

Alternatives to free molecular halogens as chemoselective reactants: Catalysis of organic reactions with reusable complexes of halogen metal salts*

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Abstract: Organometallic complexes of halogen metallic salts have been used as catalysts in different organic reactions, mainly the oxidation of organic compounds. Their use has not only allowed the reduction of the amounts of catalyst (since they can be reused) but also a lower generation of byproducts and wastes. The different reaction media developed through the research were analyzed by several green parameters, and the best results were obtained with complexes that have cyclodextrins as organic ligands. The proposed methodology is an alternative to use of molecular halogen as oxidant or catalyst when halogens are significant chemoselective reactants.

Keywords: catalyst; chemoselectivity; cyclodextrin-iron complexes; halogen derivatives; sulfoxidation.

INTRODUCTION

The development of new drugs with pharmacological application or new methodologies for industrial process is of interest to both the scientific community and the industrial sector. Two important aspects that can be studied are chemoselective sulfoxidation and heterogeneous catalyst synthesis.

Given the pharmacological importance of sulfoxides [1], the chemo- and enantioselective sulfoxidation reaction is under continuous study [2]. Also, new catalysts are necessary to obtain products through organic reactions without waste generation [3].

In addition, green chemistry concepts were introduced with the aim to overcome health and environmental problems at the source by developing cleaner chemical processes for the chemical industry through the design of innovative and environmentally benign chemical reactions [4].

Although halogen-free systems are desired, because of their particular chemical properties, there are several reaction systems where replacement is a difficult task. Such is the case of oxidation reactions mediated by halogens where a specific redox couple provides the suitable media for a highly chemoselective reaction. In previous work we have reported the synthesis of sulfoxides starting from sulfides where the redox couple between a sulfide and a halogen prevents the overoxidation to sulfone, increasing the selectivity of the reaction [5].

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There are several examples in the literature, where halogens or their complexes are involved as either oxidizing agents or catalysts in sulfoxidation reactions whether the molecular halogen is employed or generated in situ [6]. Among possible halogens, chlorine is the less used, mainly because it has a higher oxidation potential that accounts for the lack of selectivity and low yields obtained in conventional oxidations involving chlorine and chlorides [7]. For these reasons, bromine is employed more frequently. For example, bromine was used combined with hydrogen peroxide to oxidize sulfide to sulfoxide, so bromide generated in the reaction returned to Br_2 . The used ratios sulfide: Br_2 were from 10 to 0.5, halogenated compounds were obtained as byproduct [8].

Bromine complex of 1,4-diazabicycles(2.2.2)octane (DABCO) was used in the presence of 70 % acetic acid in selective sulfoxidation in a sulfide:bromine complex 1.0:0.5 molar ratio [9], although the yields were very good, the reaction waste contained bromide salts as explained in other publications [10].

Also, quaternary ammonium salts have been used in sulfoxidation reaction with good yields. So, benzyltrimethylammonium tribromide was a useful oxidant in aqueous sodium hydroxide, in this case, sulfide:quaternary ammonium salts ratio was 0.83 [11]; or cetyltrimethylammonium tribromide with a ratio of 0.84 but an important change of solvent because it used acetonitrile instead of dichloromethane [12]. In both cases, bromide derivatives were generated as waste.

For these cases where the replacement of halogens means less efficiency, specificity, or the use of rough reaction conditions, the use of catalytic amounts is a feasible alternative. In addition, if the employed halogen can be reused the environmental impact of the systems is decreased because the formation of halogenated waste or byproducts is avoided. Thus, in the last several years the aim of our work has been the optimization of the sulfoxidation reaction to the development of a "greener" oxidative system. Therefore, in this report, we present also a short review of our work based on the chemo-selective synthesis of sulfoxides with halogen derivatives such as iron(III) bromide or their complexes with organic ligands, principally their cyclodextrin complexes [13]. These complexes were as active as the inorganic salt and more stable.

Furthermore, we analyze the results obtained during our studies on the sulfoxidation as well as the literature data presented above in terms of reported green metrics and we demonstrate that the proposed methodology [14] fulfills several of the green chemistry principles since the oxidant is molecular oxygen from air, the catalyst is a non-contaminating metal, and the reactions are highly selective, producing a minimum amount of waste.

SULFOXIDATION REACTIONS

We have studied the sulfoxidation reaction in different conditions. In a first stage, we performed the sulfide oxidation in a biphasic medium formed by a nitric acid solution and nitromethane or dichloromethane [15,16]. In this medium, the proposed reaction mechanism, Fig. 1, involves in situ formation of molecular halogen from a HNO_3 solution, an excess of oxidant, and ferric halide in catalytic amount; after sulfoxidation occurs and halide ions are regenerated, the cycle continues until the reaction is complete [5].

This in situ generation of molecular halogen was more effective with bromide metallic salts for the sulfoxidation reaction, but it also occurs with chloride metallic salts [7] with potential applications in other reactions according to the metallic centers, their coordination, and capacity to activate organic compounds.

RME, MI, and AE have been proposed in the last decade as the measures of environmental sustainability in terms of minimization theoretical waste amount [25b]. RME, eq. 1, is a more sophisticated measure of *greenness* that allows the effect of yield and the excess or catalytic amount of reactants used, but it does not consider the solvent used. MI, eq. 2, takes into account the yield, stoichiometry, the solvent, and the reactant used in the reaction. Finally, AE, eq. 3, was introduced by Trost [27] and is a theoretical measure of the chemical and environmental efficiency of a chemical reaction based on the stoichiometric equation; it does not consider solvents, possible excess of reagents, formation of unwanted products, etc. In an ideal situation % RME \approx 100, MI \approx 1, and % AE \approx 100.

The green metrics were calculated using the procedures reported in the literature [25b]. They are defined as follows:

$$\text{RME} = \frac{\sum \text{Mass of products}}{\sum \text{Mass of reactants}} \times 100 \quad (1)$$

$$\text{MI} = \frac{\text{Total mass used in a process or process step (g)}}{\text{Mass of product (g)}} \quad (2)$$

$$\text{AE} = \frac{\text{Molecular weight of product}}{\sum \text{Molecular weight of reactant}} \times 100 \quad (3)$$

The revised sulfoxidation reactions were evaluated through green metrics, and the results obtained are listed in the Table 1. From the analysis of the MI values, in addition to those calculated and published in *Green Chemistry* [14], it can be said that, for high-yielding reactions, this parameter depends more on the amount of solvent used than on the use of homogeneous or heterogeneous catalyst or the oxidant employed under our reaction conditions. The value changed from MI \approx 30 when 5 mL of solvent per 1 mmol of substrate was used, to MI \approx 12 for 2.6 mL per 1 mmol, to MI \approx 4 for 0.6 mL per 1 mmol, to MI \approx 1 for the solventless reaction. This dependence was also observed in the values of MI calculated for the data of ref. [9a] (entries 2–4 and 18, Table 1) where the amount of aqueous solution decreases, or the data of ref. [12] (entries 7 and 24, Table 1) where only 2 mL of organic solvent is used.

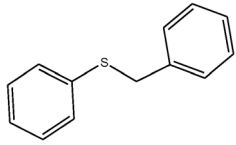
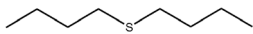
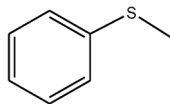
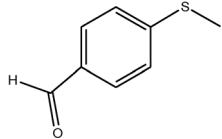
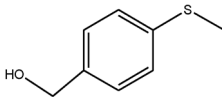
On the other hand, high values of %RME and %AE were obtained when the reactions were performed in the monophasic system and molecular oxygen was used as oxidant (e.g., entries 8–11 vs. 12–15) or the use of molecular bromine in stoichiometric or catalytic amounts (e.g., entry 16 vs. 17, Table 1).

With respect to the cyclodextrin-iron complexes, in general, the calculated parameters did not show significant differences between the use of free FeBr₃ or DMSO-FeBr₃ complex. Some exceptions were observed in entries 34–37, 38–39, 42–44, or 53–54. Also, comparing different cyclodextrins, the β -cyclodextrin-FeBr₃ complex showed the best values of the calculated parameters.

However, the development of heterogeneous catalyst improves the work-up and allows for reuse of the catalyst. In this way, the choice of the ligand plays a vital role in the final properties of the catalyst, and green chemistry principles are seldom involved in the process. β -Cyclodextrin fulfills several green chemistry principles because it is efficiently synthesized from renewable feedstock, is biodegradable, and is much less toxic than most of the organic molecules used as ligand. The choice of a green ligand did not compromise the reaction effectiveness since the process is equally complete.

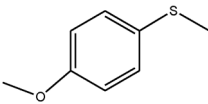
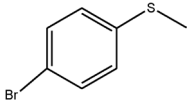
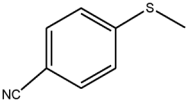
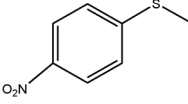
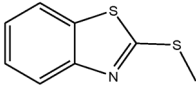
Also, and in general, different solvent trials led us to more environmental friendly reaction conditions and were more appropriate to green chemistry principles.

Table 1 Green metrics to sulfoxidation reactions.

Entry	Substrate	Oxidant ^a /catalyst ^b /solvent	%RME ^c	MI ^d	%AE ^e	Ref. ^f
1		Br ₂ /CH ₂ Cl ₂ -H ₂ O	15.7	93.9	60.1	[8]
2		C ₆ H ₁₂ N ₂ Br ₂ /AcOH _(aq)	43.5	2.3	45.8	[9a]
3		C ₅ H ₅ NBr ₂ /AcOH _(aq)	32.0	3.1	49.2	[9a]
4		C ₉ H ₇ NBr ₂ /AcOH _(aq)	38.9	2.6	44.2	[9a]
5		BTMABr ₃ -NaOH/CH ₂ Cl ₂	14.7	41.5	34.3	[11]
6		BTMABr ₃ -NaOH/ClCH ₂ CH ₂ Cl	22.2	26.3	34.3	[11]
7		Br ₂ -CTMAB/CH ₃ CN-H ₂ O	52.0	6.5	60.1	[12]
8		HNO _{3(aq)} /Fe/CH ₃ NO ₂	31.3	24.8	82.1	[15]
9		HNO _{3(aq)} /Fe/CH ₂ Cl ₂	37.8	23.7	82.1	[15]
10		HNO _{3(aq)} /DMSO-Fe/CH ₃ NO ₂	29.6	24.2	82.1	[15]
11		HNO _{3(aq)} /DMSO-Fe/CH ₂ Cl ₂	33.7	24.5	82.1	[15]
12		O ₂ -Fe(NO ₃) ₃ /α-CD-Fe/CH ₃ CN	65.7	24.8	93.1	[20]
13		O ₂ -Fe(NO ₃) ₃ /β-CD-Fe/CH ₃ CN	73.3	22.2	93.1	[20]
14		O ₂ -Fe(NO ₃) ₃ /γ-CD-Fe/CH ₃ CN	69.1	23.6	93.1	[20]
15		O ₂ -Fe(NO ₃) ₃ /HP-β-CD-Fe/CH ₃ CN	68.3	23.9	93.1	[20]
16		Br ₂ /CH ₂ Cl ₂ -H ₂ O	28.9	56.9	53.0	[8]
17		H ₂ O ₂ /Br ₂ /CH ₂ Cl ₂ -H ₂ O	61.2	66.3	90.0	[8]
18		C ₆ H ₁₂ N ₂ Br ₂ /AcOH _(aq)	33.0	3.0	38.8	[9a]
19		BTMABr ₃ -NaOH/CH ₂ Cl ₂	22.2	29.5	28.2	[11]
20		HNO _{3(aq)} /Fe/CH ₃ NO ₂	28.5	30.0	77.5	[15]
21		HNO _{3(aq)} /Fe/CH ₂ Cl ₂	32.6	30.3	77.5	[15]
22		HNO _{3(aq)} /DMSO-Fe/CH ₃ NO ₂	26.9	29.0	77.5	[15]
23		HNO _{3(aq)} /DMSO-Fe/CH ₂ Cl ₂	30.3	29.7	77.5	[15]
24			Br ₂ -CTMAB/CH ₃ CN-H ₂ O	41.4	9.5	49.4
25	HNO _{3(aq)} /Fe/CH ₃ NO ₂		17.8	50.0	74.9	[15]
26	HNO _{3(aq)} /Fe/CH ₂ Cl ₂		20.0	51.5	74.9	[15]
27	HNO _{3(aq)} /DMSO-Fe/CH ₃ NO ₂		21.5	37.6	74.9	[15]
28	HNO _{3(aq)} /DMSO-Fe/CH ₂ Cl ₂		22.3	41.8	74.9	[15]
29	O ₂ -Fe(NO ₃) ₃ /Fe/CH ₃ CN		66.0	32.0	89.8	[19]
30	O ₂ -Fe(NO ₃) ₃ /α-CD-Fe/CH ₃ CN		66.0	34.5	89.8	[20]
31	O ₂ -Fe(NO ₃) ₃ /β-CD-Fe/CH ₃ CN		62.9	36.2	89.8	[20]
32	O ₂ -Fe(NO ₃) ₃ /γ-CD-Fe/CH ₃ CN		66.0	34.5	89.8	[20]
33	O ₂ -Fe(NO ₃) ₃ /HP-β-CD-Fe/CH ₃ CN		62.1	36.6	89.8	[20]
34		O ₂ -Fe(NO ₃) ₃ /Fe/CH ₃ CN	65.5	28.4	91.3	[21]
35		O ₂ -Fe(NO ₃) ₃ /DMSO-Fe/CH ₃ CN	26.9	62.1	91.3	[21]
36		O ₂ -Fe(NO ₃) ₃ /β-CD-Fe/CH ₃ CN	75.0	26.5	91.3	[21]
37		O ₂ -Fe(NO ₃) ₃ /γ-CD-Fe/CH ₃ CN	70.9	28.0	91.3	[21]
38		O ₂ -Fe(NO ₃) ₃ /DMSO-Fe/CH ₃ CN	42.6	39.0	91.4	[21]
39		O ₂ -Fe(NO ₃) ₃ /β-CD-Fe/CH ₃ CN	62.2	31.6	91.4	[21]

(continues on next page)

Table 1 (Continued).

Entry	Substrate	Oxidant ^a /catalyst ^b /solvent	%RME ^c	MI ^d	%AE ^e	Ref. ^f
40	Methyl 4-(methylthio)phenyl ether	O ₂ -Fe(NO ₃) ₃ /Fe/CH ₃ CN	68.0	27.1	91.4	[19]
41		O ₂ -Fe(NO ₃) ₃ /β-CD-Fe/CH ₃ CN	67.9	29.0	91.4	[20]
42	4-(Methylthio)bromobenzene	O ₂ -Fe(NO ₃) ₃ /Fe/CH ₃ CN	72.0	21.3	93.2	[19]
43		O ₂ -Fe(NO ₃) ₃ /α-CD-Fe/CH ₃ CN	66.7	24.2	93.2	[20]
44		O ₂ -Fe(NO ₃) ₃ /β-CD-Fe/CH ₃ CN	75.1	21.5	93.2	[20]
45	4-(Methylthio)benzotrile	O ₂ -Fe(NO ₃) ₃ /Fe/CH ₃ CN	69.0	27.3	91.2	[19]
46		O ₂ -Fe(NO ₃) ₃ /α-CD-Fe/CH ₃ CN	66.7	30.2	91.2	[20]
47		O ₂ -Fe(NO ₃) ₃ /β-CD-Fe/CH ₃ CN	63.5	31.7	91.2	[20]
48	4-(Methylthio)nitrobenzene	O ₂ -Fe(NO ₃) ₃ /Fe/CH ₃ CN	70.1	24.8	92.0	[19]
49		O ₂ -Fe(NO ₃) ₃ /α-CD-Fe/CH ₃ CN	71.4	25.8	92.0	[20]
50		O ₂ -Fe(NO ₃) ₃ /β-CD-Fe/CH ₃ CN	71.4	25.8	92.0	[20]
51		O ₂ -Fe(NO ₃) ₃ /γ-CD-Fe/CH ₃ CN	69.0	26.7	92.0	[20]
52		O ₂ -Fe(NO ₃) ₃ /HP-β-CD-Fe/CH ₃ CN	67.3	27.4	92.0	[20]
53	2-(Methylthio)benzothiazole	O ₂ -Fe(NO ₃) ₃ /Fe/CH ₃ CN	42.2	39.3	92.5	[21]
54		O ₂ -Fe(NO ₃) ₃ /β-CD-Fe/CH ₃ CN	34.9	50.3	92.5	[21]

^aOxidant: Br₂-H₂O = molecular bromine in the presence of water; H₂O₂/Br₂/CH₂Cl₂-H₂O = molecular bromine in the presence of water and hydrogen peroxide; C₆H₁₂N₂Br₂/AcOH_(aq) or C₅H₅NBr₂/AcOH_(aq) or C₉H₇NBr₂/AcOH_(aq) = bromine complexes of tertiary amines in 70 % aqueous acetic acid; BTMABr₃-NaOH_(aq) = benzyltrimethylammonium tribromide in the presence of aqueous sodium hydroxide; HNO_{3(aq)} = 1.5 M nitric acid solution; O₂-Fe(NO₃)₃ = catalytic amount of Fe(NO₃)₃·9H₂O and O₂ present in air.

^bCatalyst: CTMAB = cetyltrimethylammonium bromide; Fe = FeBr₃; DMSO-Fe = [(FeBr₃)₂(CH₃S(O)CH₃)₃] [16]; α-CD-Fe = α-cyclodextrin-FeBr₃; β-CD-Fe = β-cyclodextrin-FeBr₃; γ-CD-Fe = γ-cyclodextrin-FeBr₃; HP-β-CD-Fe = hydroxypropyl-β-cyclodextrin-FeBr₃.

^c%RME: percentage reaction mass efficiency.

^dMI: mass intensity. The solvent used in the purification step was not considered in the calculations. The amount of cyclodextrin catalysts or CTMATB were not used in the calculations because the catalysts are recoverable by filtration and can be reused [12,20].

^e%AE: percentage atom economy. Reagents in catalytic quantities and catalyst are not considered in the calculation.

^fBibliographic reference.

Two examples of a typical calculation follow.

Entry 8, Table 1: benzylphenylsulfide (1.0015 g, 5 mmol, FW 200.30) reacts with the 1.50 M nitric acid solution (1.51 g, 24 mmol, FW 63.01) in the presence of iron(III) bromide (0.1478 g, 0.5 mmol, FW 295.56) in nitromethane (16 mL, 18.032 g) to give benzylphenylsulfoxide (FW 216.30) isolated in 77 % yield (3.85 mmol, 0.8328 g) [15]. For AE, catalyst is not considered in the calculation.

$$\text{RME} = [0.8328 / (1.0015 + 1.51 + 0.1478)] \times 100 = 31.3 \%$$

$$\text{MI} = (1.0015 + 1.51 + 0.1478 + 18.032) / 0.8328 = 24.8$$

$$\text{AE} = [(216.30 / (200.30 + 63.01)) \times 100 = 82.1 \%$$

Entry 13, Table 1: benzylphenylsulfide (0.2003 g, 1 mmol, FW 200.30) reacts with the iron(III) nitrate nonahydrate (0.040 g, 0.10 mmol, FW 404.00) and molecular oxygen (0.016 g, 0.5 mmol, FW 32.0) in the presence of iron complex (0.068 g, 0.05 mmol, FW 1369.17) in acetonitrile (5 mL, 3.93 g) to give benzylphenylsulfoxide (FW 216.30) isolated in 87 % yield (0.87 mmol, 0.1882 g) [20]. The amount of catalyst was not used in the calculations because it is recoverable by filtration and it can be reused. For AE, reagents in catalytic quantities and catalysts are not considered in the calculation.

$$\text{RME} = [0.1882 / (0.2003 + 0.040 + 0.016)] \times 100 = 73.3 \%$$

$$\text{MI} = [(0.2003 + 0.040 + 0.016 + 3.93) / 0.1882] = 22.2$$

$$\text{AE} = [(216.30 / (200.30 + 32.00)) \times 100 = 93.1 \%$$

CONCLUSIONS

In short, we have summarized the evolution of the sulfoxidation reaction from a biphasic system and homogeneous catalyst to a monophasic medium with heterogeneous and reusable catalyst, without compromising high yields or chemoselectivity, and with improved green metrics. The similar evolution process was observed in the references cited.

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