a nickel complex of allyl oxime. When the reaction is run above room temperature, the oxime ligand is released from the complex. The identity of the allyl-oxime ligand in this case was established from (a) infrared spectra which show two NO stretching frequencies corresponding to the *cis* and *trans* isomers, (b) NMR spectra, and (c) reaction with triphenylphosphine, when the allyl oxime is released. At higher temperatures the allyl oxime can readily dehydrate to acrylonitrile.

## REFERENCES

*1.* Zidan, F., Pajonk, G., Germain, J. E., and Teichner, S. J., *J. Catal.* **52**, 133 (1978).

*2.* Zidan, F., Pajonk, G., Germain, J. E., and Teichner, S. J., *Bull. Soc. Chim. Fr.*, 603, 1011, 1021 (1977).

*3.* See the bibliography cited in Ref. (*1*).

*4.* Kokes, R. J., personal discussion at Baltimore, Md., on July 9, 1971.

*5.* Kugler, B. L., and Kokes, R. J., *J. Catal.* **32**, 170 (1974).

*6.* Adams, C. R., and Jennings, T. J., *J. Catal.* **2**, 63 (1963); **3**, 549 (1964).

*7.* Sachtler, W. M. H., *Rec. Trav. Chim.* **82**, 243 (1963).

*8.* Callahan, J. L., Grasselli, R. K., Milberger, E. C., and Strecker, H. A., *Ind. Eng. Chem. Prod. Res. Develop.* **9**, 134 (1970).

*9.* Trifirò, F., and Pasquon, J., *J. Catal.* **10**, 86 (1968).

*10.* cf. Fieser, L. F., and Fieser, M., "Organic Chemistry," 3rd ed., pp. 701–702. Reinhold, New York, 1956.

*11.* (a) Nippon Kayaku Kabushiki Kaisha, Tokyo, Japan, Netherlands Patent Appl. 7006454 (1974); (b) The Standard Oil Co., Cleveland, Ohio, German Patent Appl. 2203710 (1972); (c) Sumitomo Chemical Co. Ltd., Osaka, Japan, German Patent Appl. 2133110 (1972).

*12.* Voorhoeve, R. J. H., Patel, C. K. N., Trimble, L. E., and Kerl, R. J., *J. Catal.* **54**, 102 (1978).

*13.* Clement, R. A., Klabunde, U., and Parshall, G. W., *J. Mol. Catal.* **4**, 87 (1978).

P. G. MENON

*Laboratorium voor Petrochemische Techniek*
*Rijksuniversiteit Gent*
*Krijgslaan 271, 9000 Gent*
*Belgium*

*Received October 31, 1978*