Ceric Ammonium Nitrate Catalyzed Oxidation of Aldehydes and Alcohols

Gowda, Ravikumar R. Chakraborty, Debashis*

Department of Chemistry, Indian Institute of Technology Madras, Chennai-600 036, Tamil Nadu, India

A variety of aromatic, aliphatic and conjugated aldehydes and alcohols were transformed to the corresponding carboxylic acids and ketones with a quantitative conversion in high yields with 70% *t*-BuOOH solution in water in the presence of catalytic amounts of ceric ammonium nitrate [Ce(NH$_4$)$_2$(NO$_3$)$_6$] (CAN) under room temperature conditions. The scope of our catalytic system is applicable for a wide range of aromatic, conjugated and aliphatic substrates. These aldehydes were converted to the corresponding carboxylic acids in good isolated yields in reasonable times. This method possesses a wide range of capabilities since it can be used with other functional groups which may not tolerate oxidative conditions, involves fairly simple method for work-up, exhibits chemoselectivity and proceeds under ambient conditions. The resulting products are obtained in good yields within reasonable time.

Keywords oxidation, aldehyde, alcohol, ceric ammonium nitrate (CAN), *t*-BuOOH

Introduction

The oxidation of alcohols has been of contemporary interest due to diversified potential in organic chemistry and industrial manufacturing, and is recognized a fundamental reaction.[1-5] The oxidation of primary alcohols gives aldehydes that may be further oxidized to carboxylic acids. The most popular and widely used reagent for oxidation is Jones reagent.[6-11] However, the reaction is stoichiometric and is performed under highly acidic conditions. Substrates having acid sensitive functionalities may not tolerate such acidity. In addition, the generation of Cr-based side products may be viewed as a potential environmental hazard.[12]

Other reagents that have been used successfully include Oxone,[13] calcium hypochlorite[14] and 2-hydroperoxyhexafluoro-2-propanol.[15] Catalytic methods with metals have been developed for oxidation reactions. Different methodologies for metal mediated transformation of aldehydes to carboxylic acids have been reported recently.[16-27] The catalytic oxidations of alcohols employing transition metals such as Ru, Co, Mo, Pd, V and W have been reported.[28-39] In addition, 2,2,6,6-tetramethylpiperidinyl-1-oxyl often referred to as TEMPO along with NaClO has been an efficient combination for such oxidations.[40-46]

The above reagents and methods have one or more limitations which include the use of superstoichiometric amounts of expensive reagents and use of highly basic or acidic reaction conditions. The search for catalytic processes that use environmentally benign reagents is always an attractive avenue.

Our recent results highlight the oxidation of alde-hydes to carboxylic acid using 30% H$_2$O$_2$ as the oxidant in the presence of catalytic amounts of AgNO$_3$.[47] We were successful in employing Bi$_2$O$_3$ as a suitable catalyst for oxidation.[48,49] We were interested in CAN oxidations since it is a table-top reagent familiar to a chemist from early years of education.

Experimental section

General reagents and equipments

All the substrates along with *t*-BuOOH, used in this study were purchased from Aldrich and used as received. The solvents used were purchased from Ranchem, India and purified using standard methods. ^{1}H and ^{13}C spectra were recorded with a Bruker Avance 400 instrument. Chemical shifts were referenced to residual solvent resonances and are reported relative to SiMe$_4$. 0.5 mL CDCl$_3$ was used for every NMR spectral measurements. ^{1}H NMR spectra were collected at 400 MHz using a 6000 Hz spectral width, a relaxation delay of 3.5 s, a pulse width of 38°, 30k data points, and CDCl$_3$ (δ 7.27) as an internal reference. ^{13}C NMR spectra were collected at 100 MHz using a 25000 Hz spectra width, a relaxation delay of 1.5 s, 75k data points, a pulse width of 40°, and CDCl$_3$ (δ 77.23) as the internal reference. About 8—10 mg of sample was dissolved in CDCl$_3$ and used for measurement. HPLC analysis was done with Waters HPLC instrument fitted with Waters 515 pump and Waters 2487 dual λ absorbance detector. The column employed was washed thoroughly until a consistent base line was found. Suitable methods were developed with different propotions of MeCN and alcohol.

Typical procedure for the oxidation of aldehyde to carboxylic acid

To a stirred solution of CAN (5 mg, 0.01 mmol or 50 mg, 0.1 mmol) and aldehyde (1 mmol or 10 mmol) in 2.5 mL or 25 mL MeCN was added 70% *t*-BuOOH (water) (0.13 mL, 1 mmol or 1.3 mL, 10 mmol). The progress of the reaction was monitored using TLC until all aldehyde was found consumed. The crude product was treated with saturated NaHCO₃ solution. This was extracted with ethyl acetate. Finally, the aqueous layer was acidified using 2 mol•L⁻¹ HCl and extracted with ethyl acetate. The organic layer was concentrated and subjected to column chromatography. The spectral data of the various carboxylic acids were found to be satisfactory in accord with the literature (see supplementary material for details).

Typical procedure for the oxidation of primary alcohol to carboxylic acid in MeCN

To a stirred solution of CAN (10 mg, 0.02 mmol or 100 mg, 0.2 mmol) and primary alcohol (1 mmol or 10 mmol) in 2.5 mL or 25 mL MeCN was added 70% *t*-BuOOH (water) (0.26 mL, 2 mmol or 2.6 mL, 20 mmol). The progress of the reaction was monitored using TLC until all aldehyde was found consumed. The crude product was treated with saturated NaHCO₃ solution. This was extracted with ethyl acetate. Finally, the aqueous layer was acidified using 2 mol•L⁻¹ HCl and extracted with ethyl acetate. The organic layer was concentrated and subjected to column chromatography. The spectral data of the various carboxylic acids were found to be satisfactory in accord with the literature (see supplementary material for details).

Typical procedure for the oxidation of secondary alcohol to ketone in MeCN

To a stirred solution of CAN (10 mg, 0.02 mmol or 100 mg, 0.2 mmol) and secondary alcohol (1 mmol or 10 mmol) in 2.5 mL or 25 mL MeCN was added 70% *t*-BuOOH (water) (0.26 mL, 2 mmol or 2.6 mL, 20 mmol). The progress of the reaction was monitored using TLC until all aldehyde was found consumed. The crude product was treated with saturated NaHCO₃ solution. This was extracted with ethyl acetate. Finally, the aqueous layer was acidified using 2 mol•L⁻¹ HCl and extracted with ethyl acetate. The organic layer was concentrated and subjected to column chromatography. Spectral characterization of the various ketones was found to match with the literature.

Results and discussion

Oxidation of aldehydes and alcohols

Initial attempts to optimize the reaction conditions for the oxidation of aldehydes to the corresponding carboxylic acids were done using benzaldehyde as the substrate in the presence of different solvents, oxidants and 1 mol% of CAN (Table 1).

Table 1 Optimization of the reaction conditions for the conversion of benzaldehyde to benzoic acid with different solvents, 1 equiv. 70% *t*-BuOOH (water) and 1 mol% Ce salts

Entry	Catalyst	Solvent	Time^a/h	Yield^b/%
1	CAN	EtOAc	20	85
2	**CAN**	**MeCN**	**12**	**95**
3	CAN	toluene	40	79
4	CAN	CH₂Cl₂	30	84
5	CAN	DMF	35	79
6	CAN	DMSO	32	78
7	CAN	THF	28	87
8	CAN	MeOH	18	83
9	CAN	CH₃NO₂	32	85
10	CeCl₃	MeCN	34	45
11	CeBr₃	MeCN	37	30

^{a} Time required for complete conversion with 2% standard deviation. ^{b} Isolated yield after column chromatography of the crude product with ethyl acetate and hexane with 2% standard deviation.

The conversion of benzaldehyde to benzoic acid is extremely facile in MeCN at ambient temperature in the presence of 1 mol% CAN and 1 equiv. 70% *t*-BuOOH (water) as the oxidant (Table 1, Entry 2). Oxidation with *t*-BuOOH (water) alone in MeCN was found to be negligible (<5%). With 1 equiv. 5 mol•L⁻¹ *t*-BuOOH (decane), the reaction was complete in 15 h with 90% isolated yield.

The reaction took longer for completion (18 h) when performed with 1 equiv. 30% H₂O₂ in MeCN. Among the different solvents used for optimization (Table 1, Entries 1—9), MeCN gave the best results. The other Ce(III) salts (Table 1, Entries 10 and 11) yielded poor results. In the absence of solvent, the reaction has gone to completion in 16 h with 85% yield when performed with 1 equiv. 70% *t*-BuOOH (water) and 1 mol% CAN. Since most of the aldehydes in Table 2 are solids at ambient temperature, we have chosen MeCN as appropriate solvent.

We have performed large scale reaction (10 mmol of benzaldehyde) in MeCN at ambient temperature in the presence of 1 mol% CAN and 1 equiv. 70% *t*-BuOOH (water) as the oxidant (Table 1, Entry 2), the reaction has gone to completion in 12 h and yield is found to be 95%.

Having realized the correct conditions for oxidation, we proceeded with a variety of aromatic and aliphatic substrates (Scheme 1, Table 2).

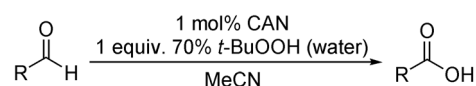**Scheme 1** CAN catalyzed oxidation of aldehydes to carboxylic acids

Table 2 CAN catalyzed oxidation of aldehydes to carboxylic acids [a]

Entry	Aldehyde	Acid	Time[b]/min	Yield[c]/%
1	Ph—CHO	Ph—COOH	12	95
2	MeO—C6H4—CHO	MeO—C6H4—COOH	10	93
3	C6H4(OMe)—CHO	C6H4(OMe)—COOH	15	94
4	MeO—C6H4—CHO	MeO—C6H4—COOH	19.5	93
5	(MeO)2C6H3—CHO	(MeO)2C6H3—COOH	10	94
6	(MeO)3C6H2—CHO	(MeO)3C6H2—COOH	15	90
7	HO—C6H4—CHO	HO—C6H4—COOH	15	88
8	Me2N—C6H4—CHO	Me2N—C6H4—COOH	45	86
9	Cl—C6H4—CHO	Cl—C6H4—COOH	10	89
10	Cl2C6H3—CHO	Cl2C6H3—COOH	27	88
11	C6H4(NO2)—CHO	C6H4(NO2)—COOH	32.5	90
12	C6H4(NO2)—CHO	C6H4(NO2)—COOH	35	91
13	O2N—C6H4—CHO	O2N—C6H4—COOH	44	92
14	furyl—CHO	furyl—COOH	15	93
15	Ph—CH=CH—CHO	Ph—CH=CH—COOH	13	94
16	CH2=CH—CH=CH—CHO	CH2=CH—CH=CH—COOH	20	92
17	alkyl—CHO	alkyl—COOH	24	85

[a] Reactions performed in MeCN with 1 mol% CAN and 1 equiv. t-BuOOH (water) under ambient conditions. [b] Time required for complete conversion with 2% standard deviation. [c] Isolated yield after column chromatography of the crude product with ethyl acetate and hexane with 2% standard deviation.

The scope of our catalytic system is applicable for a wide range of aromatic, conjugated and aliphatic substrates. These aldehydes were converted to the corresponding carboxylic acids in good isolated yields in reasonable times (Table 2).

It is pertinent to mention here that mild halogenic oxidants like hypochlorites,[14,50,51] chlorites[52,53] and NBS[54,55] are not suitable for substrates with electron rich aromatic rings, olefinic bonds and secondary hydroxyl groups. Substitutions at different positions on the phenyl ring do not hinder the reaction, although the reaction time is affected.

Our catalytic system is mild and shows sufficient selectivity in carrying out the expected oxidation without affecting other functionalities like phenol and amine (Table 2, Entries 6—9). Oxidation of α, β unsaturated derivatives (Table 2, Entries 15—16) resulted in the formation of the expected acid in very good yield.

Having made success in the transformation of the aldehyde functionality into carboxylic acid, we decided to explore the possibility of converting primary alcohols to carboxylic acids and secondary alcohols to ketones with CAN. The optimization of reaction conditions for the oxidation of primary alcohols to the corresponding carboxylic acids was performed with benzyl alcohol as a suitable substrate in the presence of different solvents, oxidants and 2 mol% of CAN (Table 3).

Table 3 Optimization of the reaction conditions for the conversion of benzyl alcohol to benzoic acid with different solvents, 2 equiv. 70% t-BuOOH (water) and 2 mol% Ce salts

Entry	Catalyst	Solvent	Time[a]/h	Yield[b]/%
1	CAN	EtOAc	23	84
2	**CAN**	**MeCN**	**15**	**96**
3	CAN	toluene	44	77
4	CAN	CH2Cl2	35	89
5	CAN	DMF	39	75
6	CAN	DMSO	42	72
7	CAN	THF	37	85
8	CAN	MeOH	29	79
9	CAN	CH3NO2	37	82
10	CeCl3	MeCN	45	30
11	CeBr3	MeCN	43	18

[a] Time required for complete conversion with 2% standard deviation. [b] Isolated yield after column chromatography of the crude product with ethyl acetate and hexane with 2% standard deviation.

The oxidation of benzyl alcohol to benzoic acid takes place rapidly in the presence of 2 mol% Ce salts and 2 equiv. 70% t-BuOOH (water) using MeCN as a suitable solvent (Table 3, Entry 2). With 2 equiv. 5 mol·L^{-1} t-BuOOH (decane), the reaction was found complete in 17 h with 90% isolated yield. Various trials

were done in the presence of different solvents (Table 3, Entries 1—9) and other Ce(III) salts (Table 3, Entries 10 and 11). In the absence of solvent, the reaction has gone to completion in 19 h with 86% yield when performed with 2 equiv. 70% *t*-BuOOH (water) and 2 mol% CAN. Since most of the alcohols in Table 4 are solids at ambient temperature, we have chosen MeCN as appropriate solvent.

We have performed large scale reaction (10 mmol of benzyl alcohol) in MeCN at ambient temperature in the presence of 2 mol% CAN and 2 equiv. 70% *t*-BuOOH (water) as the oxidant (Table 3, Entry 2), the reaction has gone to completion in 15 h and yield is found to be 96%.

We proceeded with investigation of the oxidation of various aromatic and aliphatic substrates (Scheme 2, Table 4).
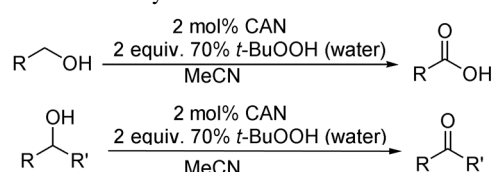
Scheme 2 CAN catalyzed oxidation of alcohols

Table 4 CAN catalyzed oxidation of primary alcohols to carboxylic acids and secondary alcohols to ketones

Entry	Alcohol	Acid/Ketone	Time[a]/ h	Yield[b]/ %
1	Ph—CH$_2$OH	Ph—COOH	15	96
2	MeO—C$_6$H$_4$—CH$_2$OH	MeO—C$_6$H$_4$—COOH	19	92
3	2-OMe-C$_6$H$_4$—CH$_2$OH	2-OMe-C$_6$H$_4$—COOH	23	95
4	3-MeO-C$_6$H$_4$—CH$_2$OH	3-MeO-C$_6$H$_4$—COOH	27	90
5	3,4-(MeO)$_2$C$_6$H$_3$—CH$_2$OH	3,4-(MeO)$_2$C$_6$H$_3$—COOH	18	88
6	(MeO)$_3$C$_6$H$_2$—CH$_2$OH	(MeO)$_3$C$_6$H$_2$—COOH	22	86
7	HO—C$_6$H$_4$—CH$_2$OH	HO—C$_6$H$_4$—COOH	24	90
8	Me$_2$N—C$_6$H$_4$—CH$_2$OH	Me$_2$N—C$_6$H$_4$—COOH	58	89
9	Cl—C$_6$H$_4$—CH$_2$OH	Cl—C$_6$H$_4$—COOH	22	92

Entry	Alcohol	Acid/Ketone	Time[a]/ h	Yield[b]/ %
10	3,4-Cl$_2$C$_6$H$_3$—CH$_2$OH	3,4-Cl$_2$C$_6$H$_3$—COOH	39	85
11	2-NO$_2$-C$_6$H$_4$—CH$_2$OH	2-NO$_2$-C$_6$H$_4$—COOH	49	84
12	3-O$_2$N-C$_6$H$_4$—CH$_2$OH	3-O$_2$N-C$_6$H$_4$—COOH	51	92
13	4-O$_2$N-C$_6$H$_4$—CH$_2$OH	4-O$_2$N-C$_6$H$_4$—COOH	58	88
14	furyl—CH$_2$OH	furyl—COOH	23	92
15	Ph—CH=CH—CH$_2$OH	Ph—CH=CH—COOH	21	88
16	CH$_2$OH (aliphatic)	COOH	30	86
17	CH$_2$OH (aliphatic alkene)	COOH	31	90
18	Ph$_2$CHOH	Ph$_2$C=O	12	80
19	PhCH(OH)CH$_3$	PhC(O)CH$_3$	28	85
20	(4-Me-C$_6$H$_4$)$_2$CHOH	(4-Me-C$_6$H$_4$)$_2$C=O	9	89
21	4-O$_2$N-C$_6$H$_4$—CH(OH)CH$_3$	4-O$_2$N-C$_6$H$_4$—C(O)CH$_3$	32	92

[a] Time required for complete conversion with 2% standard deviation. [b] Isolated yield after column chromatography of the crude product with ethyl acetate and hexane with 2% standard deviation. [c] Reactions performed in MeCN with 2 mol% CAN and 2 equiv. *t*-BuOOH (water) under ambient conditions.

Again we see that CAN actively catalyzes the transformation of different primary alcohols to the corresponding benzoic acid with variety of different substrates. Our catalyst shows sufficient selectivity in this oxidation without disturbing functional groups like phenol and amine (Table 4, Entries 6—9). Oxidation of α,β-unsaturated derivatives (Table 4, Entries 15 and 17) resulted in the formation of the expected acid in good yield. In addition, the transformation of secondary alcohols to ketones is extremely facile as indicated by Entries 18—21 of Table 4.

Kinetic studies

The kinetic studies of the oxidation with 3,4-dimethoxybenzaldehyde, 2-nitrobenzaldehyde, cro-

tonaldehyde, (3-nitrophenyl) methanol and di-*p*-tolyl-methanol were explored next. High-pressure liquid chromatography (HPLC) was used to determine the various starting materials, products and aldehyde intermediates for alcohol oxidation present as a function of time. Different trials were done under the same conditions till concordant readings were observed. The concentration of reactant, intermediate and product for the oxidation of (3-nitrophenyl) methanol is shown in Figure 1.
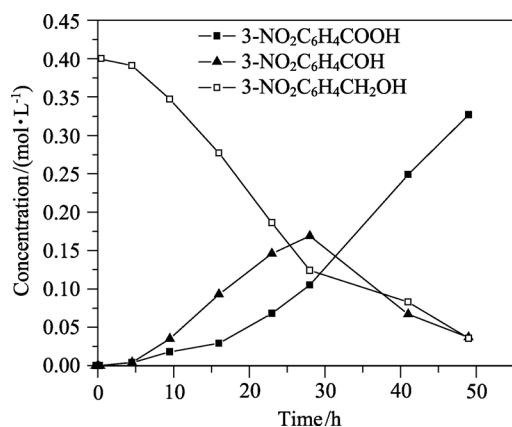

Figure 1 Concentration versus time in the oxidation of (3-nitrophenyl) methanol with 2 mol% CAN and 2 equiv. *t*-BuOOH in MeCN under ambient conditions with 2% standard deviation.

The concentration of the alcohol decreases steadily while that of the carboxylic acid increases. The concentration of the intermediate aldehyde increases, achieves a maximum and then progressively converts itself to the acid. We have calculated the rate of such reactions. As an example let us consider the oxidation of (3-nitrophenyl) methanol. The Van't Hoff differential method was used to determine the order (*n*) and rate constant (*k*) (Figure 2).
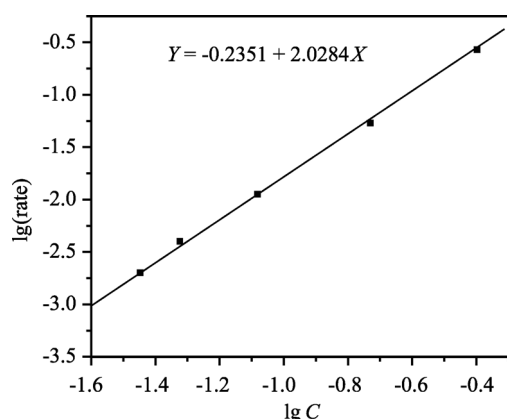

Figure 2 Van't Hoff differential plot for the oxidation of (3-nitrophenyl) methanol with 2 mol% CAN and 2 equiv. *t*-BuOOH in MeCN under ambient condition.

From Figure 1, the rate of the reaction at different concentrations can be estimated by evaluating the slope

of the tangent at each point on the curve corresponding to that of (3-nitrophenyl) methanol. With these data, lg(rate) versus lg(concentration) is plotted. The order (*n*) and rate constant (*k*) is given by the slope of the line and its intercept on the lg(rate) axis. From Figure 2, it is clear that this reaction proceeds with second-order kinetics (*n* = 2.02) and the rate constant $k = 9.699 \times 10^{-3}$ $L \cdot mol^{-1} \cdot min^{-1}$. For the other substrates namely 3,4-dimethoxybenzaldehyde, 2-nitrobenzaldehyde, crotonaldehyde, and di-*p*-tolylmethanol, the order of the reaction $n \approx 2$ with rate constants (*k*) 0.1266, 6.653×10^{-3}, 5.662×10^{-2} and 9.826×10^{-2} $L \cdot mol^{-1} \cdot min^{-1}$ respectively (see supplementary material for details).

Conclusions

In summary, we have developed a simple, efficient, chemoselective and inexpensive catalytic method for the oxidation of aldehydes to carboxylic acids, primary alcohols to carboxylic acids and secondary alcohols to ketones using a table top reagent such as CAN. It is noteworthy that this method does not use ligands and other additives.

Acknowledgements

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