Ceric Ammonium Nitrate Catalyzed Oxidation of Sulfides to Sulfoxides

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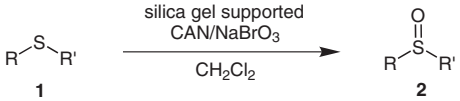
Abstract: Oxidation of sulfides to sulfoxides with a catalytic amount of ceric ammonium nitrate (CAN) reagent supported on silica gel has been achieved. Stoichiometric sodium bromate is utilized as the primary oxidant to continue the catalytic cycle involving CAN. Solid-supported CAN reagent allowed us to avoid using aqueous reaction media generally employed in CAN-promoted reactions. This heterogeneous CAN/$NaBrO_3$ reagent has simplified the reaction work-up and product isolation, produced higher product yields, and shortened reaction times compared to reactions with homogeneous CAN reagents employing aqueous media.

Key words: silica gel, solid support, CAN, sulfide, sulfoxide

Ceric ammonium nitrate (CAN) is a versatile oxidant. It has been very effective in promoting the oxidative transformations of a variety of organic substrates.[1] Ceric ammonium nitrate is a one-electron transfer reagent and has a high molecular weight; therefore, a large quantity of CAN is required for a reaction utilizing stoichiometric amounts of CAN reagent. This is a serious impediment to its large-scale use. To circumvent this limitation, stoichiometric CAN has been replaced with a dual oxidant system consisting of a catalytic amount of CAN and stoichiometric amount of $NaBrO_3$.[2–5] The purpose of the co-oxidant $NaBrO_3$ is to regenerate Ce(IV) oxidant to continue the desired oxidation activity. One of the benefits of this dual oxidant system is that $NaBrO_3$ is less expensive and has much lower molecular weight compared to CAN, therefore, a smaller amount of the co-oxidant is required to regenerate the Ce(IV) oxidizing species.

Until now, oxidation reactions with the CAN/$NaBrO_3$ dual oxidant system utilized aqueous acetonitrile reaction media. Water was necessary to dissolve CAN and $NaBrO_3$ since they both have limited solubility in common organic solvents. Solid-supported stoichiometric Ce(IV) oxidizing reagents have been reported by us[6] and by others;[7–12] however, to our knowledge, no work has been reported on using supported catalytic CAN reagent on a solid.

For some time, we have engaged in exploring solid-supported reagents and their use in organic functional group transformations as green chemistry. We have reported several reagents on solid supports.[6,13–23] One of these reagents is a silica gel supported stoichiometric CAN reagent utilized in the oxidation of sulfides to sulfoxides in nonaqueous reaction media.[6] Our previous successes in this area prompted us to investigate the possibility of developing a heterogeneous catalytic CAN reagent by supporting both CAN and $NaBrO_3$ on silica gel in the same manner and use this heterogeneous reagent in the oxidation of sulfides (Scheme 1).



Scheme 1 Oxidation of sulfides with silica gel supported CAN/$NaBrO_3$ reagent

We herein report the results of our efforts in utilizing the silica gel supported CAN/$NaBrO_3$ dual oxidizing system in the oxidation of sulfides in dichloromethane reaction media. This new procedure avoids aqueous reaction media as well as extractive aqueous work-up. One of the benefits of this procedure is that it does not produce waste water contaminated with metals. Compared to CAN-promoted reactions in aqueous organic biphasic media, our heterogeneous procedure involves fewer steps, renders the reagent safer by reducing metal mobility, and produces smaller amounts of solid waste. Our newly developed solid-supported dual oxidant shortened reaction times and produced higher yield compared to the reported results from similar oxidation reactions using homogeneous CAN/$NaBrO_3$ dual reagents in aqueous media.[3] We attribute the rate enhancement and higher yields to the dispersion of the reagents over a large surface area provided by the fine particles of silica gel.

The hygroscopic nature of silica gel allows us to immobilize CAN and $NaBrO_3$ on silica gel. The supported reagent is prepared by us by vigorously stirring a concentrated aqueous solution of a mixture of catalytic amount of CAN and stoichiometric amount of $NaBrO_3$ with silica gel until a free-flowing light yellow solid is produced (see the experimental section for details). Silica gel immobilizes the solubilized dual oxidants on its surface. The reaction was conducted by stirring a mixture of CAN/$NaBrO_3$ solid-supported reagent and the sulfide in dichloromethane at room temperature till completion of the reaction as evidenced by TLC. After cessation of stirring, the light orange colored heterogeneous reagent settled at the bottom of the reaction flask and a clear and colorless dichloromethane layer containing the product remained on the top. Oxidation of thioanisole (**1**, R = Ph, R′ = Me) using various amounts of CAN was used to optimize the amount

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of CAN to be used to prepare the heterogeneous reagent. These results are presented in Table 1.

The role of $NaBrO_3$ co-oxidant utilized in this procedure is to regenerate the Ce(IV) species which oxidizes sulfides to sulfoxides. $NaBrO_3$ does not oxidize sulfides to sulfoxides directly since $NaBrO_3$ alone supported on silica gel failed to produce thioanisole oxidation product in 24 hours reaction period (Table 1, entry 1). The rate of oxidation reaction in the presence of 1.0 mol% of CAN was extremely slow (entry 3). The rate of oxidation increased significantly as the amount of CAN increased to 5 mol% (entry 6) and produced a quantitative yield of methyl phenyl sulfoxide in 45 minutes. However, use of 10 mol% of CAN reduced the reaction time to only a few minutes (entry 7). The amount of co-oxidant $NaBrO_3$ present does not have any significant effect on the outcome of this reaction as long as it is present in greater than stoichiometric amount. The rate and the selectivity of oxidation of thioanisole remain unchanged when the amount of $NaBrO_3$ in the dual oxidation system increased from 2.2 mmol to 4.4 mmol (entry 8). The absence of any detectable amount of sulfone in the product, even when an excess amount of $NaBrO_3$ was used, indicates a high selectivity of this oxidant towards sulfoxide formation.

Table 1 Optimization of Reaction Conditions for the Oxidation of $PhSCH_3$ (**1**, R = Ph, R′ = Me)[a]

Entry	PhSMe (mmol)	CAN (mol%)	$NaBrO_3$ (mmol)	Reaction time	Yield of PhSOMe (%)[b]
1	2.0	0	2.2	24 h	0
2	2.0	1.0	2.2	5 h	0
3	2.0	1.0	2.2	6 d	4
4	2.0	2.5	2.2	7 h	15
5	2.0	2.5	2.2	5 d	99
6	2.0	5.0	2.2	45 min	ca. 100
7	2.2	10.0	2.2	13 min	99
8	2.2	10.0	4.4	15 min	92
9	10.0	2.0	12.0	5 h	5
10	10.0	2.0	12.0	2 d	20
11	10.0	2.0	12.0	5 d	99
12	10.0	5.0	11.0	5 min	99
13	10.0	10.0	11.0	5 min	99

[a] PhSMe (**1**, R = Ph, R′ = Me; 2.0 mmol) was oxidized to PhSOMe (**2**, R = Ph, R′ = Me) with silica gel supported CAN/$NaBrO_3$ at r.t. in CH_2Cl_2.
[b] Yield of isolated product.

Table 2 Oxidation of Sulfides **1** to Sulfoxides **2**

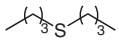
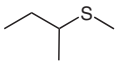
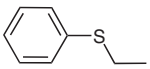
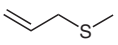
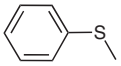
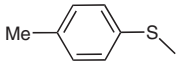
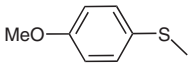
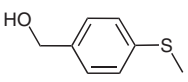
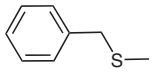
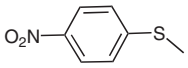
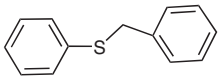
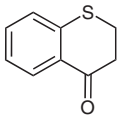
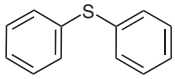
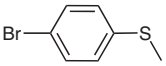
Entry	Sulfide **1**	CAN (mmol)	$NaBrO_3$ (mmol)	Reaction time (min)	Yield (%) of Sulfoxide **2**
a		0.2	2.2	14	89
b		0.05	2.2	150	96
c		0.2	2.2	10	94
d		0.1	2.2	30	98
e		0.2	2.2	15	78
f		0.2	2.2	10	93
g		0.1	2.2	120	85
h		0.2	2.2	27	70
i		0.2	2.2	15	80
j		0.2	2.2	13	99
k		0.2	2.2	10	98
l		0.2	2.2	10	97
m		0.2	2.2	30	75 (+ less than 5% of aldehyde product)

Table 2 Oxidation of Sulfides **1** to Sulfoxides **2** (continued)

Entry	Sulfide **1**	CAN (mmol)	$NaBrO_3$ (mmol)	Reaction time (min)	Yield (%) of Sulfoxide **2**
n		0.2	2.2	15	99
o		0.2	2.2	10	93
p		0.2	2.2	45	96
q		0.2	2.2	34	96
r		0.2	2.2	10 h	96
s		0.2	2.2	15	95

We employed 2.0 mmol of sulfide **1**, 0.2 mmol of CAN (10 mol% with respect to the sulfide) and 2.2 mmol of $NaBrO_3$, unless otherwise indicated, in the reactions reported in Table 2. Although as low as 2.5 mol% of CAN is capable of oxidizing sulfides to sulfoxides in days, we employed 10 mol% of CAN in these reactions to maintain short reaction times. Under these reaction conditions, it took between 10 and 45 minutes to complete the reactions. Sterically hindered sulfides took comparatively longer to complete the reaction than sterically unhindered sulfides. With 0.05 mmol of CAN (2.5 mol% with respect to sulfide), the reaction time for the oxidation of butyl sulfide (**1a/b**) increased from 14 minutes to 150 minutes to produce near quantitative yields of butyl sulfoxide (Table 2, entry **b**). Oxidation of tetramethylene sulfide (**1c/d**) and ethyl phenyl sulfide (**1f/g**) with 0.1 mmol of CAN (5 mol% with respect to the sulfides) took 30 minutes and 120 minutes, respectively, to produce a good yield of the corresponding sulfoxides (entries **d**,**g**).

None of the reactions reported in this communication produced a significant amount of sulfone. However, allyl methyl sulfide (**1h**) did not produce good yields of sulfoxides due to the susceptibility of alkene moiety towards the oxidizing reagents used (entry **h**).

All reactions were magnetically stirred. CH_2Cl_2 was used as received from the supplier without any further purification. Sulfides were purchased from Aldrich and used without further purification. Ceric ammonium nitrate was purchased from Aldrich. The silica gel used in the oxidation reactions as solid support was MN-Kieselgel 60 (0.04–0.063 mm mesh size) supplied by Fisher Scientific. NMR spectra were recorded on a Bruker DPX-300 NMR instrument (^1H at 300 MHz, ^{13}C at 75 MHz). Samples for NMR were dissolved in $CDCl_3$. Proton and carbon chemical shifts are expressed as ppm relative to tetramethylsilane. IR spectra were recorded on a Perkin-Elmer Spectrum-1000 FT-IR instrument and are reported in wave numbers (cm^{-1}). Preparative centrifugal TLC with silica gel (Merck # 7749) was done on a Chromatotron Model 7924T. Analytical TLC was done on pre-coated silica gel plates with 254 nm fluorescent indicator (Merck # 5715) and developed in a 1:4 mixture of EtOAc–hexane solvent system. Compounds were visualized by UV and/or by staining either with a *p*-anisaldehyde/H_2SO_4 or phosphomolybdic acid. The sulfoxides **2a**,**c**,**e**,**f**,**j**,**r** used for comparison are commercial products.

Oxidation of Sulfides 1 to Sulfoxides 2; Methyl Phenyl Sulfoxide (2j); Typical Procedure

Dry silica gel (5 g) was placed in a 100 mL round-bottomed flask containing a magnetic stirring bar and a loosely fitted rubber septum. An aqueous solution (2 mL) of a mixture of CAN (110.0 mg, 0.2 mmol) and $NaBrO_3$ (332.0 mg, 2.2 mmol) was added slowly from a syringe to the vigorously stirred silica gel. The contents of the flask were stirred for 5 min or until a light yellow-orange colored, free-flowing solid was produced. CH_2Cl_2 (20 mL) was added to the reaction flask. A solution of thioanisole (**1j**; 248.4 mg, 2.0 mmol) in CH_2Cl_2 (5 mL) was added slowly from a syringe through the rubber septum to the stirred heterogeneous mixture. The yellow-orange color of the reagent disappeared instantly. The mixture was stirred at r.t. for 13 min. During this period complete disappearance of the thioanisole was evident by TLC [EtOAc–hexane (1:4) as the developing solvent and *p*-anisaldehyde/H_2SO_4 as the staining agent]. The mixture was then filtered through a sintered glass funnel, the solid residue was washed with CH_2Cl_2 (60 mL), and the washings were added to the filtrate. Removal of solvent from the CH_2Cl_2 solution under vacuum produced a reddish thick oil. Radial chromatography of the crude product using silica gel solid media and EtOAc–hexane (1:4) as the eluent afforded pure methyl phenyl sulfoxide (**2j**) as a reddish thick oil (277.5 mg, 99%).

IR (film): 690, 746, 955, 1034, 1088, 1415, 1443, 1477, 2912, 2997, 3056 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.73 (s, 3 H), 7.50–7.54 (m, 3 H), 7.62–7.70 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 43.8, 123.4, 129.3, 131.0, 145.5.

Dibutyl Sulfoxide (2a)

IR (film): 1026, 1272, 1408, 1465, 2872, 2930, 2958 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92 (t, *J* = 7.2 Hz, 3 H), 1.28–1.70 (m, 2 H), 1.68–1.78 (m, 2 H), 2.60 (t, *J* = 7.62 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.7, 22.0, 24.6, 52.1.

Tetramethylene Sulfoxide (2c)
IR (film): 768, 995, 1096, 1212, 1284, 1408, 2877, 2974 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.03-2.08 (m, 2 H), 2.43–2.47 (m, 2 H), 2.87–2.92 (m, 4 H, CH_2CH_2).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.8, 53.5.

2-(Methylsulfinyl)butane (2e)
Diastereomeric mixture (~1:1).

IR (film): 943, 1023, 1152, 1214, 1383, 1404, 1460, 2879, 2935, 2973 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.04 (2 t, *J* = 7.3 Hz, 3 H), 1.07 (t, *J* = 7.4 Hz, 3 H), 1.21 (d, *J* = 6.84, 3 H), 1.27 (d, *J* = 6.84 Hz, 3 H), 1.45 (m, 2 H), 1.84–1.87 (m, 2 H), 2.42 (m, 1 H), 2.53 (2 s, 6 H), 2.69–2.71 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.7, 10.9, 11.3, 11.4, 22.6, 23.2, 33.9, 34.4, 57.7, 58.3.

Ethyl Phenyl Sulfoxide (2f)
IR (film): 748, 998, 1044, 1086, 1146, 1306, 1446, 1478, 2875, 2935, 2979, 3057 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.20 (t, *J* = 6.8 Hz, 3 H), 2.72–2.98 (m, 2 H), 7.50–7.63 (m, 5 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 6.3, 50.6, 124.6, 129.5, 131.3, 143.1.

Allyl Methyl Sulfoxide (2h)[24]
IR (film): 741, 953, 1044, 1438, 1646, 2922, 3006, 3076 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.05 (s, 3 H), 3.48 (m, 2 H), 5.10–6.20 (m, 3 H).

1,4-Thioxane 4-Oxide (2i)[25]
IR (film): 729, 826, 1014, 1039, 1095, 1274, 1320, 1382, 1403, 1461, 2863, 2922, 2976 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.72–2.78 (m, 2 H), 2.91–3.0 (m, 2 H), 3.80–3.87 (m, 2 H), 4.32–4.40 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 46.2, 59.1.

Methyl 4-Methylphenyl Sulfoxide (2k)[26]
IR (film): 812, 956, 1039, 1087, 1294, 1407, 1495, 1597, 2736, 2921, 2993, 3045 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.41 (s, 3 H), 2.72 (s, 3 H), 7.32 (d, *J* = 8.5 Hz, 2 H), 7.54 (d, *J* = 8.5 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.3, 43.8, 123.5, 129.98, 141.5, 142.3.

4-Methoxyphenyl Methyl Sulfoxide (2l)[26]
IR (film): 831, 957, 1027, 1090, 1179, 1255, 1303, 1497, 1578, 1595, 2839, 2974, 2990, 3004, 3104 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.70 (s, 3 H), 3.84 (s, 3 H), 7.04 (d, *J* = 8.8 Hz, 2 H), 7.58 (d, *J* = 8.8 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 44.2, 55.8, 115.5, 126.1, 136.8, 162.2.

4-Hydroxymethylphenyl Methyl Sulfoxide (2m)[27]
IR (film): 809, 958, 1010, 1026, 1202, 1365, 1406, 2915, 3022, 3062, 3352 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.67 (s, 3 H), 4.03 (br s, 1 H, OH), 4.70 (s, 2 H), 7.45–7.55 (m, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 43.6, 63.9, 123.8, 127.5, 143.3, 145.3.

Benzyl Methyl Sulfoxide (2n)[26]
IR (film): 767, 1028, 1201, 1301, 1422, 1455, 1496, 2916, 2976, 3031, 3056 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.45 (s, 3 H), 4.00 (2 d, *J* = 6 Hz, 2 H), 7.20–7.40 (m, 5 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 37.4, 60.3, 128.9, 129.4, 130.0, 130.5.

Methyl 4-Nitrophenyl Sulfoxide (2o)[28]
IR (film): 740, 849, 958, 1045, 1344, 1518, 2838, 2936, 3036 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.80 (s, 3 H), 7.86 (d, *J* = 8.8 Hz, 2 H), 8.41 (d, *J* = 8.8 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 43.8, 124.5, 124.64, 149.5, 153.3.

Benzyl Phenyl Sulfoxide (2p)[29]
IR (film): 690, 742, 925, 1026, 1283, 1441, 1516, 2924, 2976, 3060 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.97 (d, *J* = 12.5 Hz, 1 H), 4.10 (d, *J* = 12.5 Hz, 1 H), 6.90–6.98 (m, 2 H), 7.21–7.28 (m, 3 H), 7.38–7.48 (m, 5 H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 63.4, 124.4, 128.2, 128.4, 128.8, 129.0, 130.3, 131.2, 142.5.

Thiooxachroman-4-one *S*-Oxide (2q)[30]
IR (film): 773, 1036, 1183, 1283, 1326, 1441, 1586, 1690, 2894, 2922, 2986, 3008, 3063 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.86–2.95 (m, 1 H), 3.45–3.54 (m, 3 H), 7.70 (t, *J* = 7.5 Hz, 1 H), 7.80 (t, *J* = 7.5 Hz, 1 H), 7.90 (d, *J* = 7.6 Hz, 1 H), 8.15 (d, *J* = 7.6 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 30.7, 47.1, 128.9, 129.4, 129.6, 132.6, 135.1, 145.9, 192.5.

Diphenyl Sulfoxide (2r)
IR (film): 708, 766, 1049, 1104, 1453, 1485, 3067 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.30–7.60 (m, 10 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 126.8, 129.1, 131.0, 145.7.

4-Bromophenyl Methyl Sulfoxide (2s)[31]
IR (film): 722, 816, 960, 1007, 1045, 1085, 1386, 1420, 1472, 2910, 2995, 3044 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.74 (s, 3 H), 7.53 (d, *J* = 8.7 Hz, 2 H), 7.68 (d, *J* = 8.7 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 43.8, 125.2, 125.4, 132.5, 144.6.

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