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A Catalytic Synthesis of Nitriles from Aldehydes and Alcohols in the Presence of Aqueous Ammonia by Oxidation with $NiSO_4$-$K_2S_2O_8$

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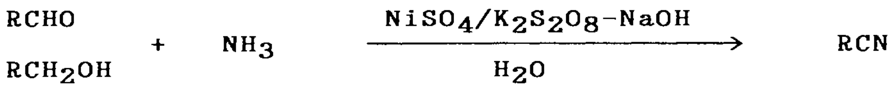
Aromatic and conjugated aldehydes were converted to nitriles by nickel-catalyzed oxidation in the presence of aqueous ammonia with $K_2S_2O_8$ under the basic aqueous conditions. This reaction could be applied to alcohols as the starting materials.

We previously reported that $NiSO_4$-$K_2S_2O_8$ in basic aqueous media was proved to be an effective catalytic oxidation system in which the catalytically active species was nickel peroxide, and that the system could be applied to the transformation of allylic alcohols to α,β-unsaturated carbonyl compounds[1] and aliphatic primary amines to nitriles.[2] Here we report a facile and one-pot conversion of aldehydes and alcohols to nitriles by nickel-catalyzed oxidation in the presence of aqueous ammonia.

There has been some reports on the one step transformation of aldehydes and alcohols to nitriles in the presence of ammonia in organic media by oxidizing agents such as oxygen-copper(II) chloride,[3] lead tetraacetate[4] and iodine,[5] but there has been no reaction using aqueous ammonia as the nitrogen source.[6]



$$\begin{matrix}\mathrm{RCHO}\\ \mathrm{RCH_2OH}\end{matrix} + \mathrm{NH_3} \xrightarrow[\mathrm{H_2O}]{\mathrm{NiSO_4/K_2S_2O_8-NaOH}} \mathrm{RCN}$$

At first, benzaldehyde was oxidized in CH_2Cl_2-H_2O as the two phase solvent system as is the case with the nickel-catalyzed oxidation of amines to nitriles.[2] Under the conditions, a considerable amount of benzaldehyde was remained even after 24 h, and benzonitrile was obtained in moderate yield (46%) along with benzoic acid (16%). The oxidation of benzyl alcohol gave almost the same result with the oxidation of benzaldehyde on the yield of benzonitrile.

To improve the low conversion of the starting materials, we investigated several reaction conditions, and found that when the reaction was carried out without using organic solvent, the aldehydes and alcohols were smoothly converted to nitriles.

The results of the oxidation of aldehydes in basic aqueous media were summarized in Table 1. The reaction was performed typically as follows: aqueous 0.050 M $NiSO_4$ (1 M = 1 mol dm^{-3}, 1.6 mL, 0.080 mmol) was added to the stirring mixture of aldehyde (4.0 mmol), $K_2S_2O_8$ (1.6 g, 6.0 mmol) and NaOH (0.80 g, 20 mmol) in H_2O (30 mL) at room temperature. Fine black precipitates of nickel peroxide were formed immediately upon the addition of $NiSO_4$. Aqueous ammonia (28%, 5.5 mL, 40 mmol) was added to the mixture, and the resulted mixture was stirred vigorously at room temperature for 3-6h. After the mixture was passed through a short Celite column to remove nickel precipitates, the filtrate was extracted with CH_2Cl_2. The CH_2Cl_2 extract was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. Nitrile was obtained from the residue by purification with silica gel PTLC or column chromatography.

In some cases, the black precipitates of nickel peroxide were dissolved into the aqueous mixture upon addition of aqueous ammonia, however, no reaction took place. When a small amount of *iso*-PrOH was added before the addition of $NiSO_4$ in these cases, the precipitates were not disappeared and the reaction proceeded smoothly (Runs 2-5). Thus the catalytically active species in this oxidation must be the black precipitate of nickel peroxide. The addition of large excess of ammonia causes dissolution of nickel peroxide through the coordination of ammonia, therefore no oxidation takes place. The α,β-unsaturated aldehydes such as cinnamaldehyde, α-methylcinnamaldehyde and citral were converted to the corresponding unsaturated nitriles in good to moderate yields (Runs 5-7). On the other hand, the non-conjugated aldehydes such as citroneral and 3-phenylpropanal gave no nitrile.

When the oxidation was carried out with alcohols as the starting materials under the similar conditions without using *iso*-PrOH, the reaction proceeded smoothly to give nitriles in good yields (Table 2). In most cases, the yields of nitriles were higher than those obtained by the oxidation of corresponding aldehydes shown in Table 1.

Aldehydes are reacted with ammonia to form aldimines which are oxidatively dehydrogenated to nitriles with $NiSO_4$-$K_2S_2O_8$. The reactions started from alcohols proceed via aldehydes, which are formed by the oxidation of the alcohols under the reaction conditions.[1)]

Nakagawa and coworkers have shown[7)] that alcohols and aldehydes could

Table 1. Synthesis of Nitriles from Aldehydes and Aqueous Ammonia[a]

Run	Aldehyde	Method[b]	Time / h	Conv. / %	Yield/%[c] Nitrile	Yield/%[c] Acid[d]
1	Benzaldehyde	A	3	100	76[e]	9
2	*p*-Methylbenzaldehyde	B	3	100	65	20
3	*p*-Methoxybenzaldehyde	B	5	97	75(78)	10(10)
4	Piperonal	B[f]	6	92	62(68)	16(18)
5	Cinnamaldehyde	B	3	100	64	ND[g]
6	α-Methylcinnamaldehyde	A[f]	6	40	21(54)	ND[g]
7	Citral	A[f]	6	95	48(51)	ND[g]

a) See text for reaction conditions. b) Method A: without *iso*-PrOH; Method B: with *iso*-PrOH (Runs 2 and 3: 2 mL; Runs 4 and 5: 5 mL). c) Isolated yields. The numbers in parentheses are the yields based on the recovered aldehydes. d) Carboxylic acids were obtained from the acidified aqueous layer by extraction with CH_2Cl_2. e) Determined by GC. f) 2 equivalents of $K_2S_2O_8$ was used. g) Not determined.

Table 2. Synthesis of Nitriles from Alcohols and Aqueous Ammonia[a]

Run	Alcohol	Time / h	Conv. / %	Yield/%[b] Aldehyde	Yield/%[b] Nitrile
1	Benzyl alcohol	3	100	0	82[c]
2	*p*-Methylbenzyl alcohol	6	100	0	75
3	*p*-Methoxybenzyl alcohol	1.5	100	8	75
4	*p*-Chlorobenzyl alcohol	4	100[d]	3	52
5	Cinnamyl alcohol	3	100	0	74[e]
6	Geraniol	6	93	15	40

a) Reaction conditions: a mixture of aqueous 0.050 M $NiSO_4$ (1.6 mL, 0.080 mmol), alcohol (4.0 mmol), aqueous 28% NH_3 (5.5 mL, 40 mmol), $K_2S_2O_8$ (3.2 g, 12 mmol) and NaOH (0.80 g, 20 mmol) in H_2O (60 mL) was stirred vigorously at room temperature. b) Isolated yields. c) Determined by GC. d) 16 mmol of $K_2S_2O_8$ was used. e) 4% of benzonitrile was also obtained.

be converted to the corresponding amides, when the stoichiometric nickel peroxide was used in ether dissolving gaseous ammonia at -20 °C. When the same reaction was performed at 78 °C in benzene, the yields of the amides lowered and the corresponding nitriles were mainly formed. On the other hand, the catalytic nickel peroxide oxidation described here proceeds at room temperature to give nitriles as the main product with aqueous ammonia.

The substrates which provide good results in this system are aromatic/conjugated aldehydes and benzylic/allylic alcohols, which are soluble in basic aqueous media or liquid at room temperature. Though the synthetic method described in this paper has such limitations, this novel catalytic system provide a facile method of one-step conversion of aldehydes and alcohols to nitriles by using aqueous ammonia as the nitrogen source.

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