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Ammoximation

III. The Selective Oxidation of Ammonia with a Number of Ketones to Yield the Corresponding Oxime

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A variety of ketones have been shown to undergo a selective oxidative amination to the corresponding oxime. The "ammoximation" of ketones described is limited by the competitive formation of a by-product which deposits on the catalyst during the course of the reaction. However, the amount of by-product which is formed is related to the ease with which the ketone reacts separately with ammonia. Further, pretreating the catalyst with a mixture of cyclohexanone, ammonia, and oxygen serves to activate the original catalyst (in this case a silica) toward other ketones. In general, the direct ammoximation of ketones does offer an attractive and alternative route for the preparation of speciality oximes where the conventional method(s) may prove to be more awkward.

INTRODUCTION

Recently, we described a new process for the selective oxyamination of ketones to oximes (*1*, *2*) indicated by Eq. (1). Ammoximation is a process applicable to a wide variety of aliphatic, aromatic, and alicyclic ketones:

$$\text{Ketone} + NH_3 + \tfrac{1}{2}O_2 \rightarrow \text{Oxime} + H_2O. \quad (1)$$

Most prior work focused on the use of cyclohexanone since the product, cyclohexanone oxime, is a key intermediate in all commercial processes for the production of caprolactam. Two previous papers (*3*, *4*) described the use of a variety of catalysts. The best of these catalysts was a pure silica–alumina which gave a selectivity to cyclohexanone oxime of 68%.

This report will summarize the results with other ketones. Using a variety of ketones enables us to gain some insight into the reaction mechanism. The direct synthesis of oximes (from the ketone plus ammonia and oxygen over a heterogeneous catalyst) offers an alternative route for the preparation of oximes in cases where the use of hydroxylamine salts may be undesirable or where by-product ammonium sulfate cannot be utilized.

EXPERIMENTAL

All ketones used in this study were of the highest grade available (generally reagent).[2] The imine of pivalone (hexamethylacetone) was prepared (*5*) from the reaction of:

$$(CH_3)_3C{-}C{\equiv}N + (CH_3)_3C{-}Li \overset{H^+}{\rightarrow} [(CH_3)_3C]_2C{=}NH. \quad (2)$$

The imine was stored under helium, and a syringe pump was used to deliver the imine into the feed stream of ammonia/oxygen and helium. The corresponding oximes were prepared via known routes (usually with $NH_2OH \cdot HX$) (*6*) or purchased directly from either the Aldrich Chemical Company or The Ames Laboratories, Inc. In some cases, the oximes (prepared by the

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[2] 7-Norbornanone was prepared under contract with Alfa Products.

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use of hydroxylamine salts) could not be isolated as solids. In these cases, the oximes were used as produced in the final product solution. Where possible, the ketones were fed into the reactor by vaporization with nitrogen with the ketone maintained at a temperature below the boiling point of the ketone. The ketone (~2% in the vapor phase) was mixed with ammonia (~50%), oxygen (~12%), and a diluent (helium or nitrogen) and the mixture allowed to pass downward through a plugged flow reactor containing 1 cm^3 of Porasil A (*3*). This catalyst was demonstrated to be quite effective for the ammoximation of cyclohexanone to its oxime at 195°C. (The more effective silica–alumina catalyst was not discovered until this study was completed.) All gases were controlled using Tylan mass flow controllers (Torrance, Calif.). Inlet and product gas streams were continually analyzed by GC, as described in earlier reports (*3*).

For the deuterium exchange studies, samples of the gaseous products exiting the reactor were trapped in narrow tubes (immersed in ice water) and frozen prior to GC/MS analysis. Products from the reaction (1) with a variety of ketones reported in this study were analyzed by GC/MS by trapping the volatile products (emerging from the reactor) in absolute alcohol (at 0°C). Confirmation of the various oximes produced was obtained by GC/MS analysis of the products (collected in ethanol traps) using a Finnigan chemical ionization (with CH_4) mass spectrometer and by a specific spectrophotometric analysis for oximes (*7*).

The yield, Y, is the [(moles of oxime produced)/(moles of ketone fed in)] × 100. The selectivity, S, is the [(moles of oxime produced)/(total moles of ketone reacted)] × 100. The conversion, C, is the ratio of $(Y/S) \times 100$. The values of Y, C, and S reported in the following tables generally represent the highest (and generally constant) selectivity during a period of 3–6 hr after initiation of the flows. No pretreatment of the catalyst is necessary.

RESULTS

The results of the reaction of ammonia and oxygen with a wide variety of ketones are summarized in Tables 1, 2, and 3. Table 1 summarizes the results obtained with a variety of methyl-substituted ketones used to assess the steric or inductive effect of the electron-donating methyl group(s).

Most of the ketones listed in Table 2 were tested to establish that it was possible to perform the ammoximation reaction of internal, aliphatic ketones as well as an aromatic ketone such as acetophenone. Acetone was the only ketone that produced any CO_2. In addition, the ammoximation of acetone resulted in mesitylene and a variety of mono-, di-, and trimethylated pyridines. Eventually, the selectivity to acetone oxime was increased to ~41% at 270°C (with 49% conversion) by using the automated reactor system to optimize the selectivity over Porasil A. With acetone, the life of the catalyst was extended to ~6 days (as opposed to ~2 days with cyclohexanone) because of the lower amounts of residue which deposited on the catalyst.

One literature report (*8*) described the oxime of benzophenone as unstable in the presence of water and base, so it is unlikely that one would be able to detect substantial amounts of the oxime in our system. However, large amounts of the imine of benzophenone (*9*) were recovered. The catalyst did not gain any weight during the reaction, although it did apparently adsorb (hold up) large amounts of the ketone at 305°C.

Table 3 summarizes the ammoximation of a variety of cycloalkanones.

Competition Experiments with Cyclohexanone and Cyclopentanone

The control experiment of cyclopentanone, ammonia, and oxygen gave a selectivity of 18% (yields of 6–11%). With cyclohexanone (alone), ammonia, and oxygen (at 180°C, 1 cm^3 Porasil A, less than optimum conditions), the selectivity was 49% (yields

TABLE 1

Ammoximation of Methyl-Substituted Ketones

Substituted Cyclohexanone[a]	Catalyst temp. (°C)	C^{*b} (%)	Y (%)	C (%)	S (%)	Deposit[c] (g)	Comments[d]
2-Methyl	195	50	10	50	20	0.2	Secondary product with m/e = 125[e]
2,6-Dimethyl	200	40	~5	80	~7	0.1	Secondary product with m/e = 139[e]
3,3,5,5-Tetramethyl	200	—	8	60	12.5	0.1	Secondary product with m/e = 167[e]
2,2,6,6-Tetramethyl	195 (or 240)	21	None	11	—		GC/MS indicates the imine was the major product
Unsubstituted	195	80 → 50	22	40	51–55	0.15	

[a] 2% by volume in gas phase with ~50% NH_3, 12% O_2 over 1 cm^3 Porasil A; total flow = 21 cm^3/min (with helium).

[b] C^* is conversion of the ketone in the absence of O_2 under conditions given in footnote *a*.

[c] Weight of residue on catalyst/7 hr of reaction/for 0.4 g of catalyst.

[d] Identified by GC/MS; emerged off Carbowax column after the oxime.

[e] These m/e values are 2 amu less than those for the corresponding oxime.

of 20–25%). With a combined mixture of cyclopentanone (1.8%) and cyclohexanone (1.1%), ammonia, and oxygen over Porasil A, the selectivities to the corresponding oximes remained the same as with the control runs. With an excess of cyclohexanone (1.6%) over cyclopentanone (1.2%), similar results were observed. If only cyclohexanone, ammonia, and oxygen were passed over Porasil A for 4 hr and then the cyclohexanone feed was replaced with cyclopentanone, the selectivity for cyclopentanone oxime immediately rose to 54%! With this tripling of the selectivity, the life of the catalyst with respect to cyclopentanone conversion to the oxime was markedly increased. If the cyclopentanone feed was turned on first (with ammonia and oxygen present) and then replaced after 2 hr by cyclohexanone, the cyclohexanone oxime selectivity reached about 40%. (This probably reflects the more extensive deposition of the cyclopentanone by-product onto the catalyst, which results in lowering the activity of the catalyst.) When cyclohexanone, ammonia, and oxygen were passed over Porasil A for 4 hr and then cyclopentanone was added to the feed, the selectivity for both oximes remained comparable to the control experiments.

2,2,6,6,-d_4-Cyclohexanone

It was hoped that a deuterated sample of cyclohexanone might provide some information about the mechanism of the ammoximation process.[3] The standard flows of ammonia (50%) and oxygen (10%) were mixed with 2% (gas volume) of 2,2,6,6,-d_4-cyclohexanone and were allowed to react over Porasil A at 195°C. Initially a Carbowax 20M on Chromosorb WAW column was used (for the GC/MS analysis) to separate the oxime from the ketone, but it was discovered that this column catalyzed the

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[3] We have looked into purchasing partially enriched [^{13}C]cyclohexanone. The only supplier seems to be Merck (Canada), and the minimum price is $1500/g m.

TABLE 2

Ammoximation of Alternative Feeds

Substituted cyclohexanone[a]	Catalyst temp. (°C)	C^*[b] (%)	Y (%)	C (%)	S (%)	Deposit[c] (g)	Comments[d]
Acetone	200	—	11	56	20	0.2	4% acetone; product had characteristic amide odor; empirical formulas of residue $(C_3H_3N_1O_x)_n$: S_{CO_2} ~7%
3-Pentanone	230	—	10	50	20	0.2	Empirical formulas of residue $(C_3H_5N_1O_x)_n$
Acetophenone	210	—	>3	34	>10	0.2	Empirical formulas of residue $(C_{20}H_{13}N_1O_x)_n$; also observed benzonitrile and phenol as products
Benzophenone	305[e]	>90	None	>90[f]	—	None	
	375		Trace				
Pivalone[g]	190	—	—	None	—		
	350			10			
2,3-Butanedione	180	—	Trace	>95	—		Empirical formulas $(C_6H_8N_2O_x)_n$; traces of both mono- + dioximes
l-1,3,3-trimethyl-2-2-norbornanone (Fenchone)	225	—	Trace	36	—		
Bicyclo[3.3.1]non-9-one	200	76	Trace	~75	—		
Bicyclo[2.2.1]heptan-7-one	200	65	None	60	—		
(7-Norbornanone)	220		31	67	46[h]		
Hexanal	135	95	Traces	>90	—		

[a] 2% by volume in gas phase with ~50% NH_3, 12% O_2 over 1 cm^3 Porasil A; total flow = 21 cm^3/min (with helium).

[b] C^* is conversion of the ketone in the absence of O_2 under conditions given in footnote *a*.

[c] Weight of residue on catalyst/7 hr of reaction/for 0.8 g of catalyst.

[d] Identified by GC/MS; emerged off Carbowax column after the oxime.

[e] Due to the high boiling point of benzophenone.

[f] The imine of benzophenone is quite stable.

[g] Also referred to as di-t-butylketone or hexamethylacetone.

[h] Over a Porasil A catalyst which was deliberately covered with the residue from the reaction of cyclohexanone, NH_3, and O_2.

H/D exchange of the ketone so a Silar column was used. A fresh sample of Porasil A indicated substantial H/D exchange of the deuterated ketone and complete H/D exchange of the oxime within 1 hr. Using cyclohexanone (d_4), NH_3, and O_2, it was found that the aged (or blackened) Porasil A as a catalyst resulted in the complete H/D exchange of the cyclohexanone and its oxime. The experiment was repeated using a blackened (but active) source of Porasil A from the cyclohexanone (d_0) + NH_3/O_2 reaction. Once the deposit was formed, the cyclohexanone (d_0) feed was replaced with cyclohexanone (d_4). This time both the cyclohexanone and its oxime showed an immediate and almost complete H/D exchange.

DISCUSSION

A wide variety of ketones can be used in place of cyclohexanone in the ammoximation reaction described by Eq. (1). These include acetone, cyclopentanone, cyclohexanone, cycloheptanone, cyclooctanone,

TABLE 3

Ammoximation of Cyclic Ketones

Cyclic ketone[a]	Catalyst temp. (°C)	C^{*}[b] (%)	Y (%)	C (%)	S (%)	Deposit[c] (g)
Cyclopentanone	150	95	15	83	18	0.4
	200				<2	
Cyclohexanone	198	80 → 50[d]	20–22	40	51–55	0.15
Cycloheptanone	195	35	26	36	73	
Cyclooctanone	200	41	20	48	41[e]	0.25
Cyclodecanone	195	49	3.8	75	5	

[a] 2% by volume in gas phase with ~50% NH_3, 12% O_2 over 1 cm^3 Porasil A; total flow = 21 cm^3/min (with helium).

[b] C^* is conversion of the ketone in the absence of O_2 under conditions given in footnote *a*.

[c] Weight of residue on catalyst/7 hr of reaction/for 0.4 g of catalyst.

[d] Conversion is ~80% early in the reaction and then falls to ~50%/8 hr.

[e] Shoulder on oxime peak in GC.

cyclodecanone, 2-methylcyclohexanone, acetophenone, and 3-pentanone. A dione such as butane-2,3-dione seems to give both mono- and dioxime products. These results will be discussed as they relate to the mechanism of ammoximation and the formation of the unwanted by-product(s). With the limited effort summarized in Tables 1, 2, and 3 (at less than optimum conditions), appreciable amounts of the oxime were generated from ammonia, oxygen, and the appropriate ketone. Recall that these early experiments were carried out over Porasil A, a catalyst which has since been replaced by the more active silica–alumina described recently (*3*, *4*).

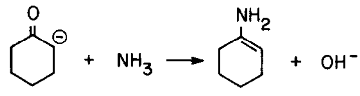
Competitive experiments between cyclopentanone (S = 18%) and cyclohexanone (S = 49%) in the presence of ammonia and oxygen over Porasil A at 195°C indicate that the catalyst is more effective when coated with the layer of the by-products from ammonia, oxygen, and cyclohexanone. These experiments suggest that the aldolization (*10*) of cyclohexanone contributes to making the Porasil A a better catalyst. Recalling our earlier work (*3*), no oxime is produced in the absence of Porasil A (with an empty catalyst tube or with the quartz chips in place of the silica gel catalyst). Further, the carbonaceous deposit occurs as soon as the feeds are initiated over the catalyst and continues during the extended period of reaction during which the selectivity remains fairly constant. The resulting surface deposit (of decomposed cyclohexanone) on the Porasil can be used to promote the ammoximation of other ketones, in this case cyclopentanone. This allows improved selectivity to the oxime for a ketone which by itself does not give rise to high selectivities for ammoximation. However, a deposit of cyclopentanone, ammonia, and oxygen on Porasil A does not provide a good surface for the ammoximation of cyclohexanone. Further, given the choice between cyclopentanone and cyclohexanone, the blackened Porasil A selectively reacts with cyclohexanone.

While a variety of mechanisms can be invoked to explain the ammoximation process, basically two types of mechanisms can be considered. In an earlier report (*3*), we suggested a mechanism invoking a common intermediate which either decomposes to yield the oxime or a residue derived from aldol condensation. Because of the residue which builds up on the catalyst with time, one must ask whether less than 1 mole of oxime is produced per mole of ketone consumed. It is well established (*11*) that ketones in basic media form anions that can be trapped by oxygen. If this occurs, the generation of a hydroperoxide is expected to result in the formation of a coproduct such as 2-hydroxycyclohexanone. For such a mechanism, the acidity of the α-hydrogens of the ketone would be expected to be an important factor in the generation of the oxime. In Table I, a variety of methyl-substituted cyclohexanones were tested. Adding one or two methyl groups alpha to the keto group of cyclohexanone seemed to reduce the selectivity to oxime. This lower selectivity might be due to the added bulk around the keto group. Adding four methyl groups beta to the keto group also lowered the selectivity.

Reaction of 2,2,6,6-tetramethylcyclohexanone with ammonia and oxygen over a variety of ammoximation catalysts did not yield significant amounts of oxime. Unlike cyclohexanone, 2,2,6,6-tetramethylcyclohexanone was not strongly adsorbed on the catalyst. Since this ketone gave essentially no oxime, one might now be tempted to conclude that acidic hydrogens alpha to the keto group are required for ammoximation. However, the high boiling point of this ketone required that the reactor be operated at very high reaction temperatures. Further, the imine of this ketone is very stable, and no further oxidation of the imine was observed.

Treating benzophenone with ammonia and oxygen produced mainly the imine and traces of the oxime. This ketone probably did not react as readily as some of the other ketones, because one must heat the catalyst beyond 300°C in order to avoid condensation of the ketone in the catalyst bed. At such high temperatures, any oxime which might form would eventually decompose. The reaction of a lower-boiling ketone without α-hydrogens, such as pivalone, with ammonia and oxygen over Porasil A did not result in any oxime production. Further, no substantial conversion of the ketone was detected. With pivalone, the methyl groups might serve to protect the keto function from attack by ammonia and/or oxygen. For ammonia to attack pivalone (to produce the imine), the C–C–C bond angle must close from 120 to 109°. If one builds a space-filling model of pivalone, it is difficult to see how one can further contract the C–C–C bond angle to 109° because of the bulky t-butyl groups. The stable imine of pivalone was also prepared. As with the imine of 2,2,6,6-tetramethylcyclohexanone, no substantial conversion of the imine of pivalone occurred. Once again we observed that stable imines did not undergo oxidation at temperatures less than 200°C. At first, these results might suggest that the imine is not the key intermediate in the ammoximation process; however, the difficulty in oxidizing the imine of pivalone must be due to the bulky methyl groups which hinder attack by oxygen. Indeed, this would explain why the imine of pivalone was only slowly hydrolyzed in the vapor phase.

In further efforts to determine the importance of α-hydrogens, we tested a variety of ketones which either did not have α-hydrogens or contained a keto group which was sterically constrained from forming the enamine. Enamines could be obtained from the reaction of ammonia with the carbanion formed by removing the acidic hydrogen of cyclohexanone.



(3)

Fenchone (*l*-1,3,3-trimethyl-2-norbornanone) with its high boiling point did not readily react with ammonia and oxygen. However, as with benzophenone, traces of the oxime of fenchone were observed. With such small amounts of oxime produced, one must be careful about drawing any firm conclusions. It is certainly apparent that the yield of oxime is markedly reduced; however, this may be due to potential oxidation of the oxime at the high temperatures used for the reaction (needed to ensure vaporization of the ketone). In addition, the steric effects of the methyl groups around the ketone serve to prevent any chemisorption of the ketone by the catalyst surface. Bicyclo[3.3.1]non-9-one gave traces of the corresponding oxime. While 7-norbornanone did not yield oxime over fresh samples of Porasil A, the blackened Porasil A did yield the corresponding oxime of this strained ketone. These last two ketones cannot readily form the enamine. The fact that we obtained some oxime suggested that enamines are not the only route to prepare the oxime.

One has to be very careful to evaluate the results in Table 2 with ketones containing either no α-hydrogens or strained keto groups. For any of the following reasons, these ketones may not provide a basis for a definite conclusion: (1) The ketone could absorb on the silica surface; therefore, it could not be activated; (2) the imine of the ketone is so hindered by the bulky methyl groups (adjacent to the carbon of the imine unit) that it is not susceptible to oxidation; (3) the ketone is too high boiling; hence, it is not reactive enough at 195 or 250°C, while at even higher temperatures overoxidation of the oxime might occur.

Experiments with 2,2,6,6-tetradeuterocyclohexanone, ammonia, and oxygen over Porasil A give the completely exchanged oxime; however, the control study without added oxygen also produces extensive H/D exchange of the α-hydrogens over the blackened Porasil A. From these experiments, it is impossible to determine the mechanism of the ammoximation reaction based on the prior exchange of the α-hydrogens on cyclohexanone as catalyzed by ammonia and Porasil A. It is interesting to point out that the α-hydrogens on cyclohexanone do undergo rapid H/D exchange consistent with the expected acidity of those hydrogens.

The acidity of the hydrogens alpha to the keto group is quite different for cyclopentanone relative to cyclooctanone. There are various arguments as to the relative acidities of the α-hydrogens (*12*). Perhaps the best report on these acidities is based on a series of base-catalyzed brominations of cycloalkanones (*13*). These brominations involve the formation of the enolate ion as the rate-determining step. The relative rates for C_5, C_6, C_7, and C_8 cycloalkanones are 9.9 : 1.0 : 1.7 : 3.4. There is an even bigger shift for the base-catalyzed isomerizations of the exo to the endo forms of the corresponding alkylidenecycloalkanes (45.4 : 1 : 5.8 : 17) (*14*). The linear correlation (represented by a log/log plot) suggests that the controlling factors for ketone enolization and isomerization of the alkylidenecycloalkanes are stereoelectronic relationships governing the ease of the rehybridization of the allylic bond (*14*). The use of the cycloalkanones provided a useful correlation between extent of aldolization (ammonia plus ketone to unwanted byproducts) and the selectivity to the corresponding oxime when oxygen was added to the feed stream. The best selectivity was obtained with cycloheptanone (S = 73 ± 5%) without any extensive attempts to optimize the reaction.

Figure 1 compares the effect of just NH_3 upon the conversion of the cycloalkanones

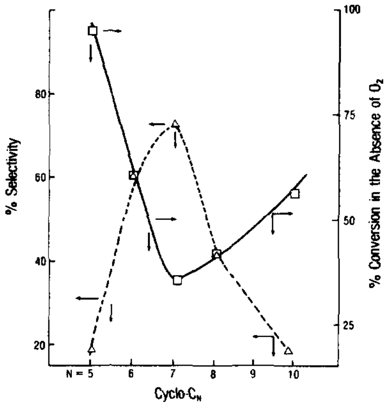


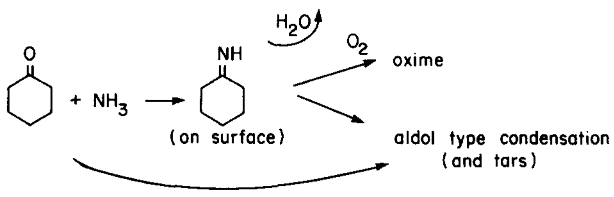
FIG. 1. Behavior of cyclic ketones. Ammoximation of cycloalkanones (△) versus ammonolysis of cycloalkanones (□). The left-hand coordinate represents the best selectivity to the oxime under any set of reaction conditions. The right-hand coordinate corresponds to the conversion of the ketone under these reaction conditions without any oxygen added to the feed stream.

over Porasil A with the selectivity for oxime formation when oxygen and ammonia are added to the gaseous cycloalkanone over Porasil A. It is clear that the best selectivity is obtained with cycloheptanone and the worst selectivity with cyclopentanone. Up to the C_{10} system, the selectivities are inversely related to the amount of aldolization which has occurred (as measured by the conversion of the ketone with no oxygen present). It is not clear why cyclohexanone is less selective than cycloheptanone. Perhaps this may be related to a faster rate for ammoximation in the C_7 case. With cyclooctanone, the selectivity again falls to the level of cyclohexanone. Therefore, there does appear to be a direct correlation between minimizing the aldolization and maximizing the ammoximation reactions. However, there may still be other competitive paths which contribute to the present selectivity of 73% for cycloheptanone. That is, one may have minimized cycloheptanone aldolization and still have other minor side reactions which now are more important than before.

This marked improvement in selectivity to the cycloheptanone oxime is certainly linked to the low conversion of just ammonia and ketone over the catalyst. The work on the bromination of cycloalkanones indicates that the enolization of C_5 is much more extensive than that of C_6 or C_7. It must be remembered that our studies deal with a gas-phase reaction where parallel paths are probably involved. By limiting the amount of enolization, we have increased the probability for ammoximation, hence the higher selectivity in going from C_5 to C_7.

With all these results in mind, a mechanism which invokes a carbanion and a peroxo complex now seems unlikely for the following reasons. (1) One does obtain traces of oximes with some ketones which do not contain hydrogens alpha to the keto group. (2) A peroxo species is not expected to be very stable at 200°C on the surface of the silica gel. (3) Upon the addition of peroxide to the feed stream, no increase in the selectivity to cyclohexanone oxime is observed. (4) The potential coproducts of a peroxo intermediate, that is, adipoin or adipic acid, are not observed. (5) The stoichiometry for a peroxo mechanism would suggest a maximum selectivity of 50% to the oxime. We have already reported a selectivity above 68% to the oxime (3). If reaction (1) was governed by the formation of substantial by-products, it is unlikely that we would have achieved a selectivity as high as 68%. (6) Equation (1) is applicable to many different types of ketones, and the selectivity appears to be strongly related to the ability of the ketone to undergo aldolization.

The above data cannot rule out any number of possible mechanisms which can be proposed for the ammoximation process. However, the data is consistent with a parallel-path process wherein some ketone goes via aldolization to a tar. Our best catalyst simply diverts more of the ketone to the desired oxime rather than to tar.



Hexanal, ammonia, and oxygen reacted even in the absence of a catalyst. Over Porasil A (135°C) some aldoxime was produced as well as large amounts of by-products. Aldehydes tend to be much more reactive than ketones (*15*), and it would appear that in the presence of ammonia and oxygen this is certainly the case. In fact, they are so reactive that by-product formation predominates over oxime formation. If hexanal is representative of aldehydes, one can conclude that aldehydes do yield some aldoxime in addition to large amounts of by-products.

In conclusion, a variety of organic substrates can be substituted for cyclohexanone in the ammoximation process. One can generate oximes from a wide variety of ketones including acetone, cyclopentanone, cyclohexanone, cycloheptanone, cyclooctanone, 2-methylcyclohexanone, 2,6-dimethylcyclohexanone, 3,3,5,5-tetramethylcyclohexanone, 3-pentanone, and acetophenone. Ketones which form stable imines such as pivalone (hexamethylacetone) and benzophenone do not produce significant amounts of oxime when treated with ammonia and oxygen in the gas phase over a variety of catalysts. This may be due to either the absence of α-hydrogens and/or the fact that the keto group is somewhat blocked for attack (as in benzophenone) for a selective oxidation. With the cyclic ketones, an inverse relationship is observed between the selectivity to the oxime and the aldolization of the ketone. This suggests that the aldolization of the ketone exerts a strong effect upon the ammoximation process.

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