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PHOTOLYSIS OF DIMETHYL SULFOXIDE IN WATER, METHANOL, ETHYL ALCOHOL, AND ISOPROPYL ALCOHOL.

EVIDENCE FOR PHOTOLYTIC DECOMPOSITION VIA NON-RADICAL PATHWAYS.

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Products and product distributions obtained during the photolysis of dimethyl sulfoxide (DMSO) in water and acetonitrile (1) indicate that two primary reactions of photochemically excited DMSO occur, one of which is a bimolecular reaction according to

$$1)\quad DMSO^{*} + DMSO \longrightarrow CH_3SO_2CH_3 + CH_3SCH_3$$

with a quantum yield of dimethyl sulfone formation of about 0.02 - 0.06, whereas the other involves fragmentation into CH_3 and methanesulfinyl species, CH_3SO, with a quantum yield of methane production of about 0.2 in both solvents.

Irradiation of perdeuterated dimethyl sulfoxide, DMSO-d_6, in oxygen-free H_2O yielded CD_3H to an extent of more than 99 % of the total amount of methane. Neither in the dark nor during the photolysis reaction did any hydrogen exchange occur as was revealed from recovered DMSO-d_6.

Irradiation of DMSO in oxygen-free O-deuterated methanol, ethyl alcohol, and isopropyl alcohol resulted in CH_4-CH_3D mixtures as shown in Table 1. Again, no hydrogen exchange was detected in the recovered DMSO.

Table 1: CH_4-CH_3D Formation during Photolysis of DMSO (1 M) in O-deuterated Alcohols *).

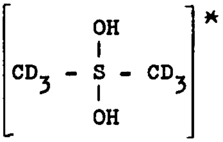
Solvent	Molar Ratio CH_4 : CH_3D	% Non-Radical Mechanism
CH_3OD	1 : 1	50
CH_3CH_2OD	3 : 1	25
$(CH_3)_2CHOD$	11 : 1	8

*) λ_{exc} = 2537 Å, Irradiation of 10^{-2} moles DMSO/10 ml solvent for one hr. after oxygen was removed by conventional freeze-pump-thaw procedures at 77°K on a mercury-free vacuum system.

Since hydrogen atom abstraction from water by methyl radicals is rather improbable (2), CD_3H may be produced via heterolytic scission of the C-S bond according to

2) $CD_3SO\text{-}CD_3 + h\nu \longrightarrow \longrightarrow \overset{\oplus}{CD_3SO} + \overset{\ominus}{CD_3} \xrightarrow{+H_2O} CD_3SO_2H + CD_3H$

which, however, would require that the solvation energies of $\overset{\oplus}{CD_3SO} + \overset{\ominus}{CD_3}$ be about 120 kcal/mole since the heterolytic C-S bond cleavage of DMSO in the gas phase needs about 230 kcal/mole (3). Or, CD_3H may be produced by a solvolytic displacement reaction of electronically excited DMSO-d_6 by H_2O via a concerted reaction or via ionic reactions one of which may include the formation of an electronically excited or a highly vibrationally excited ground state DMSO-d_6 - water adduct



$$\left[\begin{array}{c} OH \\ | \\ CD_3 - S - CD_3 \\ | \\ OH \end{array}\right]^{*}$$

that decomposes at least partly into $CD_3SO_2H + CD_3H$. (The corresponding thermalized ground state adduct would be expected to yield only DMSO-d_6 and H_2O as may be deduced from ^{16}O - ^{18}O exchange experiments of DMSO in concentrated sulfuric acid (4)). In order to get some more insight into the photofragmentation process, irradiations of DMSO in $H_2{}^{18}O$ are investigated at present.

In methanol, ethyl alcohol, and isopropyl alcohol, part of the photofragmentation obviously occurs also via one of the non-radical pathways discussed producing the corresponding alkyl methanesulfinate and methane (CH_3D). Besides these pathways, however, a radical pathway is followed which seems to be the more preferred the easier a hydrogen atom may be abstracted from the solvent molecules by the primarily formed radicals, $\cdot CH_3$ and $CH_3\underset{\bullet}{S}O$, indicating that hydrogen is abstracted from the solvent rather than from DMSO itself.

3) $CH_3SO\text{-}CH_3 + h\nu \longrightarrow \longrightarrow CH_3\underset{\bullet}{S}O + \cdot CH_3$

4) $CH_3\underset{\bullet}{S}O + R_2CHOD \longrightarrow CH_3SOH + R_2\underset{\bullet}{C}\text{-}OD$

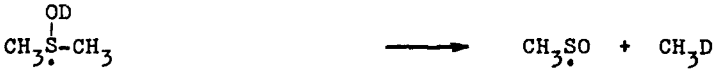
5) $\cdot CH_3 + R_2CHOD \longrightarrow CH_4 + R_2\underset{\bullet}{C}\text{-}OD$

This is supported by the fact that no products of the dimsyl radical, $CH_3SO\text{-}\underset{\bullet}{C}H_2$, could be found in either solvent. Furthermore, appreciable amounts of acetone were isolated when DMSO was photolyzed in isopropyl alcohol, due to the intermediate formation of 2-hydroxy-2-propyl radicals, and finally only CD_3H was detected when DMSO-d_6 was irradiated in non-deuterated alcohols. The observed stability of DMSO toward radical attack under the conditions used is very well in agreement with the resistance of the hydrogens of DMSO toward attack of other free radicals (5) that makes DMSO a suitable solvent for free radical reactions and polymerizations.

In view of the results obtained with DMSO-d_6 in water and the increasing amounts of CH_4 formed during the photolyses of DMSO in O-deuterated methanol, ethyl alcohol, and isopropyl alcohol, production of CH_3D in the latter solvents as a result of D-atom transfer according to a chain reaction process like

6)


$$(CH_3)_2\underset{\bullet}{C}\text{-}OD \;+\; CH_3SO\text{-}CH_3 \longrightarrow CH_3CO\text{-}CH_3 \;+\; CH_3\underset{\bullet}{\overset{\overset{OD}{|}}{S}}\text{-}CH_3$$

7)


$$CH_3\underset{\bullet}{\overset{\overset{OD}{|}}{S}}\text{-}CH_3 \longrightarrow CH_3\underset{\bullet}{S}O \;+\; CH_3D$$

$$8)\quad CH_3\underset{\bullet}{S}O \;+\; (CH_3)_2CHOD \longrightarrow CH_3SOH \;+\; (CH_3)_2\underset{\bullet}{C}\text{-}OD$$

similar to that proposed for certain photochemical benzophenone-isopropyl alcohol reactions (6) seems to be rather unlikely at the present stage of investigation. Studies on the photolysis of DMSO in optically active alcohols such as 2-butanol are under way.

In acetonitrile as solvent, fragmentation of DMSO into radicals followed by hydrogen atom abstraction to yield methane and methanesulfenic acid is very probable the only pathway by which C-S bond cleavage is achieved, since during the benzene-sensitized DMSO photolysis in acetonitrile all methanesulfinyl radicals and most of the methyl radicals could be trapped by benzene (7). As in the other solvents, the hydrogens abstracted are only those of the solvent as was shown by the exclusive formation of CD_3H when DMSO-d_6 was photolyzed in CH_3CN.

Experimental: Low conversion (0,5 - 1 per cent) irradiations were performed in quartz vessels using a Srinivasan-Griffin Photochemical Reactor RPR 100 equipped with 16 Hg-low pressure vycor lamps (2537 Å). Methane was analyzed gas chromatographically after being pumped off by a Toepler-pump at 77°K. Deuterium distribution in methane and undecomposed DMSO was determined by means of mass spectroscopy.

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References

1. K. Gollnick and H.U. Stracke, *Tetrahedron Letters*, preceding paper.
2. A.F. Trotman-Dickenson and G.S. Milne, *Tables of Bimolecular Gas Reactions*, NSRDS-NBS 9, US Gov.Print. Off. **1967**, VI, p. 49.
3. H.U. Stracke, P. Potzinger, and K. Gollnick, unpublished results.
4. S. Oae, *Quart.Rep.Sulfur Chem.*, **5**, 53 (1970).
5. W.S. MacGregor, *Quart.Rep.Sulfur Chem.*, **3**, 149 (1968).
6. J.N. Pitts, Jr., R. Letsinger, R. Taylor, S. Patterson, G. Recktenwald, and R. Martin, *J.Am.Chem.Soc.*, **81**, 1068 (1959).
7. K. Gollnick and H.U. Stracke, unpublished results.