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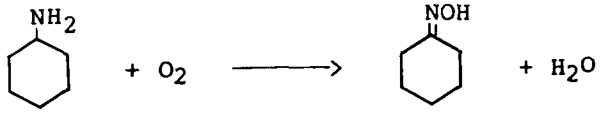
The Selective Oxidation of Cyclohexylamine to Its Oxime

We have discovered a highly specific oxidation of a primary amine to its oxime using molecular oxygen. For large scale oxidation processes, oxygen is desirable because it is certainly cheaper than other oxidants. Generally, the use of molecular oxygen for the oxidation of primary amines results in the loss of the nitrogen functionality (with ketone formation) (*1*) or extensive oxidative dehydrogenation to yield the corresponding nitriles (*2*) (via intermediate imine species) (*3*). Recently, coordinated ammonia was oxidized electrochemically (via a proposed hydroxylamine species) (*4*) to nitrate, while coordinated amines have also been oxidized to imines and nitriles electrochemically or with more precious oxidants such as Ce(IV) (*5*). Although peroxides are expensive, they do provide high selectivity and can oxidize primary amines to their oximes in the presence of tungstic acid (*6, 7*). However, there appears to be no prior report of a highly selective oxidation of the nitrogen center of an organic amine to an oxime with molecular oxygen.

The oxidation of cyclohexylamine was studied by passing the amine vapor, blended with O_2 and a diluent such as helium, through a Pyrex glass tube (~12 mm i.d.) containing the solid catalyst (20–80 mesh). Reactants and products were analyzed quantitatively by GLC using a column of Carbowax 20M on Teflon. This analysis and the reactor configuration have been described in earlier reports (*8–13*).

The vapor phase oxidation of cyclohexylamine to its oxime as described by Eq. (1) was observed over a variety of heterogeneous catalysts. Oxime was not produced in the absence of a solid catalyst or in the absence of oxygen. Oxime production occurred over an extended period of time (days) with a small amount of coke-like residue depositing on the catalyst. Over the WO_3/Al_2O_3 catalyst, the only other volatile product (at $< \frac{1}{20}$ the oxime level) of reaction (1) was the imine: *N*-(cyclohexylidene)–cyclohexylamine(I). In separate experiments (*14*), we observed that the oxime undergoes some further decomposition to the corresponding ketone over a catalyst such as WO_3/Al_2O_3. Cyclohexanone reacts rapidly with cyclohexylamine to produce the imine by-product (*15, 16*). Attempts to improve the selectivity of reaction (1) by adding NH_3 or the imine(I) to the reactants proved unsuccessful. In addition, no significant oxidation (by O_2) occurred in solutions of cyclohexylamine heated under reflux in the presence of the solid catalyst.



(1)

A variety of heterogeneous catalysts were effective for reaction (1), and these are summarized in Table 1. Other materials that proved ineffective for the catalysis of reaction (1) included quartz chips, a zeolite (ZSM-5), MgO, various silica-aluminas,

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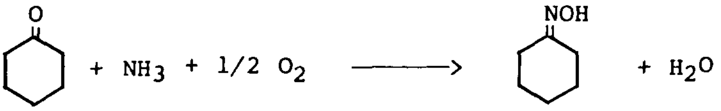
ZrO_2, activated carbon, and α-Al_2O_3. A number of common oxidation catalysts were also tested. While these catalysts demonstrated good conversions (*C*), they showed very poor selectivity (*S*) to the oxime. These included CuO/Al_2O_3 (T = 160°C; C = 47%; S = 5%), V_2O_5/SiO_2 (175°C; C = 32; S = 6), MoO_3/Al_2O_3 (152°C; C = 46; S = 17), and Bi/Mo oxides (240°C; C = 15; S = 16).

As shown in Table 1, even silica gel was found to be a good catalyst for the selective oxidation of the amine to its oxime. Also, tungstate salts were promoters of γ-Al_2O_3 for reaction (1), and these catalysts provided a 64% selectivity to the oxime. The amine was found to be strongly adsorbed on the surface of all these catalysts. Due to the strength of the Si–O bond, silica can only provide the necessary surface to activate the primary amine with the actual oxidation proceeding by some type of O_2 activated species.

Much of our work on reaction (1) focused on cyclohexylamine; however, other primary amines gave trace amounts of the oxime (e.g., isopropylamine, 2°-butylamine, 2°-hexylamine, and cyclooctylamine). In each case, the major product was the corresponding ketone.

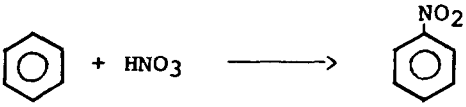
It is interesting to compare the catalysis of reaction (1) with the catalysis of the ammoximation of cyclohexanone, reaction (2).



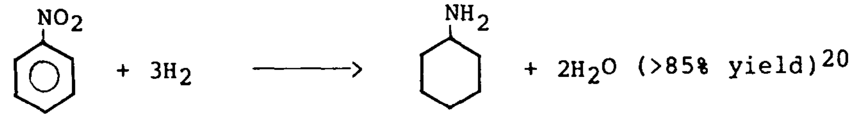
(2)

Silica (*10, 17*) was found to be an effective catalyst for both reactions. However, the silica-alumina catalysts which were so effective (*11, 12*) for reaction (2) were ineffective for reaction (1). While tungstate salts were promoters of reaction (1), these (and other metal) salts were ineffective for reaction (2). Lastly, reaction (2) was much more general, since it was demonstrated for a wide variety of ketones. Therefore, in many ways, both reactions (1) and (2) are quite different from one another.

Initially, the work on the oxidation of cyclohexylamine to the corresponding oxime was carried out to support mechanistic studies on the ammoximation of cyclohexanone [Eq. (2) (*10*)]. However, as a need arose for alternative feedstocks (*18*) for the production of caprolactam, this oxidation reaction (Eq. (1)) attracted renewed interest. If the selectivity for Eq. (5) could be improved further, the four equations below might constitute a new 4-step route to caprolactam. Present commercial routes have 8–12 process steps. This route would also greatly reduce the amount of $(NH_4)_2SO_4$ currently produced by most other processes (*22*).



(99+% yield)[19] (3)



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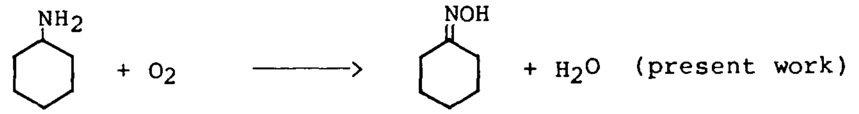
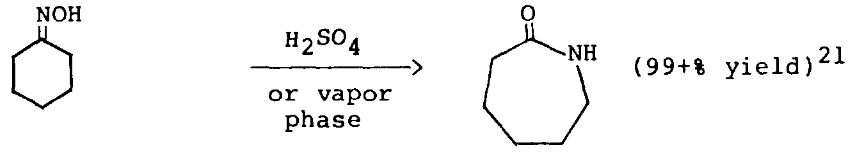


(5)



(6)

TABLE 1

Heterogeneous Oxidation Catalysts for Cyclohexylamine[a]

Catalyst	Wt (Vol) (g) (cm^3)	Temperature (°C)	*C* (%)	*S* (%)[b]
SiO_2-gel[c] (Porasil A)	1.0 (2)	155	20	50
γ-Al_2O_3[d]	(2)	170	10	40
WO_3/SiO_2[e]	1.0 (2)	159	28	54
WO_3/Al_2O_3[f]	1.5 (2)	148	16	35
		161	15	50
		191	29	29
		227	58	17
WO_3/Al_2O_3[g] via ASB	1.0 (6.6)	160	33	64

[a] Conditions: 1–4% cyclohexylamine vapor, 19% O_2, total flow 21 cm^3/min.

[b] S = Selectivity to oxime = moles of oxime produced/moles of amine consumed; $Y = C \times S/100$ = yield = moles of oxime produced/moles of amine fed.

[c] Supplied by Waters Associates (Waltham, MA); pore volume (P.V.) = 1.0 cm^3/g; surface area (S.A.) = 450 m^2/g.

[d] Supplied by United Catalyst, #T-126; S.A. = 227 m^2/g; similar results obtained with ASB (footnote *g*) as the source of γ-Al_2O_3.

[e] Prepared by impregnating ammonium metatungstate (10% by weight W) onto Porasil A.

[f] Ten percent WO_3/Al_2O_3 as supplied by Alfa products; S.A. = 145 m^2/g.

[g] Prepared by hydrolyzing aluminum *sec*-butoxide (ASB) with an aqueous solution of ammonium metatungstate (10% by weight W). P.V. = 1.9 cm^3/g; S.A. = 460 m^2/g.

In addition to the novel, selective, air oxidation of the amine to its oxime reported above, this work reports a second example of SiO_2-gel serving as a catalyst for a vapor-phase oxidation reaction (*17*). Further, it points to a dramatic difference in selectivity when using cyclohexylamine in comparison with other primary amines, as a substrate.

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