FORMATION OF HYDROQUINONE-DISULPHUR MONOXIDE CLATHRATE

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ABSTRACT

Hydroquinone is well known to form clathrates with sulphur dioxide and hydrogen sulphide. The molecular parameters of disulphur monoxide are found to be very close to the molecular parameters of the sulphur dioxide. It was, therefore, of interest to investigate whether disulphur monoxide also would give rise to a clathrate compound with hydroquinone. The formation of such a compound and its identification is reported in this paper.

A deep yellow solution of disulphur monoxide in carbon tetrachloride is obtained by passing the products of low pressure combustion of sulphur in oxygen (5-7 mm. *of* Hg.) *into the chilled solvent kept at* $-20^\circ C$ *The yellow solution of lower oxide could be freed from sulphur dioxide with the help of a vacuum pump*

When the solution is shaken with a dilute solution of hydroquinone dissolved in a mixture of carbon tetrachloride and n*-propyl alcohol, a pale yellow solid separates out. The dry solid is analysed for the sulphur oxide and hydroquinone contents by a variety of methods Hydrolytic, oxidative and reduction procedures have been employed for quantitative evaluation of the clathrate. I R. and X-ray methods have been helpful in identifying the compounds.*

1. INTRODUCTION

Hydroquinone is well known to form clathrates with sulphur dioxide and hydrogen sulphide[1]. Three molecules of hydroquinone form a hydrogen-bonded cage in which one guest molecule of appropriate size (diameter between 4-5 Å) can be accommodated. The hydroquinone phase in such caged compounds is designated as β phase. In the absence of the guest molecule the β phase is unstable and reverts to the stable α-form that exists under the usual normal laboratory conditions[2].

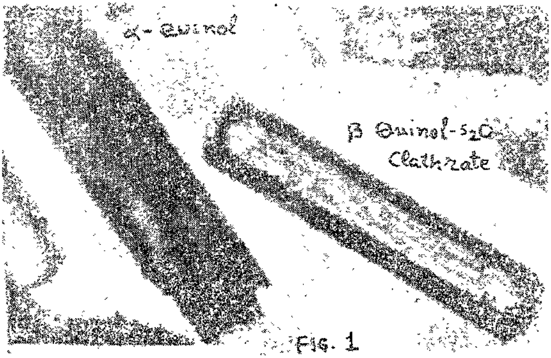


FIG. 1

The molecular parameters of disulphur monoxide are comparable to those of sulphur dioxide ; the O-S-S and O-S-O bond angles are 118°±0.5 and 119.3° respectively. The S-O bond length in SO_2 is 1 432 Å, whereas in S_2O it is 1 465 Å The S-S distance is S_2O is only 1.884 Å, which is very much shorter than the usual single bond distance of 2.1 Å. The shorter bond length indicates the double bond character between the two sulphur atoms in S_2O[3].

It was of interest therefore to investigate whether disulphur monoxide would also give rise to a clathrate compound with hydroquinone. The formation of such a clathrate and its characterisation is reported in this paper.

2. EXPERIMENTAL

(1) *Preparation of disulphur monoxide solution* :

The gaseous disulphur monoxide is very unstable under atmospheric conditions[4] whereas its solution in an inert cold solvent like carbon tetrachloride is comparatively stable[5,6]. Such solutions can be employed to study the physico-chemical behaviour of disulphur monoxide. A yellow solution of disulphur monoxide in cold carbon tetrachloride is easily prepared by sucking the products of combustion of sulphur in oxygen at low pressure (5-7 mm of Hg.) through the chilled solvent (−20°C). The solutiou can be freed from sulphur dioxide by evacuation. The solution thus obtained will be clear and lemon to orange yellow in colour. The concentration of the oxide in such solution ($\approx$ 0 05 M) can be determined by (*a*) anhydrous hydrogen iodide reaction and (*b*) by the decomposition of the oxide with mercury.

(2) *Preparation of the clathrate* :

A few drops of a cold solution of hydroquinone in *n*-propyl alcohol (50%) (−20°C) are added to the cold solution of disulphur monoxide in carbon tetrachloride (50 ml) and shaken well. A straw yellow white solid separates out which is filtered, washed with carbon tetrachloride and dried in vacuum. (About 200 mg. of the solid sample can be obtained in a batch preparation). The free flowing powder is the disulphur monoxide-hydroquinone clathrate which can be analysed and identified by methods described below.

The clathrate is found to hydrolyse and to give rise to cadmium sulphide when the solid is shaken with a suspension of cadmium hydroxide in dilute sodium hydroxide solution. Cadmium sulphide is precipitated Disulphur monoxide solution is easily decomposed when shaken with alkali ; sulphide, sulphite, thiosulphate and elemental sulphur are produced during the hydrolytic reaction. In the present case, it is rather difficult to estimate the other sulphur compounds owing to the presence of hydroquinone. The fact that cadmium sulphide is obtained from the sample indicates the presence of disulphur monoxide. The quantitative analysis is carried out by two methods.

(3) *Analysis of the clathrate* :

(*a*) The total sulphur content of the sample is estimated after oxidising a known weight of the sample with bromine and nitric acid. The resulting sulphuric acid is determined by gravimetric procedure after precipitating as barium sulphate.

(*b*) A fine suspension of the sample in carbon tetrachloride is treated with excess of anhydrous hydrogen iodide in a closed vessel. The hydrogen sulphide liberated during the reaction is isolated and estimated.

Anhydrous hydrogen iodide is known to reduce the sulphur oxide in terms of the equation[7] :

$$S_2O + 6HI \rightarrow 2H_2S + H_2O + 3I_2$$

Every gram mole of disulphur monoxide will give rise to 2 gram moles of hydrogen sulphide and 6 gram atoms of iodine. In the present case a lower value for iodine than the stoichiometric expectation was obtained. This may be attributed to the possible oxidation of hydroquinone by iodine. It is therefore more reliable to make use of the hydrogen sulphide value for estimating the disulpur monoxide content in the clathrate.

The analytical values for sulphur content by two independent methods agree reasonably well (Table I) The hydrogen iodide reaction indicates that the entire sulphur present in the form of clathrated S_2O is reduced to hydrogen sulphide. These results show that S_2O is contained in the hydroquinone crystal and is stabilised.

It is important to note, that it is rather difficult to prepare disulphur monoxide solutions of identical concentration. Considerable variation is observed in the yield of S_2O which depends on the experimental conditions of low pressure combustion such as the time, the amount of oxygen employed and its pressure, etc. The variation of the concentration is reflected in the S_2O content of the clathrate also which varies from 4 to 10%.

If the clathrate of disulphur monoxide were to be similar to that of sulphur dioxide, a molecule of the oxide should be occupied in the cage formed by three molecules of hydroquinone. The ideal composition of the clathrate would then be ($3C_6H_6O_2 \cdot S_2O$) corresponding to the total sulphur content of 15.6%. The lower results of the sulphur content in the clathrates obtained in the present study indicate that not all the vacant space in the cages is filled up. Only a fraction of the empty cages is occupied by S_2O. Similar observations have been made in the case of sulphur dioxide clathrates and hydrogen sulphide clathrates.

The formation of clathrate is confirmed by examining its morphology, X-ray powder pattern and I.R. spectra.

(4) *Morphology of Clathrate.*

The habits of α-quinol and β-quinol crystals have been observed to be different and as such they can be easily distinguished under a microscope. α-hydroquinone crystallised from water will be in the form of hexagonal prisms capped by rhombohedra. β-hydroquinone deposited from methyl alcohol will also be in the hexagonal form but is capped by trigonal pyramids with a well marked hemimorphism along the C-axis. The crystals are not so excessively acicular as those of α hydroquinune. The former tends to be fairly thick in relation to their length. SO_2-hydroquinone clathrate crystals are yellow in colour and resemble β-hydroquinone in their habits, S_2O clathrate is rather pale yellow and similar to SO_2-clathrate in their morphological features. Fig. 1.

(5) *X-Ray Power Pattern:*

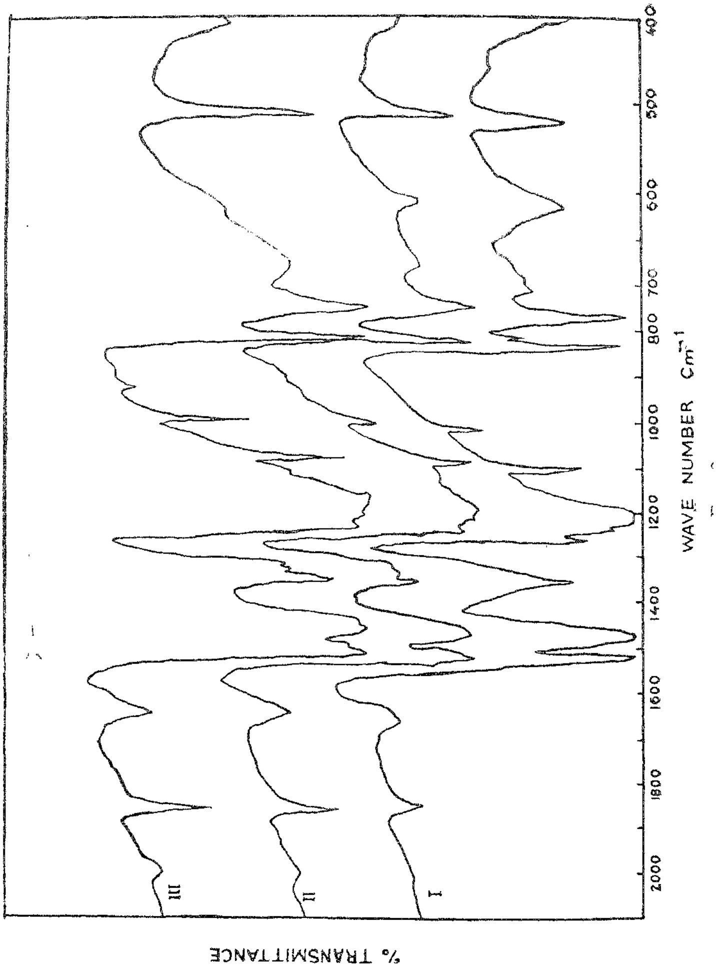
The powder pattern of hydroquinone crystals (α) differs from the powder pattern of the clathrates Three intense lines corresponding to three different *d* spacings are taken for purposes of comparison. CuK_α radiation was employed to get the powder pattern data. The three prominent lines of α-hydroquinone have been found[8] to corresponding to *d*=4.14 Å, 3 22 Å and 4.39 Å The following are the values corresponding to hydrogen sulphide and sulphur dioxide clathrates

SO_2 – hydroquinene ; *d*=3.91 Å, 4.40 Å and 4 79 Å
H_2S – hydroquinone ; *d*=3 86 Å, 4.37 Å and 4 81 Å

The *d* spacings corresponding to the three prominent lines obtained with S_2O-hydroquinone clathrate are *d*=3 867 Å, 4 392 Å and 4.769 Å. These values are distinctly different from the values for pure hydroquinone but are closely near to the values obtained for SO_2-hydroquinone clathrate and H_2S-hydroquinone clathrate. The powder pattern of the S_2O-hydroquinone clathrate sample clearly shows that pattern is due to β-hydroquinone and there is a guest molecule accammodated in the hydroquinone cage.

(6) *I. R. Spectra:*

The I.R. spectra of solid sample was recorded with K_2GR 10 recording pectrometer using KCl pellet technique (4 mg/gm). The Fig. 2 shows the R. spectra of (I) α-hydroquinone, (II) SO_2-hydroquinone clathrate and III) S_2O-hydroquinone clathrate. The spectrum of S_2O-hydroquinone clathrate esembles that of SO_2-hydroquinone clathrate indicating that the phase of ydroquinone corresponds to β-hydroquinone. The spectrum (I) is that ydroquinone which does not have any guest molecule. The space group of -hydroquinone is R_3 whereas that of β-hydroquinone is $R_{\bar{3}}$ which has an dditional element of symmetry (Centre of symmetry). The number of I.R. ands will be less in the case of species with a higher symmetry. The ands observed at the frequencies ($\bar{\nu}$) 1260, 810, 705 and 406 cm^{-1} for


400
500
600
700
800
1000
1200
1400
1600
1800
2000
WAVE NUMBER Cm⁻¹
% TRANSMITTANCE
I
II
III

α-hydroquinone (1) are absent for the samples of SO_2-hydroquinone clathrate and S_2O-hyroquinone clathrate. Similar observations are made with other guest molecules bound in the hydroquinone crystals[10]. The guest molecules in such caged compounds do not exhibit their characteristic frequencies owing to their low concentrations

TABLE I

Analysis of the disulphur monoxide-hydroquinone clathrate

Sl. No.	Weight of the sample taken for analysis mg	Total sulphur determined as $BaSO_4$ %	Sulphur obtained as H_2S in HI reaction %
1	4.0	4.53	4.37
2	14.6	4.37	4.53
3	13.9	7.49	7.48
4	15.0	5.56	5.44
5	57.7	6 85	6.55

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