The first example of direct oxidation of sulfides to sulfones by osmate-molecular oxygen system

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Electronic Supporting Information

General: ^{1}H NMR spectra were recorded on a Varian Gemini 200 / 400 MHz spectrometer. Chemical shifts are reported in ppm, using tetramethylsilane (TMS) as the internal standard. Gas chromatography was performed using following apparatus; Shimadzu LC-10AC and Shimadzu LC-10AC chromopac. ACME silica gel (100-200 mesh) was used for column chromatography and thin layer chromatography (TLC) was performed on Merck precoated silica gel 60-F_{254} plates. X-ray photoelectron spectra [XPS, or Electron Spectroscopy for Chemical Analysis (ESCA)] were recorded on a KRATOS AXIS 165 with a dual anode (Mg and Al) apparatus using the Mg Kα anode. The pressure in the spectrometer was about 10^{-9} Torr. For energy calibration we have used the carbon 1s photoelectron line. The carbon 1s binding energy was taken to be 285.0 eV. Spectra were deconvoluted using Sun Solaris based Vision 2 curve resolver. The location and the full width at half maximum (FWHM) for a species was first determined using the spectrum of a pure sample. The location and FWHM of products, which were not obtained as pure species, were adjusted until the best fit was obtained. Symmetric Gaussian shapes were used in all cases. Binding energies for identical samples were, in general, reproducible to within ±0.1 eV. Mass spectra were recorded on a Micro Mass VG 70-70H spectrometer operating at 70eV using direct inlet system. Thermogravimetric (TG), differential thermal analysis (DTA) and mass of the evolved gas during the thermal decomposition of catalyst were studied on TGA/SDTA Mettler Toledo 851^e system coupled to MS Balzers GSD 300T, using open alumina crucibles, containing samples weighing about 8-10 mg with a linear heating rate of 10°C min^{-1}. Nitrogen was used as purge gas for all these measurements.

$K_2OsO_4.2H_2O$, $MgCl_2.6H_2O$, $AlCl_3.6H_2O$, thioanisole and 4-bromothioanisole were purchased from Aldrich. Merrifield resin (2% cross-linked divinyl benzene) is purchased from Lancaster. All other sulfides listed in Table 1 are prepared using standard procedures. All the other solvents and chemicals were obtained from commercial sources and used as such without further purification.

Preparation of the catalysts

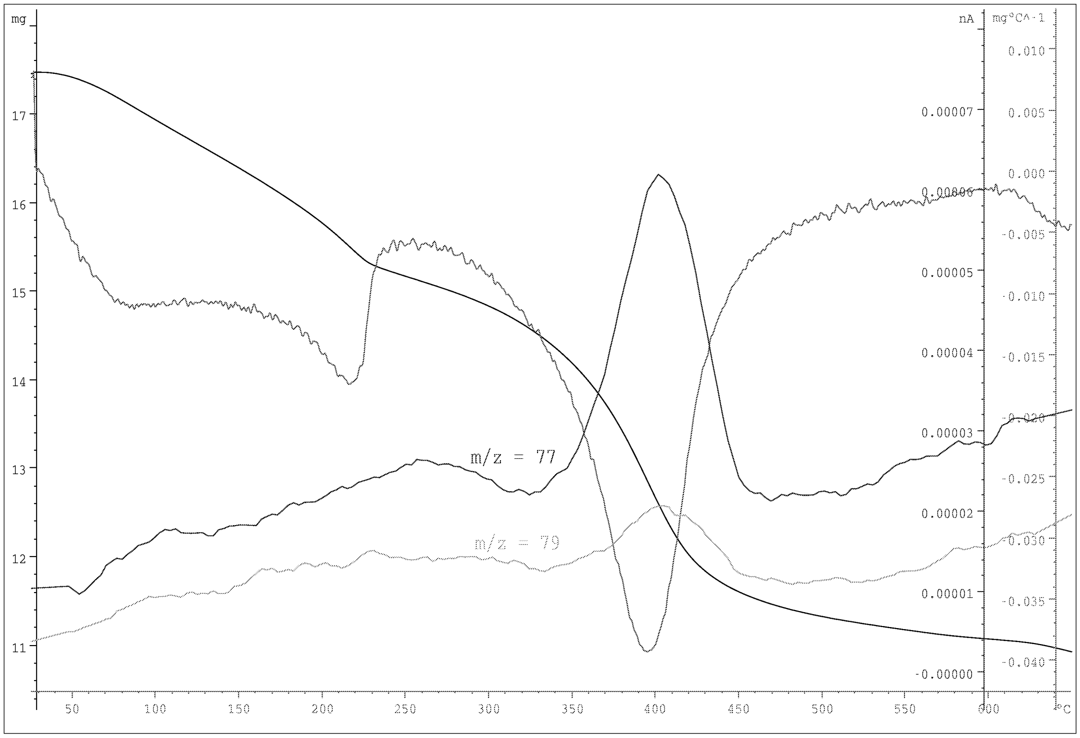
The preparation of LDH (Mg-Al-Cl) was based on literature procedure.[1] A mixture of $MgCl_2.6H_2O$ (30.49 g, 0.15 mmol) and $AlCl_3.6H_2O$ (12.07 g, 0.05 mmol) was dissolved in 200 mL of deionised water. To this aqueous solution, 100 ml of NaOH (2M) solution was slowly added at 25°C and a further amount of 2M NaOH solution was added to maintain a pH of 10 under nitrogen flow. The resulting suspension was stirred overnight at 70°C. The solid product was isolated by filtration, washed thoroughly with deionised water and dried overnight at 80°C. All the synthetic steps were carried out using decarbonated water.

LDH-OsO_4 (cat 1): One and one-half grams of Mg-Al-Cl LDH was suspended in 150 mL of 0.689 g (1.87 mmol) aqueous potassium osmate solution and stirred at 25°C for 12h under nitrogen atmosphere. The solid catalyst was filtered, washed thoroughly with 500 mL of water and vacuum dried to obtain 1.916g of LDH-OsO_4 (0.975 mmol of Os per g).

Resin-OsO_4(cat 2): Resin was obtained by quaternisation of triethylamine (2.1 mL, 21 mmol) with 1.0g of chloromethylated styrene-divinylbenzene copolymer (Merrifield resin, capacity ~2.1 mequiv/g) in chloroform (20 mL) under reflux for 24h. 1.0g of quaternary ammonium resin was suspended in 100 mL of 0.8 mmol aqueous potassium osmate solution and stirred at 25°C for 12h under nitrogen atmosphere. The solid catalyst was filtered, washed thoroughly with 300 mL of water and vacuum-dried to obtain resin-OsO_4 (0.641 mmol of Os per g).

References

1. S. Miyata, *Clay Clay Miner.,* 1975**, 23**, 369.



IICT: METTLER METTLER TOLEDO STAR^e System

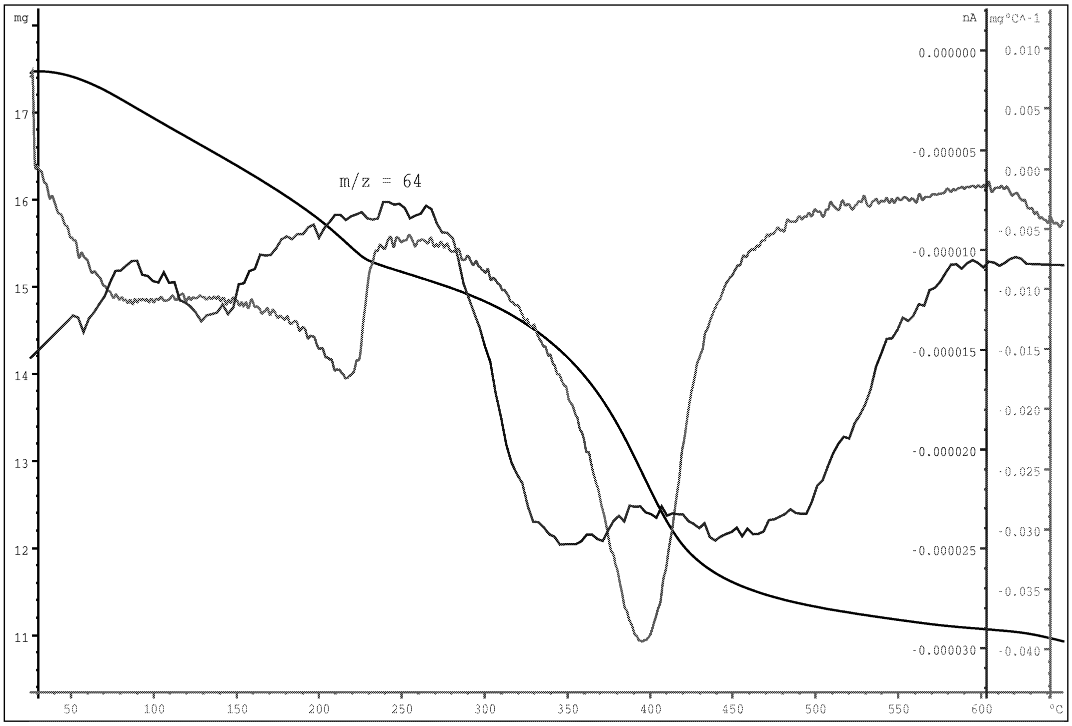


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Figure. A. TGA-DTA-MS thermogram of LDH-OsO_4®complex for C_6H_5, CH_3SO_2 and SO_2 (m/z values 77, 79 and 64 a.m.u., respectively) in nitrogen atmosphere with an heating rate of 10 °C/min.