

Electrochemical Preparation of Bismethylsulphonyl Peroxide and its Reactions with Aromatic Hydrocarbons

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A simple, safe, and high yield preparation of bismethylsulphonyl peroxide by constant current oxidation of a solution of sodium methanesulphonate in anhydrous methanesulphonic acid is described. The reactions of bismethylsulphonyl peroxide with benzene, naphthalene, and other aromatic hydrocarbons are briefly considered.

A RECENT communication¹ described the reactions of peroxydisulphonyl difluoride (FSO₃)₂ with some small aliphatic molecules in anhydrous fluorosulphuric acid. The reactions were carried out *in situ* in an electrochemical cell while the peroxydisulphonyl difluoride was generated at the anode, and led to the formation of fluorosulphonate esters. The extreme reactivity of this peroxide, however, causes its useful reactions to be limited to those with very inert substrates in fluorosulphuric acid. Thus, with a view to extending this type of synthetic reaction to a wider range of substrates, for example aromatic hydrocarbons, the preparation and reactions of the analogous but less reactive bismethylsulphonyl peroxide have been investigated.

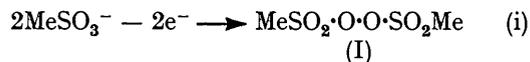
Earlier attempts² to prepare bismethylsulphonyl peroxide (MeSO₃)₂ by anodic oxidation of an aqueous 10M-solution of methanesulphonic acid led only to a poor current yield (<20%). Furthermore the product was insoluble and was deposited on the anode, and in some preparations this deposit caused local heating and an explosive decomposition of the peroxide. Preliminary studies of the reactions of the peroxide with benzene and toluene^{2,3} did, however, show that methanesulphonate esters were formed.

RESULTS AND DISCUSSION

Preparation of Bismethylsulphonyl Peroxide.—The *i*-*E* curve for a solution of sodium methanesulphonate (0.1M)

¹ J. P. Coleman and D. Pletcher, *Tetrahedron Letters*, 1974, 147.

in anhydrous methanesulphonic acid at a smooth platinum electrode showed that there was no steady state process occurring between -0.2 and +2.2 V (*vs.* a Pd/H₂ reference electrode in the same solution). The cathodic potential limit was due to hydrogen evolution, and the results reported below indicate that the anodic limit is due to formation of bismethylsulphonyl peroxide (I). Indeed a cyclic voltammogram run on the same system showed that, provided the potential sweep extends into the potential region where reaction (i)



occurs, there is an additional diffusion-controlled reduction peak at $E_p + 0.05$ V which may be attributed to the reverse of reaction (i), *i.e.* reduction of (I).

The preliminary results indicated that the product from the anodic oxidation of sodium methanesulphonate-methanesulphonic acid could conveniently be prepared by a constant current electrolysis in a divided cell with two platinum electrodes. Such an electrolysis was carried out at a current density of 16 mA cm⁻² until the theoretical concentration of a 2e⁻ product was 0.3M. The anolyte was then added dropwise to a five-fold excess of ice-water and the resulting aqueous solution was cooled in an ice-bath. A flocculent white solid

² R. N. Haszeldine, R. B. Heslop, and J. W. Lethbridge, *J. Chem. Soc.*, 1964, 4901.

³ U.S.P. 3,320,301/1967.

precipitated; this was filtered off, washed, and dried. Spectra (see Experimental section) showed the product to be the peroxide (I). The isolated yield, based on the charge passed during the electrolysis, was 65%.

In order to optimise the current yield of (I), a number of electrolyses were performed in the anhydrous acid with various concentrations of sodium methanesulphonate and at various current densities. Two types of experiment were carried out: (i) the electrolyses were continued until high concentrations of the product had accumulated and the overall yield was determined by estimating the concentration of peroxide volumetrically; (ii) the electrolyses were terminated after the passage of 100 C and the concentration of (I) was estimated by observation of the reduction peak at +0.05 V on a cyclic voltammogram using a vitreous carbon microelectrode. The height of this peak was calibrated by addition of a known amount of (I) and running a further voltammogram. The results of these experiments are reported in Tables 1 and 2.

TABLE 1

Yields of $(\text{MeSO}_3)_2$ from constant current oxidation of $\text{MeSO}_3\text{Na}-\text{MeSO}_3\text{H}$; anolyte volume 16.5 cm³

$[\text{MeSO}_3\text{Na}]/\text{M}$	Current density (mA cm ⁻²)	Charge passed (C)	Final $[(\text{MeSO}_3)_2]/\text{M}^a$	Current yield (%)
1.0	16	1600	0.32	82
	16	1500	0.30	77
	82	1400	0.31	80
0.1	16	900	0.17	69
	16	800	0.16	63
	131	800	0.17	69
0.01	16	500	0.13	86
	16	500	0.13	85

^a Determined by titration.

TABLE 2

Yield of $(\text{MeSO}_3)_2$ from constant current electrolyses of $\text{MeSO}_3\text{Na}-\text{MeSO}_3\text{H}$ terminated after the passage of 100 C; anolyte volume 16.5 cm³; current density 16 mA cm⁻²

$[\text{MeSO}_3\text{Na}]/\text{M}$	1.0	0.5	0.1	0.05	0.01
Current yield ^a of $(\text{MeSO}_3)_2$ (%)	89	82	83	82	86

^a Concentration of $(\text{MeSO}_3)_2$ determined by cyclic voltammetry using a standard addition technique.

In all experiments the current yield of (I) is good. Furthermore Table 1 shows that the acid as well as the sodium methanesulphonate must undergo oxidation to the peroxide.

The solid peroxide (I) appears to be stable indefinitely at room temperature; certainly after storage in a desiccator for 4 weeks there was no loss of oxidising power as determined volumetrically. On heating in a flame, however, the solid decomposed spontaneously. The peroxide (I) is soluble in many organic solvents although not aliphatic hydrocarbons and its stability in solution is less than in the solid state.

Direct Anodic Oxidations in Methanesulphonic Acid.—Cyclic voltammetry using a smooth platinum wire working electrode was carried out on solutions of several organic compounds in methanesulphonic acid containing

sodium methanesulphonate (0.1M). The results can be summarised as follows. (i) *p*-Methoxybenzene, tri-*sp*-bromophenylamine, and octafluoronaphthalene each gave cyclic voltammograms which indicated that these compounds underwent reversible one-electron oxidations to give stable cation radicals. The oxidation peaks occur at +0.67, +0.57, and +1.69 V, respectively. (ii) Benzene and naphthalene gave irreversible oxidation waves. Furthermore, attempts to carry out preparative-scale oxidations were hampered by polymerisation on the electrode surface. Thus the direct anodic oxidation of such hydrocarbons in this solvent would not lead to good yields of products. (iii) Cyclohexane and *n*-hexane were not oxidised prior to the solvent/electrolyte decomposition potential. Anthracene and higher polynuclear aromatic hydrocarbons were not sufficiently soluble in this medium to allow the recording of reliable voltammograms.

Reactions of Bismethylsulphonyl Peroxide.—(a) *Benzene.* The reaction with benzene was carried out both by addition of benzene to the anolyte at the end of a constant current electrolysis, *i.e.* in methanesulphonic acid-sodium methanesulphonate, and by the addition of solid peroxide to benzene. In both cases the products (yields determined by g.l.c.) were phenyl methanesulphonate (70%) and biphenyl (7%). In the latter procedure the product yields decreased slightly with increase in temperature (58 and 6% respectively at 80 °C). At room temperature the reaction takes several hours but at 80 °C it is complete in 30 min. The rate of reaction is unaffected by light.

(b) *Naphthalene.* Equimolar quantities of the reactants were mixed in ether; at room temperature the reaction was complete in 3 h. The products were 1-naphthyl methanesulphonate (46%) and the 2-isomer (3%). A low yield of disubstituted product (5–10%) was also identified. In methylene chloride the reaction is more rapid.

(c) *Other aromatic hydrocarbons.* The reaction with anthracene in ether is complete in 5 min but the product is a complex mixture containing methanesulphonate esters. In methylene chloride, 9,10-diphenylanthracene, thianthrene, and 1,4-dimethoxybenzene react immediately with the peroxide to give coloured cation radicals (blue, red, and yellow, respectively). In ether these reactions could not be detected.

(d) *Other compounds.* The peroxide reacts with ferrocene in methylene chloride to give the blue ferrocenium cation. Neither diethyl malonate nor hexane reacts with the peroxide.

These experiments show that bismethylsulphonyl peroxide is a useful reagent for the preparation of the methanesulphonate esters of the less reactive aromatic hydrocarbons. The reactions are, however, rather slow for convenience. Indeed, the reactivity both in terms of the rate of reaction and the range of compounds which could be oxidised by this peroxide contrasts markedly with that of peroxydisulphonyl difluoride. The reactions of bismethylsulphonyl peroxide, the relative

rates of its reactions with various substrates, and the marked solvent but absence of a light effect on its reaction rates all point to the initial reaction being an electron-transfer process from the substrate to the peroxide.

EXPERIMENTAL

Electrochemical experiments were carried out using a Chemical Electronics valve potentiostat and Pulse Generator, type R.B.1; i - E curves were recorded on a Bryans X-Y 26000 recorder, and the charge passed during an electrolysis was measured with an electronic integrator.

I.r., n.m.r., and mass spectra were recorded on a Perkin-Elmer 157G spectrometer, a 60 MHz Perkin-Elmer R12 spectrometer, and an A.E.I. MS12 spectrometer, respectively.

G.l.c. was carried out using a Pye-Unicam 104 instrument with a flame ionisation detector. Peak areas were measured with an electronic integrator. Two columns were used: 3 m PEGA on Celite column and 1.5 m silicone oil OV17 on Celite. The carrier gas was nitrogen (flow rate 60 cm³ min⁻¹).

High pressure liquid chromatography was performed on a Waters Associates ALC 202 instrument with a 20 × 0.5 cm Spherisorb 20 μ alumina column and 3 : 97 ethyl acetate-hexane, flow rate 4.5 cm³ min⁻¹, as solvent.

Cyclic voltammetry was carried out in a two-compartment cell; the platinum wire working electrode and a platinum helix secondary electrode were in a single compartment. The reference electrode, a palladium bead soaked with hydrogen,⁴ was in a separate compartment with a Luggin capillary to the working electrode. The constant current electrolyses were carried out in two-compartment cells, the compartments being separated by a No. 3 glass sinter. The platinum gauze electrodes were of area 5 cm².

Methanesulphonic acid (May and Baker) was distilled under reduced pressure. The sodium salt was prepared by neutralisation of a solution of aqueous acid with sodium hydroxide and removal of the water; the salt was recrystallised from ethanol and dried under vacuum at 80 °C. An i.r. spectrum showed the resulting salt was anhydrous.

The methanesulphonate esters were prepared by treatment of the phenol or naphthol with methanesulphonyl chloride in pyridine at 0 °C.^{5,6} After 2 days at 5 °C the product was precipitated with an excess of water. Solid esters were recrystallised from ethanol; liquid esters were distilled under vacuum.

Preparation of Bismethylsulphonyl Peroxide.—The preparation was carried out by constant current electrolysis of solutions of sodium methanesulphonate in anhydrous methanesulphonic acid in the cell described above. In some experiments the yield of the peroxide was determined volumetrically. A sample of the peroxide in the acid was added to an excess of standard aqueous iron(II) ammonium sulphate and the excess of iron(II) was determined by titration with standard potassium permanganate. In other experiments the solution of the peroxide was added

dropwise to a five-fold excess of ice-water and the resulting aqueous solution was cooled in ice. The peroxide precipitated and was filtered off, washed with cold water, and dried under vacuum. The resulting crystals showed ν_{\max} (Nujol) 1195, 1180, 990, 970, 775, 725, and 670 cm⁻¹, ν_{\max} (hexachlorobutadiene) 3050, 3030, 1420, 1375br, and 1330 cm⁻¹; τ (CD₃CN) 6.57 (s); m/e 79, 96, 81, 48, 65, 143, and 64.

Reactions of Bismethylsulphonyl Peroxide.—(a) *Benzene.* (i) A constant current electrolysis [16 mA cm⁻²] was performed on a solution of sodium methanesulphonate (0.1M) in methanesulphonic acid for 3 h in order to generate a solution of peroxide (ca. 0.1M). Benzene (2 ml) was added after the solution was cooled to 0 °C. The two-phase system was stirred at room temperature for 15 h. Water was then added and the organic material extracted into ether. The volatile components were removed and the residue was phenyl methanesulphonate as shown by comparison of spectral and g.l.c. properties with those of an authentic sample: τ (CCl₄) 7.00 (3H, s) and 2.67 (5H, m); ν_{\max} (CCl₄) 2955, 2900, 1590, 1490, 1440, 1395, 1170, 1140, 970, 870, and 790 cm⁻¹; m/e 94, 65, 172, 39, 93, 95, 66, and 63; yield 72%, based on the charge passed during the electrolysis. G.l.c. also showed the presence of biphenyl (5%).

(ii) The peroxide (1 mmol) was added to benzene (50 ml) and the solution was set aside at room temperature. The reaction was monitored by g.l.c. and after 24 h the product consisted of phenylmethanesulphonate (77%) and biphenyl (7%) (yields based on the peroxide used). Similar experiments were carried out at 50 and 80 °C and in the absence of light.

(b) *Naphthalene.* Naphthalene (2.3 mmol) and the peroxide (2.3 mmol) were added to ether at room temperature. After 3 h the reaction was complete and the ether was washed with water and dried. The ether was removed and the residue was examined by t.l.c. (silica; 3 : 2 light petroleum-ethyl acetate). Two products were seen, which were then separated by preparative t.l.c. The least polar was shown by high pressure liquid chromatography to have two components. Comparison of retention times and of n.m.r., i.r., and u.v. spectra with those of an authentic sample showed the major component to be 1-naphthyl methanesulphonate (46%), τ (neat) 7.04 (3H, s) and 1.80–2.70 (7H, m); ν_{\max} (film) 3070, 3030, 1600, 1505, 1390, 1365, 1180, 1150, 1075, 1045, 970, 890, 815, and 775 cm⁻¹; λ_{\max} (EtOH) 280 and 270 nm. The minor component had a retention time consistent with it being 2-naphthyl methanesulphonate (5%). (Yields are based on peroxide conversion.)

(c) *Anthracene.* As naphthalene. The reaction was complete in 5 min. T.l.c. showed several components; i.r. indicated them to be methanesulphonate esters.

(d) *Diethyl malonate.* As naphthalene. G.l.c. analysis indicated no reaction even after several days.

(e) *Other species.* The peroxide (0.1 mmol) was added to a solution of the compound in methylene chloride. The colour changes noted were instantaneous.

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⁴ M. Fleischmann and N. Hiddlestone, *J. Instrument Sci.*, 1968, **1**, 667.

⁵ B. Helferich and P. Papalambrou, *Annalen*, 1942, **551**, 235.

⁶ T. Kametani, O. Umezawa, K. Sekine, T. Oda, M. Ishiguro, and D. Mizuno, *Yakugaku Zasshi*, 1964, **84**(3), 237 (*Chem. Abs.*, 1964, **61**, 600d).