

# STUDIES ON THE CHEMISTRY AND TECHNOLOGY OF DIMETHYL SULPHOXIDE

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Recently, the importance of aliphatic sulfoxides has grown considerably because the production of the intermediary dimethyl sulphide from sulphite wastes of cellulose manufacture proved an economically favourable process. This gave a considerable impetus to research aimed at producing dimethyl sulfoxide.

Considering this, the main subject of my studies was to elucidate the conditions of a laboratory synthesis of dimethyl sulfoxide in the presence of various catalysts, e.g. of phosphorus pentoxide.

Sulphoxy-compounds are characterized by an =S=O sulphonyl group. These compounds form a transition between sulphides and sulphones. Formally, they may be regarded as ketones that have a sulphur atom substituted for their carbonyl-carbon.

## I. Characteristics of dimethyl sulphoxide

This compound is the most simple member of the group of sulfoxides. It is a liquid, transparent like water, strongly polar, and miscible with water in any proportion. Being an excellent solvent it easily dissolves aromatic compounds as well as inorganic salts and is miscible with all current solvents. It is a highly hygroscopic compound, at 20 °C, and excepted the saturated aliphatic hydrocarbon's 60 per cent relative humidity it absorbs 70 per cent by weight of water. According to determinations I have carried out, its more important physical data are the following:

Molecular weight	78.1
Solidification point	18.45 °C
Boiling point (760 torr)	188 °C
Density, at 20 °C	1.1009 g/ml
at 35 °C	1.0891 g/ml
Coefficient of thermal expansion	0.0008
Specific heat,	
solid phase, at 18.45 °C	0.5 cal/g
liquid phase, at 18.45 °C	0.7 cal/g
Heat of evaporation, at 189 °C	132 cal/g

Heat of fusion, at 18.45 °C					20 cal per g
Heat of combustion					6050 cal per g
Dielectric constant					45
Viscosity	°C	20	25	35	45
	cP	2.14	1.99	1.65	1.39
Vapour tension	°C	20	30	40	50
	torr	0.417	0.853	1.656	3.07

## 2. Experimental

SEYTZETT [1] was the first to have synthesized, in 1867, dimethyl sulphoxide from dimethyl sulphide with concentrated nitric acid; up to 1950 this method was of theoretical interest only. Commercial production of dimethyl sulphoxide was started in 1955, by STEPAN et al. [2]. Generally, the not too vigorous oxidation methods were applied. Demands rising from 1950 on made the use of more economical processes necessary [3]. In production at commercial scale, oxygen and hydrogen peroxide proved suitable oxidants, though in order to enhance conversion, this necessitated the search for, and application of, novel catalysts.

### 2.1 Oxidation in the vapour phase [4, 5, 6]

Oxidation was carried out with oxygen, and a gas containing oxygen (air). Nitrogen dioxide was the catalyst. Dimethyl sulphide, of low boiling point (37.3 °C) was easily brought into the gas phase. Dimethyl sulphide, and nitrogen dioxide, together with oxygen, were fed into the reactor. The reaction took place at 50 °C in a reactor tube, cooled or heated as necessary. The products leaving the reactor had to be cooled. Dimethyl sulphoxide, having a high boiling point, was readily condensed and entrained nitrogen dioxide and dimethyl sulphide dissolved, these, however, could be recovered without difficulty at 80 to 100 °C. Unreacted dimethyl sulphide and catalyst were recovered easily and fed back into the reactor. Care had to be taken that mole ratios of catalyst and dimethyl sulphide be maintained between 0.1 and 0.3 during reaction. Even when re-circulated, the catalyst had to be replaced since part of it was reduced to nitrogen and ammonia, and also the gases vented entrained some catalyst. When oxidation was carried out with air, the reaction mixture contained substantial quantities of dimethyl sulphide and nitrogen dioxide, these could be recovered by deep cooling, or washing with sulphoxide. The crude product could be purified by neutralization with ammonia and distillation in vacuum.

In the course of these experiments the effect of two factors had been studied at 50 °C (Fig. 1), *viz.* that of (1) the mole ratio of dimethyl sulphide to the P<sub>2</sub>O<sub>5</sub> catalyst, and (2) the changes of space velocity.

In order to increase the utilizable surface, the reactor tube was filled with Raschig rings. For the measurement of inner temperature two mercury

thermometers were used. One of them measured the temperature in the main reaction zone, i.e. that at the confluence of the oxidizing agent and the dimethyl sulphide. The spiral condenser was joined to the reflux condenser, the

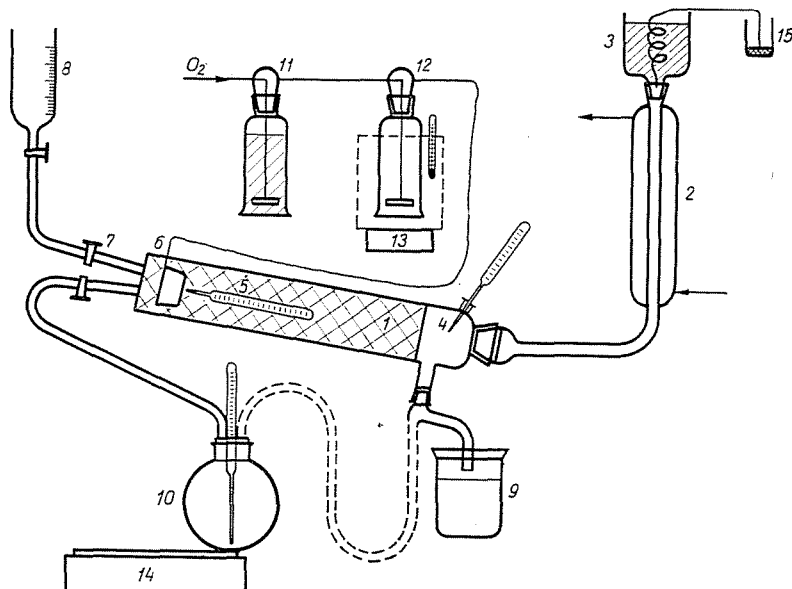


Fig. 1. Oxidation of dimethyl sulphide in the vapour phase. 1 Tubular reactor, 2 reflux condenser, 3 condenser, 4 thermometer, 5 thermometer, 6  $O_2$  and  $NO_2$  inlet, 7  $(CH_3)_2S$  feed cock, 8  $(CH_3)_2S$  feed tank, 9  $(CH_3)_2SO$  receiver, 10 flask, 11 sulphuric acid scrubber, 12 nitric acid scrubber, 13 heating, 14 heating

coolant in it was salt ice. The scrubber filled with nitric acid served the addition of the catalyst to the oxygen. Concentrated nitric acid at temperatures above  $30^\circ C$  decomposes according to the following formula



The tension of  $NO_2$  is a function of temperature; this allowed the ratio, between the oxygen passed through and the catalyst, to be controlled. In order to prevent the dilution of the nitric acid, a calculated amount of acetic anhydride was added as a dehydrating agent. The role of the scrubber filled with sulphuric acid was the drying of oxygen prior to its use in the reaction. Oxygen was fed into the reactor by a feeder operated by water overpressure.

### Experiments

Using half a mole of dimethyl sulphide, a quantity of oxygen equivalent to this was needed for each test. Excess oxidant increased the reaction rate

but allowed the product to further oxidize. The volume of the oxidant gas mixture differed from case to case since molecular oxygen was capable to oxidize twice as much dimethyl sulphide as was nitrogen dioxide. In the course of the experiments, mole ratios of dimethyl sulphide to nitrogen dioxide were 3 : 1, 4 : 1 and 6 : 1. The amount of the dehydrating agent was calculated on the basis of nitrogen dioxide consumption, with a slight excess. Into the nitric acid scrubber a relatively great quantity of nitric acid (with 1 to 3 g of  $P_2O_5$  added) was fed, thus the tension-reducing effect of the acetic anhydride used as dehydrating agent could be kept at a low level (Table 1).

Table 1  
Oxidation of dimethyl sulphide in vapour phase

	Unit	Test No.		
		1.	2.	3.
Dimethyl sulphide . . . . .	mole	0.5	0.5	0.5
	g	31	31	31
	ml	37	37	37
Nitrogen dioxide . . . . .	mole	1	1	1
	litre	12	$\frac{8}{5}$	$\frac{5}{5}$
	at 20 °C	$\frac{2}{2}$	3	4
$P_2O_5$ . . . . .	g	1	2.5	3
Acetic anhydride . . . . .	g	5	7.5	10
Oxygen . . . . .	litre			
	at 20 °C	5	4.5	4
Tension of $NO_2$ . . . . .	torr	218	310	380
Temperature of $HNO_3$ . . .	°C	50	60	70
Quantity of $HNO_3$ . . . . .	g	100	100	100
Reaction time . . . . .	hour	1.5	1.5	1.5
Space velocity . . . . .	litre/hour	77	77	77
Retention time . . . . .	sec	47	47	47
Crude product . . . . .	ml	33	34	34
Loss . . . . .	ml	4	3	3
Conversion, measured . . . .	% by vol.	41.5	55.5	69.5
Conversion, corrected . . . .	% by vol.	37	51	63

In the experiments here described, carried out under identical reaction conditions, only ratios of dimethyl sulphide, nitrogen dioxide and phosphorus pentoxide were varied. As is to be seen in Table 1, the conversion could be raised from 41.5 to 69.5 per cent by volume; this was due to the effect of the addition of more phosphorus pentoxide (1 g, 2.5 g and 3 g).

## 2.2 Oxidation in the liquid phase, by oxygen [7, 8]

Oxidation in the liquid phase could be carried out with oxygen, or a gas containing oxygen. As a catalyst, nitrogen dioxide admixed to the oxygen,

or concentrated nitric acid admixed to the dimethyl sulphide, could be used. These experiments covered also the effect of the addition of phosphorus pentoxide in quantities between 1 and 5 mole per cent referred to dimethyl sulphide.

The reactor was a tube filled with Raschig rings, and could be heated or cooled.

The temperature at the start of the reaction was 20 to 25 °C, and rose to 35 or 40 °C. At 25 °C, the heat of reaction was 19.8 kcal per mole. It was found advisable to control the oxygen feed so as to be fully consumed during the reac-

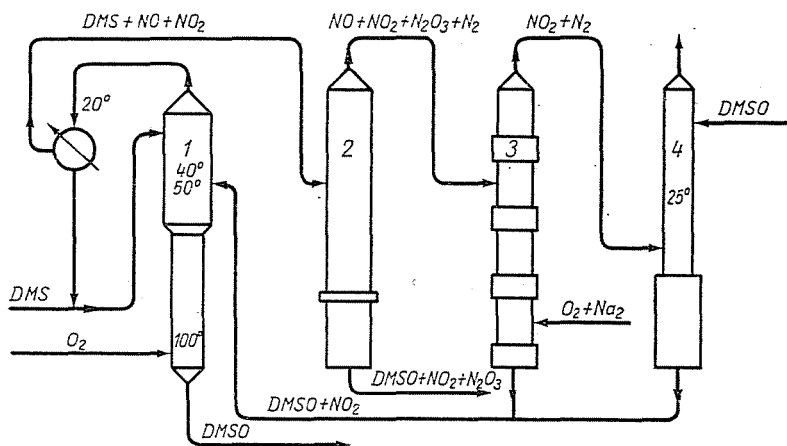


Fig. 2. The oxidation of dimethyl sulphide in the liquid phase, with molecular oxygen.  
DMS = dimethyl sulphide, DMSO = dimethyl sulphoxide

tion. To reach full conversion, 20 to 25 hours were needed. Increase of the quantity of the catalyst and a rise of temperature accelerate the reaction up to a certain limit. At the same time this was harmful, since then the reaction proceeded further in the gas space because of the excess oxygen, as recognized by the brown colour of the gas space and by a sudden rise of its temperature. The greatest problems involved with this process are, first, how to make it safe for commercial operation, and second, how to provide economically for the recovery of nitrogen dioxide and sulphide. A satisfactory technology could be based on the fact that dimethyl sulphoxide dissolves nitrogen dioxide but does not dissolve nitrogen monoxide. This allowed the oxidation to be carried out with nitrogen dioxide dissolved in dimethyl sulphoxide, insoluble nitrogen monoxide being recovered and regenerated with oxygen, then absorbed by dimethyl sulphoxide and recirculated. The flow-sheet of this process is presented in Fig. 2. The technological design of the plant prevented the formation of an explosive gas mixture of dimethyl sulphoxide and oxygen. (The explosive

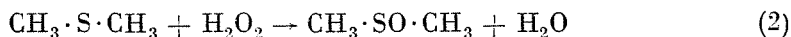
domain of dimethyl sulphide in oxygen is from 1 to 83.5 per cent by volume that of dimethyl sulphoxide from 2.5 to 45 per cent by volume [9].)

Dimethyl sulphide was fed at the reactor-head 1 where, admixed to nitrogen dioxide dissolved in dimethyl sulphoxide, its temperature rose to 40 to 50 °C, and partial oxidation occurred. The dimethyl sulphide that remained in the dimethyl sulphoxide drained off the lower part of the reactor was brought into contact with oxygen at 100 °C and the reaction went to completion. As a bottom product crude dimethyl sulphoxide, contaminated with a small quantity of sulphone, was obtained. The unreacted and uncondensed part of the dimethyl sulphide, together with nitrogen oxide, entered a second reactor 2 where the oxidation was completed at 25 °C. The bottom product of column 2 was dimethyl sulphoxide with nitrogen dioxide dissolved in it.

Nitrogen-monoxide and -sesquioxide left at the head of this column and entered the regeneration column 3, where auto-oxidation with oxygen took place. The head product gas from column 3 was carried into scrubber 4 at its lower section and the dimethyl sulphoxide that entered scrubber 4 at its upper section removed the head product and the nitrogen dioxide still present from this gas mixture. The tail gas vented held less than a total of 1 per cent made up of carbon dioxide, nitrogen, oxygen, and nitrogen dioxide.

### 2.3 Oxidation with hydrogen peroxide, in the liquid phase

A more economical method was oxidation with hydrogen peroxide alone.



A drawback in this process was the formation of dimethyl sulphoxide as an aqueous solution of 40 to 44 per cent strength. Oxidation was carried out at pH 8 to 9, adjusting the medium to this value with the help of ammonia. A scheme of the apparatus used is shown in Fig. 3. Reaction started in the mixer where hydrogen peroxide and dimethyl sulphide were brought into contact. Feed molar ratio was 0.8 : 1. Retention time in the mixer was 10 minutes, at a temperature of 20 °C, under stirring at 600 r.p.m. The mixture flowed into the reactor where reaction proceeded for 1.5 hours at 20 to 25 °C, then entered the separator wherefrom dimethyl sulphide was piped off through the upper and dimethyl sulphoxide through the lower exit ducts. Dimethylsulphide was recirculated through the corresponding feed tank. After separation, dimethyl sulphoxide must not contain more than 0.8 per cent of active oxygen.

Refractive index 1.390 to 1.4000,

Dimethyl sulphide content max. 0.2 per cent,

Colour, light yellow.

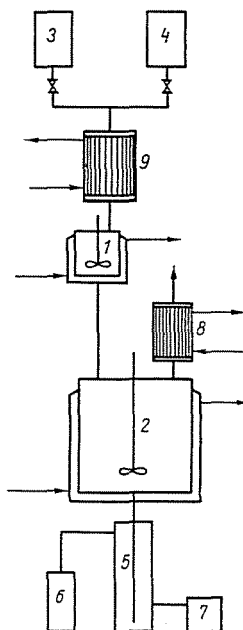


Fig. 3. Oxidation of dimethyl sulphide with hydrogen peroxide, in the liquid phase. 1 Mixer (emulsifier vessel), 2 reactor, 3 hydrogen peroxide feed tank, 4 dimethyl sulphide feed tank, 5 separator, 6 dimethyl sulphide receiver tank, 7 dimethyl sulphoxide receiver tank, 8 Condenser, 9 cooler

2.3.1 *Processing of the dimethyl sulphoxide mixture.* The crude product contained 40 to 44 per cent dimethyl sulphoxide, 5 to 15 per cent dimethyl sulphide, and 50 to 60 per cent water. Concentration of this product in commercial practice can be carried out by distillation on a 5-plate column at atmospheric pressure.

Qualitative and quantitative estimation of dimethyl sulphoxide was made by means of the boiling point curve. Prior to distillation, the product was made slightly alkaline with ammonia. Distillation started at 37 °C, when dimethyl sulphide was removed, temperature rose to 100 °C. Along with the decrease of the water quantity in the reboiler increased that of dimethyl sulphoxide in the distillate; from 188 °C on, pure dimethyl sulphoxide distilled over. Further purification of the aqueous dimethyl sulphoxide was attempted by repeated distillation, but these attempts failed. Thus, in the evaluation, the quantity of dimethyl sulphoxide distilled over with water was also taken into account. Yields referred to hydrogen peroxide and the way of evaluation are shown in Table 2 and Fig. 4.

Attempts were made to separate dimethyl sulphoxide from water with benzene. Addition of benzene started at 100 °C, at a rate to avoid temperature

rise. After separation, the organic phase of the distillate was recirculated into the benzene feeder. Azeotropic distillation was continued till water was present in the product.

Estimating the yields in tests Nos 2, 3 and 4 in a similar way, and converting for hydrogen peroxide, the data in Table 3 have been obtained.

Changes of temperature during distillation are shown in Fig. 5.

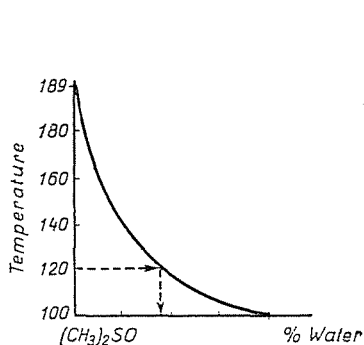


Fig. 4. Evaluation of the distillation curve of dimethyl sulphide

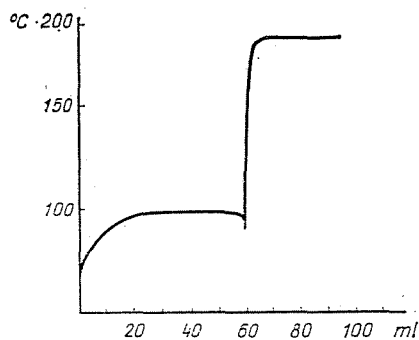


Fig. 5. Azeotropic distillation with benzene

**Table 2**  
Quantitative evaluation of the distillation curve of dimethyl sulphoxide

ml	°C	Percentage of DMSO in water, %	DMSO, g/10 ml
0	37		
10	100	2	0.2
20	102	2	0.2
30	104	5	0.5
40	120	8	0.8
50	140	10	1
60	160	14	1.4
70	188		4.1
80	189	30.5	
90	189		
95	190		

Distillation residue, 2 ml  
Distillation loss, 2.5 ml  
Product, 36 ml



Table 3

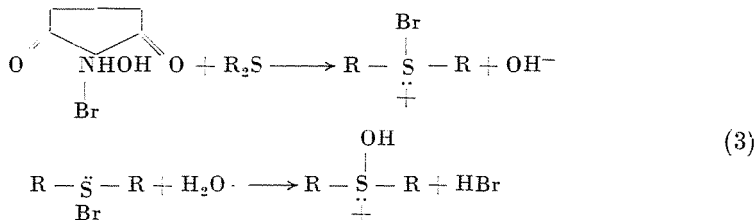
Test No.	1	2	3	4	5*
Yield	89	87	89	88.5	83

\* Yield measured by azeotropic distillation with benzene (Fig. 5). Unreacted dimethyl sulphide could be recovered almost without loss.

#### 2.4 Oxidation with bromo-succinimide

The significance of oxidation with bromo-succinimide lies in that the purity of the product obtained by it is much better than possible by other methods, and that this reaction is very fast (5 to 10 minutes) and can be carried out in an aqueous medium at room temperature, in the presence of 0.01 mole of  $P_2O_5$  as the catalyst.

Mole ratio in my experiments was 1 : 1. Formation of sulphone was very low indeed. This method is useful in the case of compounds which are sensitive to oxidation



#### 2.5 Oxidation with nitrogen tetroxide, in the liquid phase

To nitrogen tetroxide (18.4 g) dissolved in chloroform (60 ml),  $P_2O_5$  catalyst (0.1 g) was added. At 20 °C, dimethyl sulphide (12.4 g) dissolved in chloroform (20 ml) was added dropwise under stirring during 8 to 10 minutes. The mixture of chloroform and nitrogen sesquioxide was distilled off while oxygen was bubbled through the liquid. Oxygen was passed through till condensation in the condenser began. The product could be further purified by distillation in vacuum, thus chloroform and nitrogen tetroxide could be recovered and used again.

### Summary

The oxidation of dimethyl sulphide with hydrogen peroxide, and molecular oxygen in the presence of nitrogen dioxide and  $P_2O_5$  catalyst in the liquid and in the gas phase was studied. With hydrogen peroxide, yield was nearly 90 per cent, unchanged dimethyl sulphide was easily recovered. In spite of the substantial evolution of heat of oxidation, the reaction mixture did cause no difficulties thanks to the good heat transfer of the substance.

Oxidation with molecular oxygen yielded acceptable results only when carried out in the vapour phase. In the liquid phase the rate of reaction could be controlled through the  $P_2O_5$  catalyst.

When oxidation is carried out in the vapour phase, uniform distribution of gases and adequate cooling are important because dimethyl sulphide and oxygen may form an explosive mixture.

On the basis of experimental findings the hydrogen peroxide method, and the use of  $P_2O_5$  as catalyst, proved to increase conversion.

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