

## FLASH PHOTOLYSIS OF DIMETHYLSULPHOXIDE

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### SUMMARY

The photolysis of dimethylsulphoxide in aqueous solution produces two transitory species which are the result of excitation rather than photoionization processes. In alkaline media the less stable species, to which we attribute the formula  $\text{CH}_3\text{SOHCH}_3$  ionizes, the  $\text{p}K_a$  of the equilibrium being between 10.3 and 11.3. In neutral solutions, the rate constant for decay of this species is  $(3.0 \pm 0.3) \times 10^3 \text{ s}^{-1}$ . It is suggested that the second species, stable during our experimental observations is methyl sulphinic acid,  $\text{CH}_3\text{SO}_2\text{H}$ .

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### INTRODUCTION

The special physical properties of dimethylsulphoxide (DMSO) as a polar aprotic solvent led us to study its radiolysis<sup>1,2</sup>. The results obtained, and in particular those from pulse radiolysis experiments, have led us to examine its photochemical behaviour. Three absorption bands, corresponding to three distinct unstable species, were observed in DMSO irradiated with 30 ns pulses of 2 MeV electrons and it was not possible to relate one of these transient species to the electrons or positive ions formed upon irradiation by:



It seemed possible that this species (absorbing in the u.v. below 300 nm) might be formed *via* excited molecules,  $\text{DMSO}^*$ , which are also produced by the electron pulse and that evidence for their existence might be obtained by flash photolysis of DMSO.

While this work was in progress Gollnick *et al.*<sup>3</sup> published results of a study on the steady state photolysis of DMSO in which a number of stable products were identified. Our technique, which allows measurements to be made in times

of the order of 50  $\mu\text{s}$  and enables the formation and decay of unstable species to be followed, leads us to suggest a reaction mechanism somewhat different from that proposed by these authors.

#### EXPERIMENTAL

The apparatus was partly described in a previous publication<sup>4</sup>. In the present work a coaxial photolysis lamp filled with oxygen (10 Torr) was used and gave, with an energy expenditure of 1300 J, a flash duration of 4  $\mu\text{s}$  at half intensity, although the tail of the flash emission precluded oscillographic measurements at times shorter than 30–40  $\mu\text{s}$  after the flash; the distance between the electrodes was 13 cm. Other equipment included a xenon arc (Osram XB0450W) as analyzing light source, a McPherson Model 218 monochromator and RCA IP28 photo-multiplier tube of which only the first six dynodes were used in order to improve the signal to noise ratio. The absorption cell (Pursil 453, Quartz et Silice) was 18 cm long and 1.5 cm in diameter.

Dimethylsulphoxide (Merck, Livasol) was distilled under reduced pressure of argon, both with and without calcium hydride, to remove traces of water and dimethyl sulphide, the principal impurities. Infra-red analysis confirmed that if the DMSO was already very pure, the presence of calcium hydride led to no significant improvement in the quality of the distillate but rather to some decomposition with the formation of water<sup>5</sup>. For this reason, simple distillation under reduced pressure through a 1 m column with rejection of the initial distillate was retained as the method of purification.

DMSO is transparent from 1800 to 300 nm. Absorption begins below 300 nm with a "cut off" at 261 nm. Since our first results showed that the transients formed by photolysis absorbed in the region of 300 nm, the DMSO was diluted with water to reduce absorption due to the solvent and make possible more precise measurement of optical densities below 300 nm. Most of our experiments were carried out with solutions containing 5% by vol. DMSO, *i.e.* 0.7 M.

Water was triple-distilled. Other reagents (Merck) were used without preliminary purification.

#### RESULTS

The variation of the initial optical density (40  $\mu\text{s}$  after the start of the flash) was followed as a function of wavelength. Figure 1 shows this variation in the case of pure DMSO and it can be seen that one or several species absorbing in the region of 300 nm are formed during the flash.

Figure 2 shows the variation of initial optical density with wavelength for a 5% aqueous DMSO solution for a flash of the same duration. The solution was renewed between each flash.

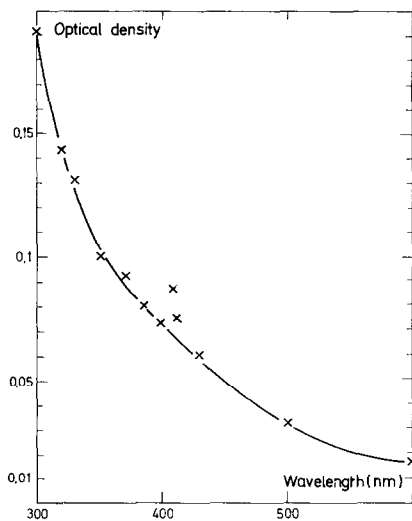


Fig. 1. Initial optical density of the transient formed in pure DMSO vs. the wavelength.

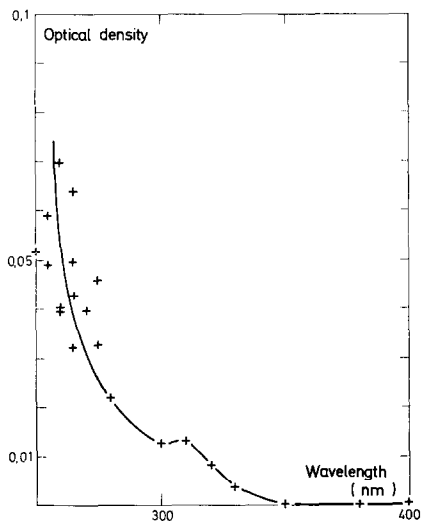


Fig. 2. Initial optical density of the transient formed in 5% DMSO aqueous solution vs. the wavelength.

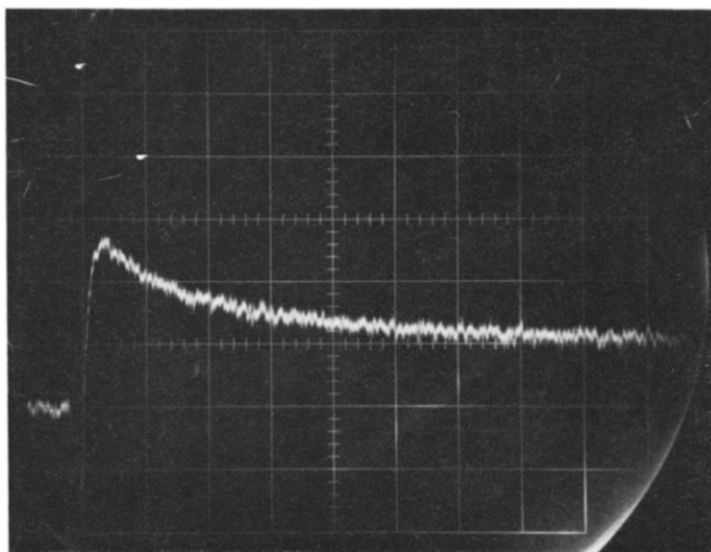


Fig. 3. Oscillogram of flash photolysis of DMSO at  $\lambda = 260$  nm. (hor. div. =  $200 \mu s$ , vert. div. = 5%)

We established from the oscillogram (Fig. 3) at  $\lambda = 260$  nm, that after the total decay of the absorption (after about 1 ms) attributable to an unstable transitory species, a permanent absorption remained. At 300 nm and above no decay was observed but only the appearance of an absorption corresponding to a

species stable over the time range of our experiments. We conclude, therefore, that two species were formed during the flash. Figure 4 shows the optical density of the solution measured 1.4 ms after the flash ( $d_{\infty}$ ) as a function of wavelength. It corresponds therefore either to the optical density of the more stable transient formed during the flash or to the sum of the optical densities of this species and that formed after the flash by decay of the more unstable species. Taking the optical density at 1 ms as reference, the decay of the latter follows a first order law with a rate constant of  $(3.0 \pm 0.3) \times 10^3 \text{ s}^{-1}$  (Fig. 5). This allows us to exclude dismutation of this species from any proposed reaction mechanism.

In summary the formation of two species absorbing in this spectral region is similar to that obtained by radiolysis of DMSO, leading us to believe that their formation was not the result of photoionization of DMSO.

Various ionization potentials have been reported for DMSO, but the most probable values for the gas phase appear to be about 8.85–9.6 eV<sup>6</sup>. It is known, however, that in the liquid phase the ionization potential may be lower and that photoionization of a molecule can be produced by photons of lower energy than are required in the gas phase<sup>7</sup>. Although the spectrum of the discharge lamp we used had its maximum intensity at about 360 nm, its spectrum extended beyond this to the quartz cut-off around 180 nm, so that photoionization of the molecule is not *a priori* excluded. We therefore looked for evidence of this process, trying to detect hydrated electrons, by their absorption at a wavelength of 600 nm. To

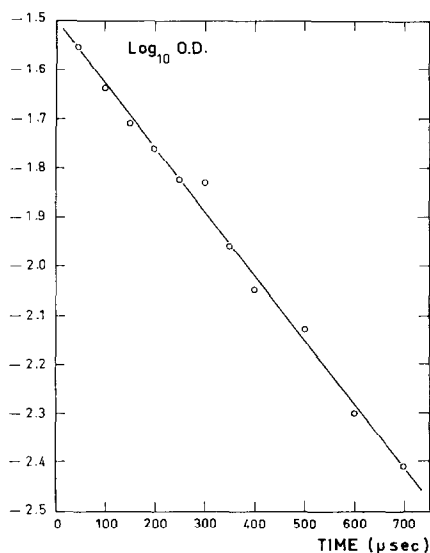
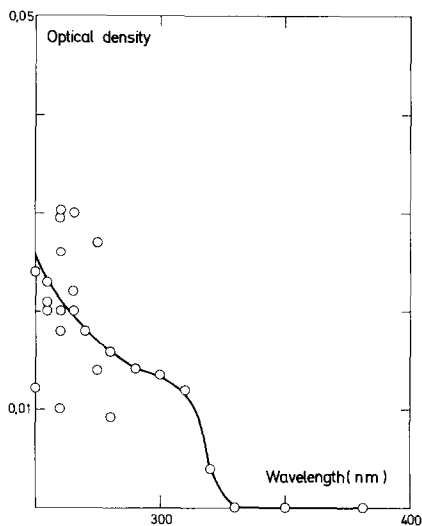


Fig. 4. Optical density 1.4 ms after the flash vs. the wavelength.

Fig. 5. Decay of the transient as function of time.

this end we photolyzed de-aerated aqueous solutions  $0.7$  and  $1.4 \times 10^{-4} M$  in DMSO. The reactivity of  $e_{aq}^-$  with DMSO is small ( $k \approx 3 \times 10^6 M^{-1} s^{-1}$ )<sup>8</sup>. No absorption was observed at this wavelength. In other experiments we confirmed that it was possible to detect  $e_{aq}^-$  under our conditions by photolyzing  $10^{-2} M$   $Br^-$  aqueous solutions.

In conclusion, our observations confirm that the formation of transient species by the photolysis of DMSO is not a consequence of ionization but rather of excitation of the molecule.

We extended this work to study the properties of the two absorbing species with a view to establishing their identity and the mechanism of their formation. The first point examined is the possible identification of the less stable transient as a triplet state of DMSO. Since oxygen is generally considered as an excellent deactivator of triplet states, we photolyzed a DMSO solution saturated with oxygen ( $1.2 \times 10^{-3} M$ ) but found no effect either on the spectrum of the species or its lifetime. Thus, this species is probably not a triplet state of DMSO. This experiment also enabled us to discard a number of other hypotheses, namely: the presence of the radical  $HO_2$  which also absorbs in the same region and consequently a mechanism of dissociation of  $DMSO^*$  such as:



and the formation of a peroxide from stable and unstable species, which would necessarily change the absorption spectrum or at least the decay kinetics.

Using concentrations of  $H_2SO_4$  up to  $1 M$  we also established that there was no effect of  $H^+$  ions on the rate of decay of the transitory species at  $\lambda = 260$  nm showing that the latter does not react with  $H^+$ . This observation excludes that in neutral media the transient is the basic form of an acid having a  $pK_a$  between 7 and 0.3. It also proves that all species taking part in the observed decay process are uncharged since the rate constant of the reaction is not influenced by the change in ionic strength<sup>9</sup>. On the other hand, a very important effect of  $5 \times 10^{-4}$  to  $1 M$  potassium hydroxide has been observed at  $\lambda = 260$  nm on the formation of the transients. We established that for the highest concentrations of KOH the absorption due to  $OH^-$  is negligible in comparison with that of DMSO (of the order of 2%) and that therefore the effects observed cannot be attributed to photochemical decomposition products of the hydroxide ion ( $e_{aq}^-$  or  $OH^-$ ). The oscillograms in Figs. 6–8 show that as the KOH concentration increases the disappearance of the initially observed transient is gradually replaced by the formation of some other undefined species.

Such a change in kinetics as a function of pH may generally be interpreted as due to an acid–base equilibrium<sup>10,11</sup>. In our case, the change in kinetics produced between pH 10.3 and 11.3 suggests that the initial transitory species is a very weak acid. This effect of  $OH^-$  on the transient absorbing at 260 nm encouraged us to study the absorption spectra of alkaline solutions,  $10^{-2}$  and  $1 M$ , after the light

flash. Figure 9 shows these spectra. They differ from those of Fig. 2, obtained in neutral solutions, and establish the appearance of a new peak, very sharp, at 270 nm due to the formation of a new species.

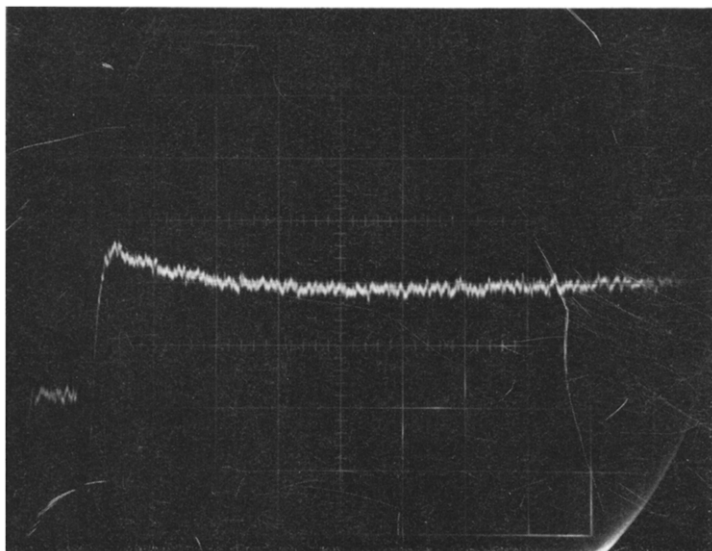


Fig. 6. Oscillogram of flash photolysis of DMSO showing the effect of  $10^{-3} M$  KOH. (hor. div.  $\approx 200 \mu s$ , vert. div.  $\approx 5\%$ )

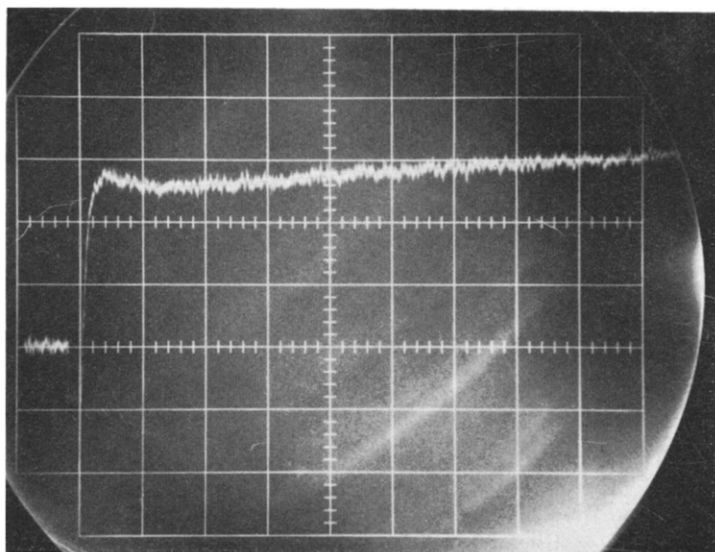


Fig. 7. Oscillogram of flash photolysis of DMSO showing the effect of  $5 \times 10^{-3} M$  KOH. (hor. div.  $\approx 200 \mu s$ , vert. div.  $\approx 5\%$ )

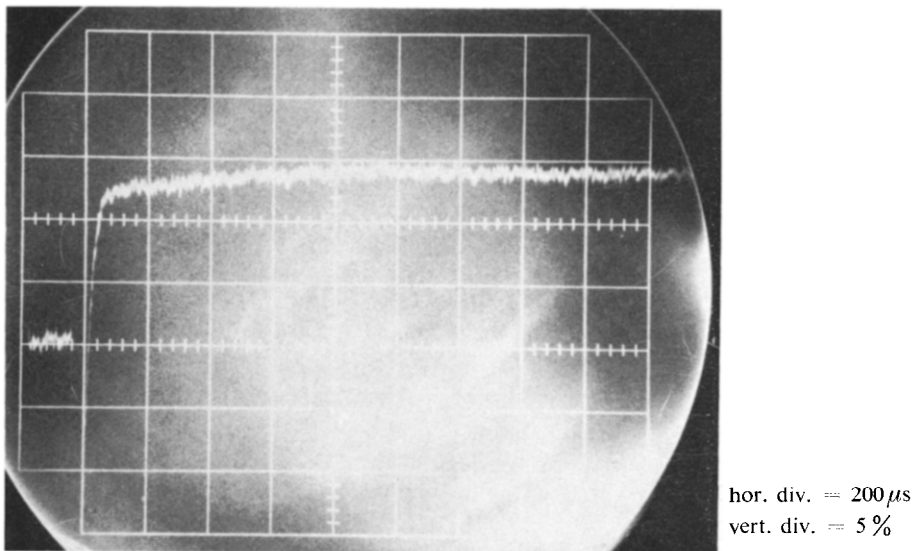


Fig. 8. Oscillogram of flash photolysis of DMSO showing the effect of  $10^{-2} M$  KOH.

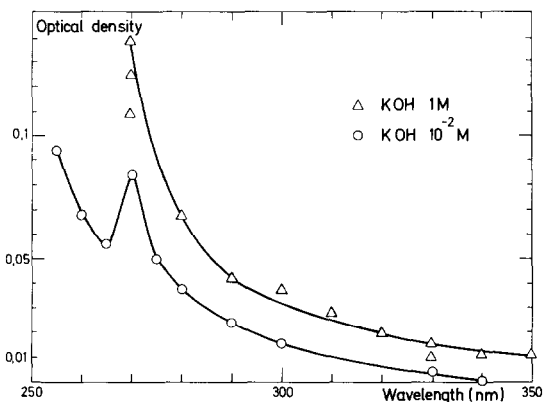


Fig. 9. Initial optical density of the transient in 5% DMSO alkaline solution.

DISCUSSION

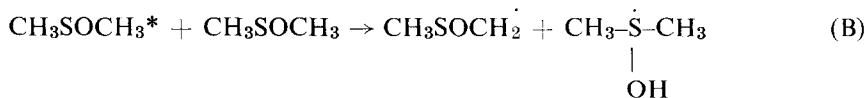
A satisfactory interpretation of the photolysis of DMSO should explain not only the positive results of this work but also the negative effects observed and, in addition, the data of previous steady-state studies<sup>3,12</sup>.

The mechanism of decomposition of DMSO, in a triplet or singlet state, can be envisaged as following several independent, but simultaneous, paths.

(I). As Gollnick *et al.*<sup>3</sup> pointed out, basing their conclusion on the identification of the final products of the photolysis, part of the  $CH_3SOCH_3^*$  may disappear according to:

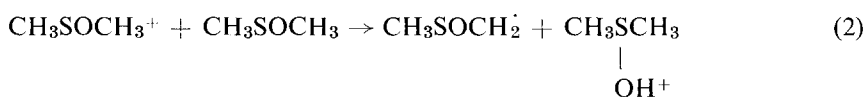


(II). Although acetone and DMSO have very different properties due to the replacement in the molecule of an atom of carbon by an atom of sulphur, one can also envisage a  $\text{CH}_3\text{SOCH}_3^*$  dissociation mechanism analogous to that proposed by Hayon *et al.*<sup>13</sup>, namely:



Such a mechanism is not incompatible with the absence of an effect of molecular oxygen in the transients formed in view of the high DMSO: oxygen concentration ratio ( $\sim 6 \times 10^2$ ).

In this reaction scheme, the species  $\text{CH}_3\text{SOCH}_2\dot{\phantom{C}}$  is identical with that expected to be formed in the radiolysis of pure DMSO<sup>2</sup> by the following mechanism:



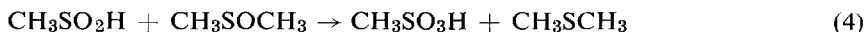
In the pulse radiolysis study an absorption band at 625 nm was attributed to an oxidizing species arising from  $\text{CH}_3\text{SOCH}_3^+$  and which is most probably  $\text{CH}_3\text{SOCH}_2\dot{\phantom{C}}$ . Such an absorption is absent in the photolysis of 5% of aqueous DMSO but is, however, present in the photolysis of pure DMSO. This leads to the conclusion that in the photolysis of 5% DMSO in water the species  $\text{CH}_3\text{SOCH}_2\dot{\phantom{C}}$  is found in too small a concentration to be detected (the extinction coefficient is  $2200 \text{ M}^{-1} \text{ cm}^{-1}$ )<sup>2</sup> and that  $\text{CH}_3\text{SOCH}_2\dot{\phantom{C}}$  is formed but reacts with water in a time shorter than 30  $\mu\text{s}$  by:



The water concentration in our system being about 53  $M$ , the rate constant of this reaction need only be  $2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ , for the radical  $\text{CH}_3\text{SOCH}_2\dot{\phantom{C}}$  to disappear in 30  $\mu\text{s}$ . In an attempt to determine the rate constant of this possible reaction a pulse radiolysis study of DMSO-water mixtures, saturated with  $\text{N}_2\text{O}$ , has been undertaken<sup>14</sup>. The results already obtained show that the species absorbing at 625 nm no longer appears in 5% DMSO solution. Although this result is compatible with the hypothesis (B) it is still not sufficient to prove that the radical  $\text{CH}_3\text{SOCH}_2\dot{\phantom{C}}$  disappears by reaction with water. This species could also disappear by a second order reaction with itself or an another radical, for example  $\text{CH}_3\text{SO}\dot{\phantom{C}}$  giving again by hydrolysis  $\text{CH}_3\text{SOCH}_3$  and other stable products such as dimethyl sulphone of methane sulphonic acid.



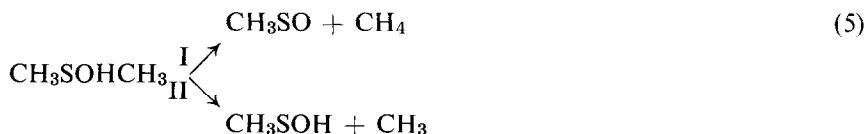
According to these hypotheses the relatively stable sulphinic acid,  $\text{CH}_3\text{SO}_2\text{H}$  would correspond to the more stable of the two species we have detected. The sulphinic acids are known to be strong acids and powerful reducing agents which are easily converted into the corresponding sulphonic acids<sup>15</sup>, for example by the reaction:



This mechanism is suggested by the fact that these compounds have been identified among the final products of the steady state photolysis of DMSO<sup>3</sup>.

If  $\text{CH}_3\text{SOCH}_2\cdot$  disappears by reaction with water, the  $\text{CH}_3\cdot$  radical formed could give  $\text{C}_2\text{H}_6$  by dimerization, or  $\text{CH}_3\text{SOCH}_3$  by reaction with the radical  $\text{CH}_3\text{SO}\cdot$ . This gas has been detected in the photolysis<sup>12</sup> and radiolysis<sup>1,16</sup> of DMSO. Gollnick *et al.*<sup>3</sup> do not say, however, if they have looked for  $\text{C}_2\text{H}_6$  among their final photolysis products.

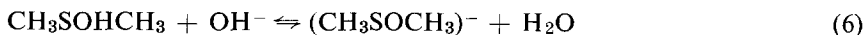
The second radical,  $\text{CH}_3\dot{\text{S}}\text{OHCH}_3$ , formed by reaction (B) would then correspond to the less stable of the two species absorbing at 260 nm. We have seen that its decay follows first order kinetics and that the rate constant is independent of the concentration of DMSO. We conclude from this that it disappears by one of the following two processes:



Disappearance by path (I) appears the most plausible in view of the results of Gollnick *et al.*<sup>3</sup>. These authors showed that the photolysis of DMSO- $d_6$  in aqueous solution leads to methane in the form  $\text{CD}_3\text{H}$  (99%). This is only possible by path (I) and not by path (II). The radical  $\text{CD}_3\cdot$  formed by path (II) leads by reaction with DMSO- $d_6$  to  $\text{CD}_4$ . We must nevertheless admit that an exchange of hydrogen occurs between water and the radical  $\text{CH}_3\text{SOHCH}_3$  though not between  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{SOCH}_3$ . This is not impossible given that this radical has an H atom on the oxygen which has not the DMSO itself.

The radical  $\text{CH}_3\text{SO}\cdot$  would either react as previously suggested or after dimerization give  $\text{CH}_3\text{SO}_2\text{SCH}_3$ , one of the end products found by Gollnick *et al.*<sup>3</sup>.

In alkaline media, the transient species we have attributed to  $\text{CH}_3\text{SOHCH}_3$  behaves quite differently. The appearance of the oscillograms suggests that an acid-base equilibrium is established between two forms of the same entity. Two forms of such an equilibrium may be written:

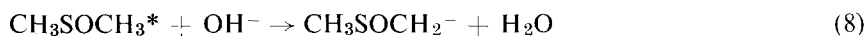


The second reaction seems the more probable because the ion  $(\text{CH}_3\text{SOCH}_3)^-$  is the anion of DMSO, a species whose existence has not been proved unequivocally by pulse radiolysis (the solvated electron would be more probably formed<sup>2</sup>). In any case its lifetime is so short that it could not be detected and the equilibrium must lie towards the left.

On the other hand, it is known that the H atoms of  $\text{CH}_3$  radicals are quite labile in the DMSO molecule<sup>17</sup>. The dimsyl anion,  $\text{CH}_3\text{SOCH}_2^-$  is the basic form of  $\text{CH}_3\text{SOCH}_3$ . The p*K* of the equilibrium between these two forms has the value 33<sup>18</sup>.  $\text{CH}_3\text{SOHCH}_2^-$  would be the analogous basic form of  $\text{CH}_3\text{SOHCH}_3$  of which the p*K* according to our results lies between pH 10.3 and 11.3 making this radical a much stronger acid than DMSO. It would have been interesting to know if the isotopic form of  $\text{CH}_4$  is influenced by the pH.

In very basic media ( $10^{-2}$  M to 1 M KOH), we have seen the appearance of a new peak at 270 nm in the spectrum of photolyzed DMSO. It is known<sup>19</sup> that the spectrum of the dimsyl ion shows an absorption peak at 272 nm ( $\epsilon = 40,000 \text{ M}^{-1} \text{ cm}^{-1}$ ) and a shoulder at 330 nm. We have not observed the shoulder at 330 nm, but in our experiments the concentration of the species is always very low (equal to or less than  $10^{-5}$  M). Consequently the corresponding optical densities are very small. Assuming the peak at 270 nm is due to the dimsyl ion we can calculate from the observed optical density and the known extinction coefficient that its concentration is  $10^{-6}$  M, a value which appears reasonable given that the process formation of this species only represents a small part of the total photolytic decomposition of DMSO. It is not impossible that under these conditions the shoulder at 330 nm is not observed.

The formation of this anion could be explained by the reaction of  $\text{OH}^-$  ions with excited DMSO molecules, forming thereby a dimsyl ion:

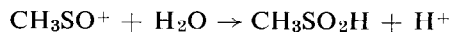


The corresponding reaction with DMSO in its ground state is endothermic by about 20 kcal, but the excitation energy of  $\text{DMSO}^*$  is probably very much higher. As van der Donckt<sup>20</sup> points out "when the site of deprotonation is carbon atom the proton loss may involve a certain amount of activation energy and in this case deactivation of the electronic energy might occur during the process". The  $\text{DMSO}^*$  might thus be able to loose a proton more easily than the ground state molecule and would therefore be a stronger acid than the latter<sup>21-23</sup>.

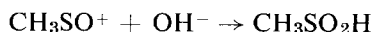
(III). Regarding the mechanism of decomposition proposed by Gollnick *et al.*<sup>3</sup>, namely:



(the corresponding purely radical mechanism having been rejected by these authors as incompatible with their experimental results) the transitory species that we observe would have to be  $\text{CH}_3\text{SO}^+$  which would disappear, for example by:



In alkaline media one would have:



The species formed would be the same whatever the pH and probably would be  $\text{CH}_3\text{SO}_2^-$  because the sulphinic acids are known to be strong acids; Wudl *et al.*<sup>24</sup> give  $\text{p}K_a = 2.28 \pm 0.04$  for methane sulphinic acid. This mechanism does not include, therefore, the possibility of an acid-base equilibrium, and we cannot describe the transitory species we have observed by the formula  $\text{CH}_3\text{SO}^+$ .

In conclusion, the flash photolysis of DMSO in aqueous solution has provided evidence of two different unstable species absorbing in the u.v. which we attribute to  $\text{CH}_3\text{SOHCH}_3$  and  $\text{CH}_3\text{SO}_2\text{H}$  respectively. In alkaline media, an acid-base equilibrium is established and a third species is formed which we attribute to the dimsyl ion.

The decay kinetics observed for the first two species suggest a new partial interpretation of the formation of products obtained by continuous photolysis. It would have been interesting to obtain evidence of the transitory species  $\text{CH}_3\text{SOHCH}_3$  in another way, for example by photolyzing dimethylsulphide in alkaline media and under an atmosphere of  $\text{N}_2\text{O}$ . This was not possible because dimethylsulphide absorbs too strongly in the u.v.

Finally, the fact of having shown that the photolytic decomposition of DMSO is not brought about by photoionization provides strong support for the hypothesis that some of the transient species formed in the radiolysis of DMSO originate from excited DMSO molecules, thus answering the major question posed at the start of this study.

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