

# Aerobic oxidation of sulfides catalysed by cobalt(II) complexes under homogeneous and heterogeneous conditions

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Received 2 August 1995; accepted 15 November 1995

## Abstract

The Co(II)-catalysed oxidation of alkyl- and aryl-sulfides was achieved under homogeneous and heterogeneous conditions using oxygen or air as the oxidant in the presence of excess aldehyde. The reactions in the homogeneous phase were carried out using the soluble  $\text{Co}(\text{acac})_2$  or  $\text{Co}(\text{AAEMA})_2$  complexes ( $\text{AAEMA}^-$  = deprotonated form of 2-(acetoxycetoxy)ethyl methacrylate) whereas the heterogeneous catalytic tests were carried out using the copolymers obtained by reaction of  $\text{Co}(\text{AAEMA})_2$  with acrylamides. Under suitable conditions excellent conversions and very good selectivities were achieved both in homogeneous and in heterogeneous phase. The supported complexes were recyclable with negligible loss of efficiency and did not suffer from metal leaching.

**Keywords:** Sulphoxidation;  $\beta$ -Ketoesters; Heterogeneous reactions; Cobalt; Supported catalysts; Polymer-supported catalysis

## 1. Introduction

The oxidation of sulfur compounds is arousing great interest in the academical and industrial communities. Recent work showed that sulfoxidations can be achieved by charcoal-supported sterically hindered cobalt(II)-phthalocyanines/ $\text{O}_2$  [1], *t*-butylhydroperoxide [2], hydroxyl radicals [3], 1,4-dimethoxynaphthalene promoted photooxidation [4], sodium hypochlorite and oxoammonium salts [5], ruthenium trichloride/sodium periodate [6], methylrhenium trioxide/hydrogen peroxide [7], metal phthalocyanines/iodosylbenzene [8],  $\text{HNO}_3/\text{Fe}(\text{III})$  [9], sodium perruthenate [10] and

that catalytic asymmetric reactions can also be accomplished [11].

We have recently shown that a mixture of branched aldehyde, oxygen and a polymerizable Fe(III), Ni(II) or Co(II) complex can oxidize sulfur compounds such as dimethylsulfide or di-*n*-butylsulfide to the corresponding sulfoxides or sulfones [12]. Cobalt(II) based system was shown to be superior both in activity and in selectivity when compared to the analogous Ni(II)- and Fe(III)-based systems.

Starting from those preliminary results, in this paper we propose a general method for the oxidation of sulfur compounds by means of cobalt(II) complexes under homogeneous and heterogeneous phase.  $\text{Co}(\text{AAEMA})_2$  or the commercially available  $\text{Co}(\text{acac})_2$  were used

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under Mukaiyama's oxidation conditions (1 atm dioxygen in the presence of excess *i*-valeraldehyde) for the reactions carried out in the homogeneous phase.

The copolymer obtained by reaction of Co(AAEMA)<sub>2</sub> with *N,N*-dimethylacrylamide (DMAA) and *N,N'*-methylenebisacrylamide (MBAA) in *N,N*-dimethylformamide (DMF) [13] (see Scheme 1) was used as the heterogeneous catalyst.

## 2. Results and discussion

The aerobic oxidations of dimethylsulfide (1), di-*n*-butylsulfide (2) and diphenylsulfide (3) in the homogeneous phase were accomplished both with Co(acac)<sub>2</sub> and Co(AAEMA)<sub>2</sub> using O<sub>2</sub> or air as the oxidant. The reactions were carried out in concentrated 1,2-dichloroethane solutions

with an aldehyde/substrate ratio equal to 3 in the case of (1) and (2), equal to 4.5 in the case of the oxidation of (3) by oxygen and equal to 6 in the case of the oxidation of (3) by air. Moreover, the sacrificial aldehyde was added at the beginning of the reaction for the substrates (1) and (2), whereas it was added dropwise during the course of the reaction for substrate (3). This procedure was suggested by the observation that, when the oxidation of (3) was carried out in the presence of an initial aldehyde/substrate ratio equal to 3, the reaction stopped before completion in consequence of the consumption of the sacrificial aldehyde. The oxidation could be restarted if successive additions of fresh aldehyde were made to the reaction mixture. In these conditions the total amount of sacrificial aldehyde necessary for the completion of the reaction was a 4.5-fold excess in the O<sub>2</sub> promoted reaction, and a 6-fold excess in

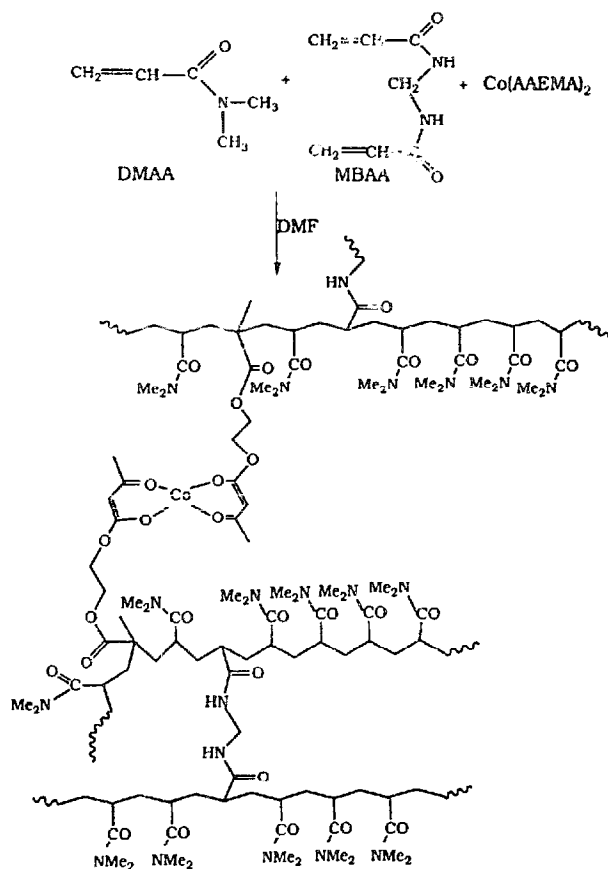
Table 1

Aerobic oxidation of sulfides (1.20 mmol) by Co(II) complexes (0.020 mmol) in the presence of *i*-valeraldehyde in 1,2-dichloroethane (2.0 ml) at room temperature and atmospheric pressure

Entry	Substrate	Catalyst	mmol aldehyde	Oxidant	Time (h)	Conv. (%)	Yield (%)	
							Sulfoxide	Sulfone
1	CH <sub>3</sub> -S-CH <sub>3</sub>	Co(acac) <sub>2</sub>	3.6	O <sub>2</sub>	2	100	–	100
2	CH <sub>3</sub> -S-CH <sub>3</sub>	Co(acac) <sub>2</sub>	3.6	air	4	70	100	–
3	CH <sub>3</sub> -S-CH <sub>3</sub>	Co(acac) <sub>2</sub>	3.6	air	15	100	–	100
4	CH <sub>3</sub> -S-CH <sub>3</sub>	Co(AAEMA) <sub>2</sub>	3.6	O <sub>2</sub>	2	100	–	100
5	CH <sub>3</sub> -S-CH <sub>3</sub>	Co(AAEMA) <sub>2</sub>	3.6	air	6	80	100	–
6	CH <sub>3</sub> -S-CH <sub>3</sub>	Co(AAEMA) <sub>2</sub>	3.6	air	15	10	–	100
7	Bu-S-Bu	Co(acac) <sub>2</sub>	3.6	O <sub>2</sub>	6	92	88	12
8	Bu-S-Bu	Co(acac) <sub>2</sub>	3.6	O <sub>2</sub>	7	100	7	93
9	Bu-S-Bu	Co(acac) <sub>2</sub>	3.6	air	22	97	88	12
10	Bu-S-Bu	Co(acac) <sub>2</sub>	3.6	air	32	100	20	80
11	Bu-S-Bu	Co(AAEMA) <sub>2</sub>	3.6	O <sub>2</sub>	8	91	94	6
12	Bu-S-Bu	Co(AAEMA) <sub>2</sub>	3.6	O <sub>2</sub>	9.5	100	–	100
13	Bu-S-Bu	Co(AAEMA) <sub>2</sub>	3.6	air	38	95	91	9
14	Bu-S-Bu	Co(AAEMA) <sub>2</sub>	3.6	air	60	100	1	99
15 <sup>a</sup>	Ph-S-Ph	Co(acac) <sub>2</sub>	5.4	O <sub>2</sub>	2	100	6	94
16 <sup>b</sup>	Ph-S-Ph	Co(acac) <sub>2</sub>	5.4	air	3	95	94	6
17 <sup>b</sup>	Ph-S-Ph	Co(acac) <sub>2</sub>	5.4	air	11	100	15	85
18 <sup>a</sup>	Ph-S-Ph	Co(AAEMA) <sub>2</sub>	5.4	O <sub>2</sub>	2	100	4	96
19 <sup>b</sup>	Ph-S-Ph	Co(AAEMA) <sub>2</sub>	7.2	air	2	90	94	6
20 <sup>b</sup>	Ph-S-Ph	Co(AAEMA) <sub>2</sub>	7.2	air	12	100	11	89

<sup>a</sup> The aldehyde was added as follows: 0.9 mmol were present at the beginning of the reaction and 4.5 mmol dissolved in 2.0 ml of 1,2-dichloroethane were added dropwise in the course of the reaction at a rate of 2.5 mmol/h.

<sup>b</sup> The aldehyde was added as follows: 0.9 mmol were present at the beginning of the reaction and 6.3 mmol dissolved in 2.0 ml of 1,2-dichloroethane were added dropwise in the course of the reaction at a rate of 1.0 mmol/h.

Scheme 1. Synthesis of supported  $\text{Co(AAEMA)}_2$ .

the reaction carried out in the air. Since the procedure of adding the aldehyde in successive stages was rather inconvenient, we carried out tests with (3) by adding at the beginning of the experiment the total amount of aldehyde required by the reaction. Unexpectedly these reactions were slower and did not reach completion probably owing to the preferential oxidation of the aldehyde respect to the sulfur compound by the oxidant species present in solution. The resolutive idea was to maintain the concentration of the aldehyde in the reaction mixture sufficient to create the oxidant species, but low enough not to compete with the substrate for the oxidation. This was realized, as previously stated, by adding a part of the aldehyde dropwise during the course of the reaction.

The results obtained in homogeneous phase using (1), (2) and (3) as the substrates are summarized in Table 1. For all three substrates the reactions carried out under dioxygen led,

both with  $\text{Co(acac)}_2$  (entries 1, 8, 15) and  $\text{Co(AAEMA)}_2$  (entries 4, 12, 18) to the corresponding sulfones. In all cases the conversions achieved were quantitative and the selectivities towards sulfone higher than 93%. When the reactions were carried out under air it was possible to find the time when the conversion of the substrate into sulfoxide was as high as possible. So (1) gave 70% conversion and 100% yield in sulfoxide after 4 h with  $\text{Co(acac)}_2$  under air (entry 2), whereas when the reaction was prolonged up to 15 h, the resulting conversion was 100% and the only sulfur compound detectable in the reaction medium was dimethylsulfoxide (entry 3). Analogous results were achieved using  $\text{Co(AAEMA)}_2$  as the catalyst (entries 5, 6). Substrate (2) was more reluctant to react and it was possible, even under oxygen, to separate the two oxidation stages (sulfide  $\rightarrow$  sulfoxide and sulfoxide  $\rightarrow$  sulfone). The reaction of substrate (2) with  $\text{Co(AAEMA)}_2$  under oxygen took 8 h to give 91% conversion and 94% yield in sulfoxide (entry 11) and further 1.5 h to effect the quantitative transformation into sulfone (entry 12). Entries 7, 8 show comparable results obtained with  $\text{Co(acac)}_2$ . The oxidation of (2) carried out under air gave the results reported in entries 9, 10, 13, 14. It is apparent that the reaction rate is significantly lower compared to the case of dioxygen as the oxidant. Substrate (3) was found to be very active and gave almost complete conversion into sulfone both with  $\text{Co(acac)}_2$  and  $\text{Co(AAEMA)}_2$  under  $\text{O}_2$  in 2 h (entries 15, 18).

The results discussed up to here point up two aspects: it is possible to oxidize sulfur compounds using Mukaiyama's procedure with the commercially available  $\text{Co(acac)}_2$  and the reaction still works when the polymerizable  $\text{Co(AAEMA)}_2$  complex is used. Therefore there are the foundations for effecting the sulfoxidation under heterogeneous conditions using the polymeric analogue of  $\text{Co(AAEMA)}_2$  already tested by us in the epoxidation of olefins [13].

The results obtained when substrates (1), (2) and (3) were exposed to oxidizing conditions in

the presence of supported  $\text{Co}(\text{AAEMA})_2$  are summarized in Table 2. It is apparent that the heterogeneous catalyst is active, selective and reusable. Three cycles of oxidation of (3) under  $\text{O}_2$  were carried out with the same resin and in all cases quantitative conversion of the substrate into sulfone was achieved after 1 h (entries 1, 2, 3).

The results obtained with (3) under air showed the same selectivity exhibited by the soluble  $\text{Co}(\text{II})$  complexes e.g. high conversion in sulfoxide at relatively short times, and complete transformation into sulfones at sufficiently long times both in the first cycle (entries 5, 6) and in the recycles (entries 7, 8).

Reactions of substrates (1) and (2) were

slower and it was possible to find the time when, also under  $\text{O}_2$ , the oxidation of the sulfides gave high yields of sulfoxides (entries 9, 17, for the first cycles; entries 11, 19 for the recycles). The reactions of (1) and (2) under air (entries 13, 14, 21, 22 for the first cycles, 15, 16, 23, 24 for the recycles) gave, in accord with expectation, first high yields of sulfoxides and then almost complete transformation into sulfones.

Eventually, we have made use of the most relevant findings stemmed from this study to oxidize substrates such as di-*t*-butylsulfide, dibenzylsulfide and *p*-tolylmethylsulfide to sulfones, both in homogeneous phase, with  $\text{Co}(\text{acac})_2$  and in heterogeneous phase, with the

Table 2

Aerobic oxidation of sulfides (1.20 mmol) by supported  $\text{Co}(\text{AAEMA})_2$  (0.020 mmol of cobalt) in the presence of *i*-valeraldehyde in 1,2-dichloroethane (2.0 ml) at room temperature and atmospheric pressure

Entry	Substrate	mmol aldehyde	Oxidant	Time (h)	Conv. (%)	Yield (%)	
						Sulfoxide	Sulfone
1 <sup>a</sup>	Ph-S-Ph	5.4	$\text{O}_2$	1	100	2	98
2 <sup>a,b</sup>	Ph-S-Ph	5.4	$\text{O}_2$	1	100	5	95
3 <sup>a,b</sup>	Ph-S-Ph	5.4	$\text{O}_2$	1	100	7	93
5 <sup>c</sup>	Ph-S-Ph	7.2	air	3	100	70	30
6 <sup>c,d</sup>	Ph-S-Ph	7.2	air	8	100	6	94
7 <sup>b,c</sup>	Ph-S-Ph	7.2	air	2	67	94	6
8 <sup>c,d</sup>	Ph-S-Ph	7.2	air	15	100	11	89
9	$\text{CH}_3\text{-S-CH}_3$	3.6	$\text{O}_2$	4	72	100	—
10 <sup>d</sup>	$\text{CH}_3\text{-S-CH}_3$	3.6	$\text{O}_2$	5	100	—	100
11 <sup>b</sup>	$\text{CH}_3\text{-S-CH}_3$	3.6	$\text{O}_2$	5	75	95	5
12 <sup>d</sup>	$\text{CH}_3\text{-S-CH}_3$	3.6	$\text{O}_2$	6	95	—	100
13	$\text{CH}_3\text{-S-CH}_3$	3.6	air	8	80	100	—
14 <sup>d</sup>	$\text{CH}_3\text{-S-CH}_3$	3.6	air	20	100	—	100
15 <sup>b</sup>	$\text{CH}_3\text{-S-CH}_3$	3.6	air	22	85	100	—
16 <sup>d</sup>	$\text{CH}_3\text{-S-CH}_3$	3.6	air	46	100	—	100
17	Bu-S-Bu	3.6	$\text{O}_2$	10	100	92	8
18 <sup>d</sup>	Bu-S-Bu	3.6	$\text{O}_2$	20	100	—	100
19 <sup>b</sup>	Bu-S-Bu	3.6	$\text{O}_2$	28	90	81	19
20 <sup>d</sup>	Bu-S-Bu	3.6	$\text{O}_2$	40	100	—	100
21	Bu-S-Bu	3.6	air	21	93	89	11
22 <sup>d</sup>	Bu-S-Bu	3.6	air	37	100	8	92
23 <sup>b</sup>	Bu-S-Bu	3.6	air	33	75	80	20
24 <sup>d</sup>	Bu-S-Bu	3.6	air	42	100	7	100

<sup>a</sup> The aldehyde was added as follows: 0.9 mmol were present at the beginning of the reaction and 4.5 mmol dissolved in 2.0 ml of 1,2-dichloroethane were added dropwise in the course of the reaction at a rate of 2.5 mmol/h.

<sup>b</sup> Recycle of the previous run.

<sup>c</sup> The aldehyde was added as follows: 0.9 mmol were present at the beginning of the reaction and 6.3 mmol dissolved in 2.0 ml of 1,2-dichloroethane were added dropwise in the course of the reaction at a rate of 1.0 mmol/h.

<sup>d</sup> Same reaction mixture of previous entry.

Table 3

Aerobic oxidation of sulfides (1.20 mmol) by Co(II) complexes (0.020 mmol of Co(acac)<sub>2</sub> or supported metal) in the presence of *i*-valeraldehyde (3.6 mmol) in 1,2-dichloroethane (2.0 ml) at room temperature and atmospheric pressure of dioxygen

Entry	Substrate	Catalyst	Time (h)	Conv. (%)	Yield in sulfone (%)
1	<i>t</i> -Bu-S- <i>t</i> -Bu	Co(acac) <sub>2</sub>	3	100	100
2	<i>t</i> -Bu-S- <i>t</i> -Bu	Co(II)-polymer	3	100	100
3	PhCH <sub>2</sub> -S-CH <sub>2</sub> Ph	Co(acac) <sub>2</sub>	3	100	100
4	PhCH <sub>2</sub> -S-CH <sub>2</sub> Ph	Co(II)-polymer	8	100	100
5	<i>p</i> -Tol-S-CH <sub>3</sub>	Co(acac) <sub>2</sub>	2	100	94
6	<i>p</i> -Tol-S-CH <sub>3</sub>	Co(II)-polymer	2	100	100

Co(II) supported resin. In all cases (see Table 3) after suitable times (2–8 h) excellent yields were obtained.

### 3. Experimental

#### 3.1. Materials and apparatus

Chromatographic analyses were carried out on a Varian Vista 6000 instrument by using a capillary 30 m Carbowax 20M column or on a Hewlett Packard 5890 chromatograph using a 25 m SPB-1 capillary column. GC-MS data were acquired on a HP 5890 chromatograph (30 m SE30 column) coupled with a mass selective detector HP 5970B, 70 eV.

The oxidized products were identified by comparison of their MS spectra and retention times in GC analysis with those of authentic samples.

Conversions were calculated by GLC analyses as moles of oxidized products per mole of starting sulfur compound by using the internal standard method.

Co(acac)<sub>2</sub> was purchased by Aldrich and used as received; Co(AAEMA)<sub>2</sub> [14] was prepared by reacting in absolute ethanol Cobalt(II) nitrate and NaAAEMA; the supported Co(II) complex [13] contained 2.98% cobalt and was prepared by stirring in *N,N*-dimethylformamide under nitrogen at 50°C Co(AAEMA)<sub>2</sub>, *N,N*-dimethylacrylamide (DMAA) and *N,N'*-methylenebisacrylamide (MBAA) in molar ratio 14:35:1.

#### 3.1.1. Catalytic runs: homogeneous phase

A Schlenk tube was charged with the sulfur substrate, (1.2 mmol), the Co(II) catalyst (Co(AAEMA)<sub>2</sub> or Co(acac)<sub>2</sub>, 0.020 mmol), the sacrificial aldehyde (added, for substrate (3), as described in the legend of Table 1) and 1,2-dichloroethane (2 ml) and stirred at room temperature till completion of the reaction, as monitored by GLC.

#### 3.2. Catalytic runs: heterogeneous phase

A Schlenk tube was charged with the sulfur substrate (1.2 mmol), the Co(II) supported catalyst (0.020 mmol of cobalt), the sacrificial aldehyde (added, for substrate (3), as described in the legend of Table 2), 1,2-dichloroethane (2 ml) and stirred at room temperature till completion of the reaction, as monitored by GLC. After reaction, the supported catalyst was recovered by addition of petroleum ether to the suspension and subsequent filtration. The recovered resin was washed with acetone and diethyl ether, dried under vacuum and opportunely recycled. Analyses carried out on the resins recovered after the reactions showed that negligible loss of metal occurred during the procedure.

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