Carbonyl Sulphide Formation *via* Transient Sulphenes

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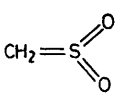
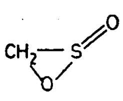
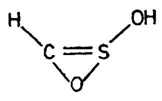
Summary An inner ester of hydroxymethanesulphonic acid, α-sultine, is proposed as an intermediate for carbonyl sulphide formation, in the coupling reactions of methylene and sulphur dioxide, in the photolytic and solid state electron impact decomposition of dimethyl sulphone and tetramethylene sulphone, and in the pyrolysis of methanesulphonyl chloride.

Reactivities of sulphene (**1**), an intermediate in many organic reactions,[1] have been studied spectroscopically[2] and theoretically.[3] We report here that carbonyl sulphide and its decomposition products always form when sulphene is produced in unreactive media and that transient α-sultine is an intermediate in the formation of carbonyl sulphide, which has never been reported in sulphene chemistry, although it has been postulated in several reactions.[4]

Typical results of the reaction of methylene and sulphur dioxide are shown in the Table. Irradiation of keten at 300 nm gave methylene, which reacted with sulphur dioxide to yield carbonyl sulphide and water. The dark reaction did not yield carbonyl sulphide. Carbon dioxide and carbon disulphide found in the products can be attributed to a secondary reaction of carbonyl sulphide.[5] In a low temperature solid film experiment the relative yield of the secondary reaction products became small. Irradiation of a gaseous mixture of carbonyl sulphide and sulphur dioxide at 254 nm results in the rapid disappearance of the former, yielding carbon dioxide, carbon disulphide, carbon monoxide and sulphur. The total yield of carbonyl sulphide, carbon dioxide and carbon disulphide in the gas phase methylene addition to sulphur dioxide amounted to 35% of the keten used. Addition of methylene to sulphur dioxide results in highly vibrationally and possibly electronically excited states (**1**) and (**2**) which undergo enolization to yield (**3**) or rearrange to (**4**) followed by dehydration to yield carbonyl sulphide. Similar additions of methylene to double bonds have been reported, e.g. to allene[6] and carbon dioxide.[7] Enolization of sulphoxides, followed by dehydration, is also known.[8] The rearrangement of (**2**) to (**4**) is analogous to the pyrolysis of alkyl sulphoxides.[9] Molecular dehydration of (**2**) is supported by the lack of inhibi-


(1)


(2)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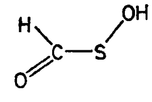
(4)

tion of nitric oxide on the pyrolysis of methanesulphonyl chloride, as described later. α-Sultine has been postulated as a source of formaldehyde in a flash pyrolysis of 3-thietanol 1,1-dioxide at 935°, which yielded many other aldehydes as major products.[4] A trace or small yield of formaldehyde in our case, as shown in the Table, may be ascribed to its rapid polymerization. Another reason for the different result may be due to different electronic states involved, possibly T_1 state in our case. When diazomethane was used as the methylene source instead of keten, a small amount of carbonyl sulphide was also formed together with a large amount of ethylene. Liquid phase addition of sulphur dioxide to diphenyl diazomethane was reported to yield a sulphene *via* cyclic azo compounds.[10]

Solid state photolysis of dimethyl sulphone yielded a significant amount of carbonyl sulphide (Table). One of the primary reactions in solid dimethyl sulphone photolysis is intra-molecular elimination of methane, leaving behind CH_2SO_2, which undergoes dehydration to yield carbonyl sulphide. Photochemical and electron impact-induced intra-molecular elimination of propene from tetramethylene sulphone also yields CH_2SO_2, resulting in carbonyl sulphide formation. The gas phase $Hg(^3P_1)$ photosensitized reactions of the two sulphones did not yield any trace of carbonyl sulphide. Instead, elimination of sulphur dioxide to yield respectively ethane and cyclobutane is the major reaction. Condensed phase photolysis of methyl sulphoxide and tetramethylene sulphoxide did not yield carbonyl sulphide, supporting CH_2SO_2 to be the precursor of carbonyl sulphide.

Although methanesulphonyl chloride is reported to decompose to methyl chloride and sulphur dioxide below 450°,[11] decomposition to hydrogen chloride and sulphene becomes important at higher temperatures; as the end products carbonyl sulphide and its secondary reaction products appear. The presence of nitric oxide does not inhibit carbonyl sulphide formation, indicating its molecular mechanism. A mass spectroscopic study of the thermolysis of methanesulphonyl chloride also suggests sulphene formation.[12]

TABLE

Relative yields compared with [A] used, or formed

	State (Temp.)	A	CH_4	C_2H_4	C_2H_6	CH_2O	H_2O	CO_2	CS_2	SCO	Other products
$:CH_2 + SO_2$[a]	gas (25°)	keten	—	0·18	—	trace	0·33	0·16	0·12	0·02	allene
$:CH_2 + SO_2$[b]	solid (−196°)	keten	—	0·13	—	trace	0·06	0·03	0·01	0·01	allene
Dimethyl sulphone + e^-[c]	solid(−196°)	SO_2	[d]	43	23	2·3	—	—	1·7	3·3	MeOH, Me_2S, Me_2S_2
Dimethyl sulphone + $h\nu$[e] ..	solid (24°)	SO_2	7·6	3·6	0·4	0·3	—	—	0·2	1·4	MeOH, Me_2S
Tetramethylene sulphone + $h\nu$[f]	liquid (30°)	SO_2	—	1·2	—	—	—	—	—	0·04	$C_3H_6(0{\cdot}2)$[g] $C_4H_8(0{\cdot}5)$
Methane sulphonyl chloride + NO[h]	gas (610°)	SO_2	0·63	0·04	—	—	0·03	0·05	0·02	0·03	HCl, MeCl

[a] A mixture of 55·1 torr keten and 377 torr SO_2 was irradiated for 24 h at 300 nm. [b] A mixture of 31·8 torr keten and 200 torr SO_2 was condensed at 77 K, and irradiated at 254 nm for 5 h. [c] An apparatus similar to that described by W. H. Hamill *et al.* (*J. Phys. Chem.*, 1970, **74**, 1883) was used with 100 eV incident electron energy. [d] The yield was not measured, but methane formation during electron impact was confirmed by continuous monitoring with a mass spectrometer. [e] A Philips zinc lamp with quartz envelope was used. [f] Neat tetramethylene sulphone was irradiated with a medium pressure mercury lamp for 3 h. Tetrahydrothiophene and $O_2(^1\Delta)$ were also formed. [g] Relative yields are given in parentheses. [h] A mixture of 30 mg methanesulphonyl chloride and 137 torr NO was pyrolyzed for 100 s in a 15 ml pyrex glass vessel.

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