



Electrosynthesis of dimethylsulfone from dimethylsulfoxide at a dimensionally stable anode

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Abstract

Galvanostatic electrochemical oxidation of dimethylsulphoxide (DMSO) to dimethylsulfone (DMSO₂) has been effected at a dimensionally stable anode (DSA) under different conditions of current density and reaction media, in both a batch and a flow reactor (membrane cell with an ion-exchange membrane between the two working electrodes) functioning in batch recirculation mode. Excellent yields of the sulfone have been obtained under both conditions. The product has been characterized by various physicochemical techniques. The operational conditions giving maximum yield of the product have been established. The electrochemical oxidation of DMSO has also been studied by cyclic voltammetry at a glassy carbon (GC) electrode. The mechanism of electrochemical oxidation and the advantages of the present methods over existing ones, are discussed.

1. Introduction

Dimethylsulfone (DMSO₂) is useful as a high temperature solvent in extractive distillation, in electroplating baths, in making ink, adhesives and many other substances of organic or inorganic nature [1]. Molten DMSO₂ is a suitable electrolyte for lithium intercalation batteries [2]. It is found in primitive plants and in the adrenal cortex of cattle. It is prepared by chemical and electrochemical methods from dimethylsulfide (DMS) or dimethylsulfoxide (DMSO). Oxidations of DMS to DMSO₂ by 6 N HNO₃ or N-oxides at 120–125 °C in the presence of OsO₄ catalyst with 71% yield [3], 30% H₂O₂ catalysed by H₂SO₄ at 110–120 °C [4], O₃ at 0–100 °C with 15% yield at 30 °C [5] or in the presence of trialkyl phosphites at –30 to –40 °C [6] and with atmospheric O₂ in the presence of transition metal compounds in acetic acid medium at 20–130 °C [7] are known in the literature. The oxidation of DMSO in hot HNO₃ at 120–150 °C with 86% yield [8] and its disproportionation in 6 N HNO₃ or N-oxides over OsO₄ catalyst at 110–120 °C with 83% yield of DMSO₂ [9] are also reported. The addition of alkaline H₂O₂ is also reported to effect the oxidation of both DMS and DMSO in ethanolic solution [10]. DMSO₂ is also produced photochemically from DMSO using photosensitizers [11].

Electrochemical synthesis of DMSO₂ has been reported by the oxidation of DMS in acetonitrile in presence of 1% H₂O [12] or DMSO at PbO₂ anode in a single compartment cell having 0.05–1.0 N H₂SO₄/Na₂SO₄ solutions at 20–40 °C [13]. The yield in the latter method was 79% at 40 mA cm⁻² in 0.2 N H₂SO₄. In an other patent [14], the complete conversion of DMSO to DMSO₂ with 76–93% current efficiency (CE) is reported when the electrolysis was carried out between 10–54 mA cm⁻² at a high density graphite anode in 0.4 M HCl at 5 °C in the presence of W, V, Mo or Se salt or oxide as catalyst.

The above methods involve expensive catalysts, corrosive chemicals, cumbersome procedures, or the use of DMS which has a pungent odour [1]. Although, the yields of sulfone and current efficiencies in some of the above processes are good, the requirement of adding a supporting electrolyte, saturation of the medium with the sulfone before electrolysis and the problems such as the separation of supporting electrolyte and catalyst from the reaction mixture/product limit their wide utility.

The present paper reports a novel and simple method of oxidation of DMSO to DMSO₂ at a DSA in both a batch and a flow reactor with batch-recirculation, to overcome the above said disadvantages. DSA has been extensively used in chloralkali industries as a catalytic

anode for chlorine evolution and is lately gaining prominence in organic oxidations [15, 16]. The effects of current density and the nature of the electrolyte (0.53 M H_2SO_4 , 0.2 M Na_2SO_4) on the yield and CE of DMSO_2 formation have been studied and the conditions for obtaining the maximum yield of DMSO_2 have been established. The advantages of the flow reactor over the batch reactor have been discussed. Cyclic voltammetric studies on the oxidation of DMSO to DMSO_2 have also been made in aqueous-acetonitrile media at a gc electrode and the mechanism of electrochemical oxidation has been discussed.

2. Experimental details

2.1. Reagents

High purity dimethylsulfoxide (DMSO) (S.D Fine Chemicals Ltd, India) was used as received. All other chemicals used in these investigations were of either AR or spectroscopic grade. All the solutions were prepared in doubly distilled water.

2.2. Electrochemical reactors and galvanostatic electrolysis

Galvanostatic electrolysis under batch reactor conditions was carried out in an undivided cell with provisions for introducing expanded DSA (area 48 cm^2) and stainless steel cathode. 20 g of DMSO (0.256 mol) was dissolved in 500 ml of 0.53 M H_2SO_4 or 0.2 M Na_2SO_4 and oxidised at current densities of 25.0, 62.5 and 100.0 mA cm^{-2} with passage of 2 faradays.

A rectangular Perspex cell of $18\text{ cm} \times 15\text{ cm}$ consisting of an expanded DSA (area 60 cm^2) and a stainless steel cathode was used as a flow reactor. A cation exchange membrane [17, 18] (an interpolymer of polyethylene and styrene-divinylbenzene copolymer with sulfonic acid as functional group having aerial resistance, $1.5\ \Omega\text{ cm}^{-2}$, ion exchange capacity, 1.8 m equivalent g^{-1} and moisture content, 29.8% after drying) of 100 cm^2 exposed surface area was placed between the cathode and the anode, which were separated by 3 mm, thus dividing the cell into two compartments each having an inlet and an outlet. The anolyte consisted of 250 ml of aqueous solution containing 20 g of DMSO and the catholyte was 250 ml of 0.1 M H_2SO_4 both of which were recirculated through the respective compartments. The flow in both the cases was regulated at 10 ml min^{-1} . The current was passed corresponding to anode current density of 35 mA cm^{-2} . The cell voltage between the cathode and the anode, and the potential at the anode vs Ag/AgCl (3 M NaCl) were monitored.

The progress of the electrolysis was followed in both the cases, by recording UV-vis. or H^1 -NMR spectra of 1 ml sample withdrawn periodically and diluted suitably. After completion of the electrolysis, the solution

was evacuated (after neutralization in case of H_2SO_4 as electrolyte) using a rotary evaporator and the resulting solid was recrystallized from ethanol. DMSO_2 was obtained as white prisms having a melting point of $109\text{ }^\circ\text{C}$.

2.3. Cyclic voltammetric studies

Cyclic voltammetric studies were made in a conventional three electrode cell with provisions for introducing the working, reference and counter electrodes. Glassy carbon (area 0.0314 cm^2), Ag/AgCl (0.222 V vs NHE) in 3 M NaCl and a platinum wire served as the working, reference and counter electrodes, respectively. Cyclic voltammograms for DMSO in the concentration range 0.05–0.10 M, were recorded in acetonitrile $-0.1\text{ M Bu}_4\text{NBF}_4$ medium.

2.4. Instrumentation

An Aplab d.c. power supply (model L 1285) was employed as a constant current source. Cyclic voltammograms were recorded with EG&G PARC model 273A potentiostat/galvanostat coupled with a three electrode assembly and Gateway 2000 (4DX2-66) computer. The NMR spectra were recorded in D_2O solvent using a Bruker Avance DPX-200-FT NMR 200 MHz spectrometer. IR spectra (KBr pellet) were recorded using a Perkin Elmer Spectrum (GX FTIR system while the UV-vis. spectra were recorded using a Hewlett Packard diode array spectrophotometer (model 8452). Elemental analysis was made on a Perkin Elmer CHNS/O 2400.

3. Results and discussion

3.1. Galvanostatic electrolysis

The results of galvanostatic oxidation studies on DMSO in different media at different current densities and reactor types are given in Table 1. Under the batch reactor conditions, the percentage yield of DMSO_2 in 0.53 M H_2SO_4 increased by 8.3% when the current density was increased from 25.0 to 62.5 mA cm^{-2} , while the CE rose by about 9%. When the current density was further increased to 100 mA cm^{-2} , the yield of DMSO_2 along with the CE was reduced, possibly due to competing oxygen evolution. In 0.2 M Na_2SO_4 medium, the yield of DMSO_2 increased slightly (4.2%) at 62.5 mA cm^{-2} , though the cell voltage was relatively much higher (10 V) which is generally not advisable. The cell voltage in all other experiments was between 4–6 V while the potential at the anode maintained to about +1.5 to +2.0 V vs Ag/AgCl, depending on the current density applied and the DMSO composition used.

The percentage yield of DMSO_2 and the CE were relatively high even at low current densities in the flow

Table 1. Data on the galvanostatic oxidation of DMSO to DMSO₂ at a DSA in batch and membrane flow reactors

Sl no.	DMSO* /g	Electrolyte /M	Anode current density /mA cm ⁻²	Cell current /A	Cell [†] voltage/A	% Yield of DMSO ₂ [‡]	CE [§] /%
1	20	H ₂ SO ₄ (0.53)	25.0	1.21	4.0	71.0	78.0
2	20	H ₂ SO ₄ (0.53)	62.5	3.02	5.0	79.3	87.1
3	20	H ₂ SO ₄ (0.53)	100.0	4.83	6.0	71.1	78.2
4	20	N ₂ SO ₄ (0.20)	62.5	3.02	10.0	83.5	91.9
5	20	^a	35.0	2.20	2.5	96.2	95.1
6	20	^b	35.0	2.20	2.5	97.5	98.1

* S. nos. 1–4 at a batch reactor; S. nos. 5 and 6 at a membrane flow reactor

[†] Voltage between the cathode and the anode

[‡] With respect to the isolated yield of DMSO₂

[§] CE for DMSO₂ formation

^a No anolyte was used, 0.1 M H₂SO₄ was the catholyte

^b No anolyte was used, 0.1 M Na₂SO₄ was the catholyte

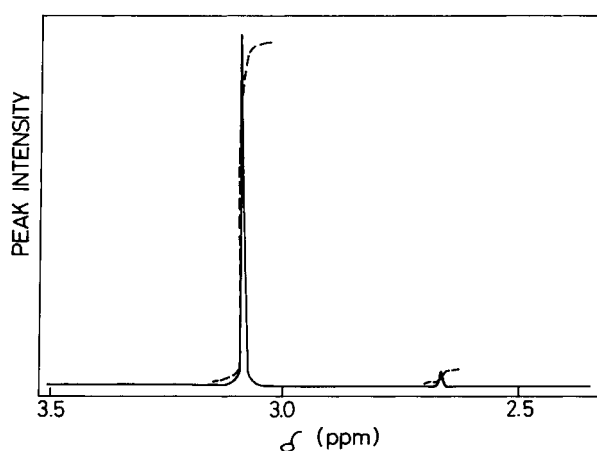


Fig. 1. H¹-NMR spectrum showing the 96% conversion of (5%) DMSO to DMSO₂ after 7 h of electrolysis at 15 mA cm⁻².

reactor as compared to those obtained in batch reactor, (S. No. 5, 6; Table 1). The yield and CE values were further improved when Na₂SO₄ was used as catholyte. However, the H₂SO₄ medium is preferable as the cell voltage is less. In both the cases, the flow of counter ion, H⁺ across the membrane occurs from the water auto decomposition equilibrium at the membrane–solution interface of the anode compartment into the cathode compartment and carries the cell current.

3.2. Product analysis

The H¹-NMR spectrum of DMSO exhibited a single sharp peak at 2.66 δ corresponding to six protons of the two symmetric methyl groups. With the progress of electrolysis, the intensity of this signal was reduced and a new peak at 3.05 δ corresponding to six protons of two symmetric methyl groups was observed whose intensity increased. The H¹-NMR spectrum of DMSO (5%) after 7 h electrolysis is depicted in Figure 1. The low intensity peak at 2.66 δ and the high intensity peak at 3.05 δ correspond to the unconverted (4%) and converted (96%) DMSO, respectively. The isolated products obtained by using both the reactors showed a single peak at 3.05 δ indicating DMSO₂ as the sole product.

The FTIR spectrum of the isolated DMSO₂ exhibited strong absorption bands at 1136 cm⁻¹ corresponding to symmetric >S=O stretch and at 1298 and 1336 cm⁻¹ due to asymmetric >S=O stretch. Besides, the other absorption bands observed at 3020, 936, 763 and 699 cm⁻¹ are typical for DMSO₂ as reported in the literature [19]. The strong band at 1030–1080 cm⁻¹ corresponding to >S=O stretch of DMSO was absent in these spectra.

DMSO showed absorption maximum at 208 nm (959 M⁻¹ cm⁻¹) while no such absorption was found for the product in the UV–vis. spectra. This is as per literature [20] reports that sulphone shows absorption due to $\Pi-\Pi^*$ transition in the far UV at wavelength less than 180 nm but not in the near UV, whereas sulfoxide shows weak absorption in the near UV due to $n-\Pi^*$ transition at wavelengths longer than 200 nm. The elemental analysis of the purified product indicated % C as 24.74 and % H as 6.05 which are close to the calculated values 25.52 and 6.42, respectively, for DMSO₂.

3.3. Cyclic voltammetry

Typical cyclic voltammograms obtained at a GC electrode for various amounts of DMSO in acetonitrile –

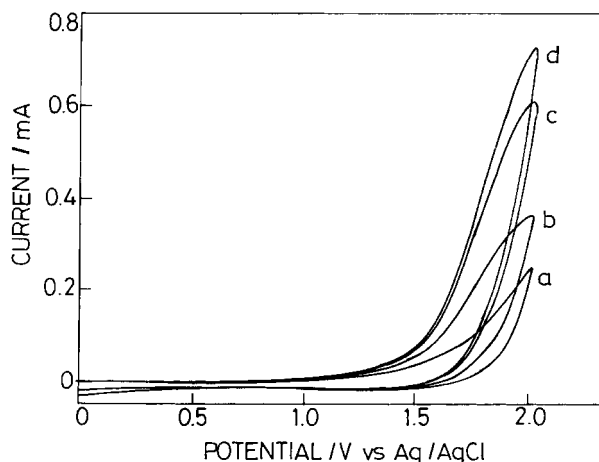


Fig. 2. Cyclic voltammetric response for CH_3CN -0.1 M $n\text{-Bu}_4\text{NBF}_4$ containing DMSO (a) 0.00 M, (b) 0.05 M (c) 0.10 M (d) 0.10 M with 2 mmol of H_2O at a GC electrode.

0.1 M $n\text{-Bu}_4\text{NBF}_4$ are shown in Figure 2. A single irreversible anodic peak is observed at around 1.9 V corresponding to the two-electron oxidation of DMSO to DMSO_2 as follows:

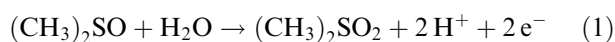


Figure 2 a shows the cyclic voltammetric response for the solvent-supporting electrolyte system. With increasing concentration of the added DMSO to the acetonitrile - 0.1 M $n\text{-Bu}_4\text{NBF}_4$, a peak starts to appear, whose height increases, indicating the oxidation of DMSO to DMSO_2 (Figure 2b, c). Further enhancement in the current was seen with the addition of 2 mmol of water (Figure 2d), indicating the participation of trace quantities of water present in the solvent in the electrochemical oxidation of sulphoxide to sulfone at +1.9 V as in Equation 1 (above).

4. Conclusion

Dimethylsulfone was obtained in excellent yields by electrochemical oxidation of DMSO in batch and flow reactors. The present method avoids the use of dimethylsulfide, a liquid with disagreeable odour, used in the earlier methods. Further, the study has demonstrated the advantage of a flow reactor (membrane cell with an ion-exchange membrane between the two working electrodes) in avoiding, the use of supporting electrolyte in the anolyte and hence, the requirement of additional neutralization and/or separation steps as required in the conventional methods.

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