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$VO(acac)_2$-catalyzed oxidation of sulfoxides to sulfones using chlorine dioxide

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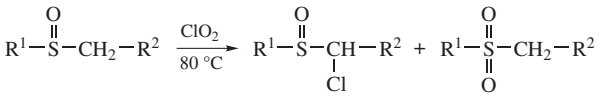
The catalytic effect of $VO(acac)_2$ in the oxidation of sulfoxides to sulfones with chlorine dioxide was found.

Chlorine dioxide (ClO_2) is a convinient industrial oxidant. The oxidation of amines, phenols, olefins and carbonyl compounds by chlorine dioxide was described.[1]

Previously,[2–5] it was shown that the oxidation of sulfides with ClO_2 at a substrate-to-oxidant molar ratio of 1:0.5 in CH_2Cl_2, CCl_4, AcOEt or without solvent results in 95–100% conversion of the sulfide to give the corresponding sulfoxide in 80–95% yields; the formation of sulfones does not exceed 2–3%.

In the oxidation of dipropyl and methyl phenyl sulfoxides at a substrate-to-oxidant molar ratio of 1:0.5 in CH_2Cl_2 and AcOH at room temperature, the conversion of sulfoxides does not exceed 20–25%. The reaction products are sulfones and monochlorinated sulfoxide derivatives (Scheme 1).† At 80 °C, the conversion of sulfoxides was 98–100% in AcOH. In the case of methyl phenyl sulfoxide, the yields of methyl phenyl sulfone and (chloromethylsulfinyl)benzene are 25 and 75%, respectively. Dipropyl sulfoxide gave a sulfone (yield 15%) and two monochlorinated sulfoxide derivatives (10 and 75%).



R^1 = Ph, Pr R^2 = H, Et

Scheme 1

Probably, the formation of chlorinated derivatives is associated with the reactions of radicals formed on the thermolysis of chlorine dioxide. For instance, among the oxidation products of substituted phenols with chlorine dioxide, the following products have been identified: 2-chloro-1,4-benzoquinone and 2,6-dichloro-1,4-benzoquinone.[1] Cycloalkanes and benzene homologues slowly interact with chlorine dioxide to form chlorinated products.[6] The main oxidation products of lower alcohols at 70–80 °C are ketones and chloroketones.[7,8]

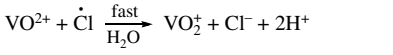
Therefore, the oxidation of sulfoxides to sulfones can be a useful model for catalytic oxidation.

The preparation of sulfones usually involves the direct oxidation of sulfides and sulfoxides using hydrogen peroxide, peracids, hydroperoxides, chlorine, nitrogen oxides, oxygen or ozone.[9–11] The most common oxidant is hydrogen peroxide, generally in acetic acid.[12–13] Various transition metal compounds are utilised in the preparation of sulfones from sulfoxides with homogeneous catalysts (W, Mo, V).[14–16]

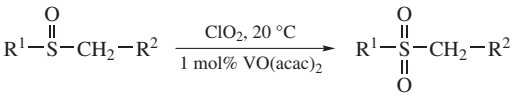
Vanadium(V) compounds are one-electron oxidants (V^V–V^{IV}) widely used in organic reactions. $VO(acac)_2$ is used as a catalyst for oxygen transfer in the oxidation reactions of alkanes, alkenes, alcohols, amines, sulfides, sulfoxides, *etc*. in the presence of TBHP or molecular oxygen as an oxidant.[17]

Previously,[18] it was found that chlorine dioxide oxidizes the vanadyl ion to a vanadium(V) dioxo cation at a high rate. Among the products of this reaction are the chlorate ion and chlorine, which oxidize the vanadyl ion to vanadium(V) dioxo cation at a lower rate. Note that, in comparison with the chlorate ion, chlorine dioxide reacts with vanadium(IV) approximately 100 times faster.

Presumably, among the reaction intermediates, there is a radical of chlorine which also rapidly oxidizes vanadium(IV).[19]



Here, we report on the oxidation of sulfoxides with chlorine dioxide in the presence of catalytic amounts of $VO(acac)_2$. The catalytic oxidation of dipropyl and methyl phenyl sulfoxides with $VO(acac)_2$ at a substrate-to-oxidant molar ratio of 1:0.5 leads to the formation of sulfones in CH_2Cl_2 or AcOH at room temperature (Scheme 2).† The yields of sulfones in product mixtures are 80–95%. The minor products are mono-chlorinated sulfoxides.



R^1 = Ph, Pr R^2 = H, Et

Scheme 2

† GC analysis was performed on a Chrom 5 chromatograph; argon was used as a carrier gas, and the column was packed with 5% SKTFT-50 on Chromaton N-AW-DMCS. The mass spectra were acquired on a Finnigan Trace DSQ instrument (column RM-5MS, 30 m×0.25 mm, T_{col} = 50–220 °C, 4 K min^{-1}). IR spectra were recorded on a MIR-8000 instrument in a thin layer (0.2–0.5 mm) and KBr pellets at 400–4000 cm^{-1}. ^1H NMR spectra were recorded on a Bruker DPX 300 instrument (300.13 MHz).

General procedure for the catalytic oxidation of sulfoxides. A sulfoxide (5 mmol) and $VO(acac)_2$ (0.05 mmol) were dissolved in 10 ml of acetic acid (or CH_2Cl_2) to give a pale green solution. After stirring for 5 min, a solution of chlorine dioxide in acetic acid was added dropwise with rapid stirring at room temperature to produce a brown solution. The mixture was stirred for 3–4 h at ambient temperature to give afresh pale green solution. After removing the solvent at low pressure, the residue was diluted with 100 ml of diethyl ether and washed with 50 ml of a saturated aqueous solution of $NaHCO_3$. The organic phase was dried with Na_2SO_4, and the solvent was evaporated. The concentrations of the products were determined by GLC and GC/MS. Sulfone was recrystallized from ethanol. The yields were 80–95%.

The batchwise addition of an oxidant changed the colour of the reaction mixture from pale green to brown; after the exhaustion of the oxidant, the colour became light green.

The direct oxidation of methyl phenyl sulfide and dipropyl sulfide at a substrate-to-oxidant molar ratio equal to 1:1 in AcOH with catalytic amounts of $VO(acac)_2$ gives corresponding sulfones in 75–92% yields.

Thus, the ClO_2–$VO(acac)_2$ system is suitable for the oxidation of sulfoxides to sulfones.

Methyl phenyl sulfoxide: ^{1}H NMR (80 MHz, $CDCl_3$) δ: 2.5 (s, 3H, Me), 7.23–7.41 (m, 5H, Ar). IR (ν/cm^{-1}): 1046 (S=O). MS, *m*/*z* (%): 140 (40) $[M]^{+\cdot}$, 125 (100) $[PhSO]^+$, 109 (10) $[PhS]^+$, 97 (40), 77 (27) $[Ph]^+$.

Methyl phenyl sulfone: mp 86–88 °C. ^{1}H NMR ($CDCl_3$) δ: 2.96 (s, 3H, Me), 7.44–7.60 (m, 3H, Ar), 7.79–7.91 (m, 2H, Ar). IR (ν/cm^{-1}): 1151, 1306 (O=S=O). MS, *m*/*z* (%): 156 (65) $[M]^{+\cdot}$, 141 (32) $[PhSO_2]^+$, 125 (5) $[PhSO]^+$, 94 (45), 77 (100) $[Ph]^+$.

(Chloromethylsulfinyl)benzene: ^{1}H NMR ($CDCl_3$) δ: 4.16–4.45 (m, 2H, CH_2Cl), 7.23–7.41 (m, 5H, Ar). IR (ν/cm^{-1}): 1058 (S=O). MS, *m*/*z* (%): 174.5 (6) $[M]^{+\cdot}$, 125 (100) $[PhSO]^+$, 110 (5) $[PhS]^+$, 97 (20), 77 (13) $[Ph]^+$.

Dipropyl sulfoxide: mp 22–23 °C. ^{1}H NMR ($CDCl_3$) δ: 0.85 (t, 3H, $MeCH_2CH_2$, *J* 7.2 Hz), 1.45–1.76 (m, 2H, $MeCH_2CH_2$), 2.45 (t, 2H, $MeCH_2CH_2$, *J* 7.25 Hz). IR (ν/cm^{-1}): 1038 (S=O). MS, *m*/*z* (%): 134 (70) $[M]^{+\cdot}$, 117 (14) $[Pr_2S]^+$, 92 (100) $[PrSO]^+$, 77 (8) $[CH_2CH_2SO]^+$, 63 (72) $[CH_2SO]^+$.

Dipropyl sulfone: mp 29.5–30.5 °C. ^{1}H NMR ($CDCl_3$) δ: 0.99 (t, 3H, $MeCH_2CH_2$, *J* 7.2 Hz), 1.54–2.00 (m, 2H, $MeCH_2CH_2$), 2.86 (t, 2H, $MeCH_2CH_2$, *J* 7.2 Hz). IR (ν/cm^{-1}): 1125, 1310 (O=S=O). MS, *m*/*z* (%): 150 (10) $[M]^{+\cdot}$, 134 (11) $[Pr_2SO]^+$, 108 (100) $[PrSO_2]^+$, 93 (4) $[CH_2CH_2SO]^+$, 63 (6) $[CH_2SO]^+$.

1-Chloro-2-(propylsulfinyl)propane [in the mixture with 1-chloro-3-(propylsulfinyl)propane]: ^{1}H NMR ($CDCl_3$) δ: 4.20–4.45 [m, 1H, $MeCH(Cl)CH_2$]. MS, *m*/*z* (%): 168 (10) $[M]^{+\cdot}$, 92 (100) $[PrSO]^+$, 77 (16) $[CH_2CH_2SO]^+$, 63 (37) $[CH_2SO]^+$.

1-Chloro-3-(propylsulfinyl)propane [in the mixture with 1-chloro-2-(propylsulfinyl)propane]: ^{1}H NMR ($CDCl_3$) δ: 3.69–3.90 [m, 2H, $CH_2(Cl)CH_2CH_2$]. MS, *m*/*z* (%): 168 (10) $[M]^{+\cdot}$, 92 (100) $[PrSO]^+$, 77 (16) $[CH_2CH_2SO]^+$, 63 (37) $[CH_2SO]^+$.

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