

185 nm PHOTOLYSIS OF LIQUID SULPHOLAN

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Summary

The main products of the 185 nm photolysis of neat liquid sulpholan are ethylene ($\phi = 0.22$), acid ($\phi(\text{H}^+) = 0.30$) and 1,2-oxathian-2-oxide ($\phi = 0.1$). Minor products are cyclobutane ($\phi = 0.04$), 1-butene ($\phi = 0.012$) and methylcyclopropane ($\phi = 0.01$), together with traces of *cis*-2-butene, acetylene and propylene. The photolysis of aqueous sulpholan presents a similar picture. Whereas in neat sulpholan the acid consists mostly of SO_2 , in aqueous sulpholan it appears to be, for the most part, a sulphinic acid with a small amount of SO_2 . These results are in agreement with the hypothesis that β -sultine could be an intermediate product in a major reaction pathway.

1. Introduction

Studies of the photochemistry of aliphatic cyclic ethers and acetals at 185 nm (for a review see ref. 1) have shown that there are two major modes of reaction: (i) ring opening by homolytic cleavage of a C—O bond (formation of a diradical) and (ii) fragmentation into smaller molecules. The latter type of process would not involve the diradical intermediate. In these systems the excited state is of the *n*-Rydberg type.

The question may be posed whether other kinds of cyclic compounds show photolytic similarities [2, 3]. In the sulpholan system investigated here, which is also cyclic and in which the SO_2 group is the chromophore, the excited state produced by excitation at 185 nm appears to be characterized by a shift of electron density from the oxygen lone pairs to the sulphur d orbitals (*cf.* dimethyl sulphone [4]).

Some aspects of sulpholan photochemistry have been studied before and volatile products have been identified [3, 5] without, however, measuring the quantum yields. It was the purpose of the present work to determine the quantum yields of gaseous and liquid products in the 185 nm photolysis of neat sulpholan and of sulpholan containing 20% H_2O . These data allow us to propose a more detailed mechanism including rearrangement and possible deactivation processes.

2. Experimental details

Sulpholan (Merck) was purified by fractionation until it was 99.96% pure. The purity was determined using gas chromatography (flame ionization detection). The substrate was photolysed in the neat form as well as in an 80% aqueous solution. 2 ml samples enclosed in a quartz Suprasil cell were deaerated by purging with argon for 30 min and were exposed to the unfiltered light of a low pressure mercury lamp (a photograph of the experimental arrangement is shown in ref. 6 where its use is described). The dose rate was 7.0×10^{15} quanta s^{-1} (at 185 nm) per sample, as determined using a Farkas actinometer [7]. The 254 nm light was only slightly effective. This was established by interposing a Vycor quartz plate between the lamp and the cell which blocked the 185 nm light, whereupon it was found that the quantum yield of all the hydrocarbon products was much smaller at 254 nm than at 185 nm (ethylene, $\phi(254) \approx 4 \times 10^{-4}$ and $\phi(\text{unfiltered}) = 0.22$; 1-butene, $\phi(254) \approx 0.002$ and $\phi(\text{unfiltered}) = 0.012$; cyclobutane, methylcyclopropane and *cis*-2-butene are not formed at 254 nm).

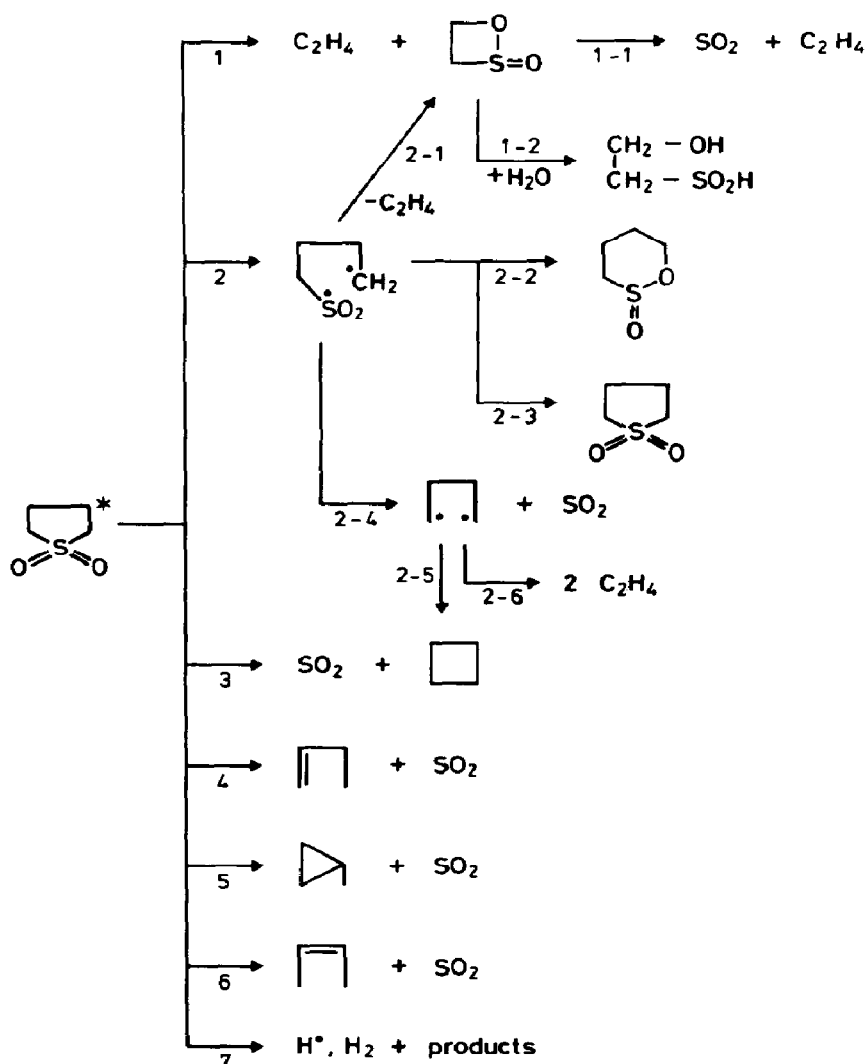
The products were identified by comparison with reference materials. The hydrocarbons were flushed out of the irradiated liquid into a sample bulb and aliquots were subjected to gas chromatography on an alumina column (120 m long; 120 °C; carrier gas, nitrogen). Hydrogen was purged from the irradiated sample by the carrier gas (argon), passed directly into the gas chromatograph and measured using thermal conductivity detection. Gas chromatography of the liquid products was performed using an OV-1-coated glass capillary column (53 m long; temperature programmed from 70 to 250 °C at 0.1 °C s^{-1} ; carrier gas, hydrogen).

The sample became acidic on irradiation. To determine the acidity, the samples were diluted to 10 ml and titrated with 0.01 M NaOH solution.

3. Results and discussion

The products and their quantum yields (Table 1) present a similar picture for both the neat and the 80% aqueous sulpholan, except for one characteristic difference. On titration of irradiated neat sulpholan a titration curve is obtained showing two steps of almost equal height, and more than 90% of the acidity can be removed by purging it with argon before dilution. In the case of aqueous sulpholan the titration curve appears to be one step, and purging with argon leads to only a moderate (about 20%) loss of acidity. It is known that SO_2 is one of the products of the gas phase photolysis of sulpholan [3]. Accordingly we expect SO_2 to account for some if not all the acidity determined in the present work. It has not been feasible to measure SO_2 directly, but the titrimetric results indicate that in the neat sulpholan essentially all the acidity is due to SO_2 whereas in the aqueous sulpholan SO_2 is less important, a large part of the acidity being due to a monovalent

acid. This acid is expected to be β -hydroxyethylsulphinic acid, formed on hydrolysis of the unstable [8] 1,2-oxathietan-2-oxide (a β -sultine):



1,2-oxathietan-2-oxide is the hypothetical primary product of reaction (1). The acid could not be identified, but the assumption agrees with the following facts: (i) in the solid phase photolysis of sulpholan a compound was observed whose mass spectrum indicated the 1,2-oxathietan-2-oxide structure [3]; (ii) this type of compound is known to be labile with respect to decomposition into olefin and SO_2 , even at room temperature [8, 9], and hence ethylene formation in the neat sulpholan is considered to be a two-step process with a prompt (reaction (1)) and a delayed (reaction (1-1)) component.

TABLE 1

Products and quantum yields of the 185 nm photolysis of deaerated sulpholan in the liquid state

	<i>Aqueous sulpholan (20% H₂O)^a</i>	<i>Neat sulpholan^a</i>
Hydrogen	Not determined	0.01
Ethylene	0.19	0.22
Acetylene	0.0024	0.0013
Propylene	0.0004	0.0006
Cyclobutane	0.045	0.040
1-butene	0.016	0.012
Methylcyclopropane	0.011	0.010
<i>cis</i> -2-butene	0.0005	0.0004
Total acid (H ⁺)	0.22	0.30
1,2-oxathian-2-oxide	0.1	0.1

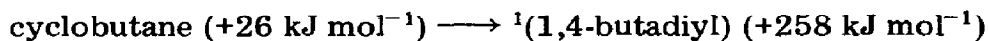
^aThe results are accurate to $\pm 10\%$.

Although it is possible that the β -sultine is formed by ethylene loss from the alkyl sulfonyl diradical generated in reaction (2) (reaction (2-1)), it is more likely to originate in the true molecular process given by reaction (1). In fact true molecular processes appear to play a significant role in many systems excited by 185 nm light [1]. The general reluctance of alkyl radicals to undergo a fast β cleavage at room temperature is in line with such an interpretation. More specifically, only traces of ethylene are observed in the 185 nm photolysis of oxepane where a similar diradical plays an important role [10]. The 1,5 diradical formed in reaction (2) may, however, be the precursor of another sulphur compound, 1,2-oxathian-2-oxide (a δ -sultine) (reaction (2-2)). Most of the 1,5 diradical may reclose to the educt (reaction (2-3)); the overall quantum yield of product formation is about 0.25 and it may well be that reaction (2) followed by reaction (2-3) is a major deactivation pathway. Homolytic photocleavage of the C—S bond in sulphones is well documented [11, 12], and it has been suggested that restitution of the C—S bond is favoured over other radical reactions in these systems [11, 13].

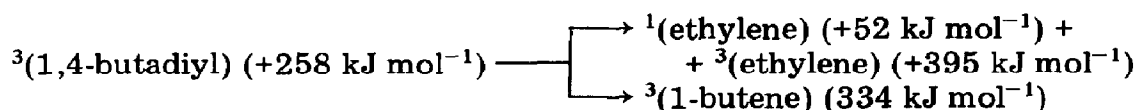
Cyclobutane could be formed via a molecular process (reaction (3)). An alternative route might involve the 1,5 diradical as a precursor. Elimination of SO₂ would result in the formation of 1,4-butadiyl (reaction (2-4)). The chemistry of this species has been extensively investigated (for a review see ref. 14). Most of it is expected to cyclize (reaction (2-5)) and only a small amount to split into two ethylene molecules (reaction (2-6)) at room temperature [15]. The other C₄ hydrocarbons (1-butene, *cis*-2-butene and methylcyclopropane) cannot be accounted for by assuming that the 1,4-butadiyl is an intermediate. Its internal disproportionation to 1-butene is unlikely as is shown by the fact that the 1-butene-to-cyclobutane ratio from pyrolytically generated 1,4-butadiyl is 0.01 or less [16, 17]. Products of this kind were

not found in the thermal and photochemical decomposition of substituted 3,4,5,6-tetrahydropyridazines [18] where 1,4 diradicals are implicated.

It has been suggested [3] that 1,4-butadiyl in its triplet state might be involved in the formation of the C₄ hydrocarbons other than cyclobutane. In the present case this seems unlikely on two counts: (i) when such diradicals are generated in the triplet-sensitized decomposition of 3,4,5,6-tetrahydropyridazines, disproportionation products are not found [18]; (ii) the formation of triplet olefin from 1,4-butadiyl is estimated to be endothermic, as is indicated by the following relations (the heats of formation are given in parentheses):

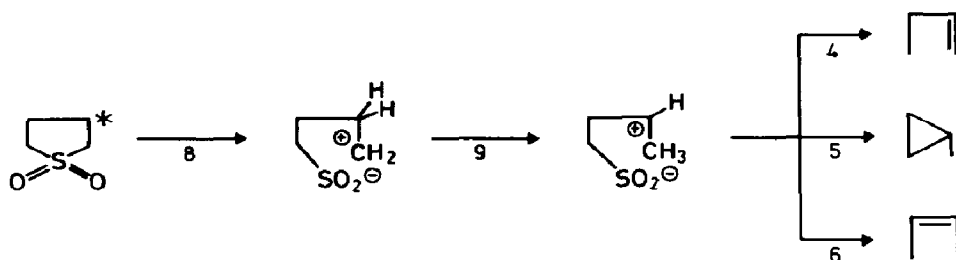


${}^1(1,4\text{-butadiyl)}$ approximately isoenergetic with ${}^3(1,4\text{-butadiyl)}$



The heat of formation of 1,4-butadiyl was estimated from thermochemical group increments [19].

Since 1,2 hydrogen shifts from a primary to a secondary carbon are common in carbo-cation chemistry but not in free-radical chemistry and, as discussed above, the 1,4-butadiyl diradical is not a probable intermediate, a zwitterionic intermediate may account for the formation of the minor products 1-butene, methylcyclopropane and *cis*-2-butene:



Propene has also been detected previously and has been considered to be formed together with carbonyl sulphide and water [5]. Because of the low quantum yield of propene such a process is of very minor importance here.

$\phi(\text{H}_2)$ is very low, and products that would allow us to distinguish between H₂ elimination and hydrogen atom formation (reaction (7)) have not been observed.

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