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PHOTOLYSIS OF DIMETHYL SULFOXIDE IN WATER AND ACETONITRILE. PRODUCT ANALYSIS.

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Despite the fundamental importance of organic sulfoxides as sulfur analogues of ketones, rather little is known of their photochemistry (1). Irradiation of neat dimethyl sulfoxide (DMSO) is reported to yield CO, methane and ethane (2), whereas trimethylsulfonium methanesulfonate is found if the irradiation is carried out in the presence of iodine (3). Sulfinyl radicals thought to be rather stable intermediates during certain C-S bond cleavage reactions have as yet not been detected or trapped (1).

We irradiated (Srinivasan-Griffin-Reactor, λ_{exc} = 2537 Å) DMSO in water ($\varepsilon_{2537} = 0{,}1\ \underline{M}^{-1}\ cm^{-1}$) as well as in acetonitrile ($\varepsilon_{2537} = 0{,}2\ \underline{M}^{-1}\ cm^{-1}$) and observed the formation of methane, methanesulfonic acid, dimethyl sulfide, dimethyl sulfone, methyl methanethiolsulfonate, and dimethyl disulfide. Table 1 shows the results in 10^{-6} mole units.

Table 1: Irradiation of DMSO (2 $\underline{M}$) in Water and Acetonitrile.
Products and Product Distribution in 10^{-6} Moles*).

Products / Solvent	CH_4	CH_3SO_3H	CH_3SCH_3	$CH_3SO_2CH_3$	$CH_3SO_2SCH_3$	CH_3SSCH_3
Water	190	110	90	60	10	30
Acetonitrile	170	65	110	20	traces	55

*) λ_{exc} = 2537 Å, Irradiation of $4 \cdot 10^{-2}$ moles DMSO/20 ml solvent for one (in acetonitrile) or two (in water) hrs. after oxygen was removed by conventional freeze-pump-thaw procedures at 77°K on a mercury-free vacuum system.

Assuming methane and methanesulfinic acid to be the primary stable products of the photolysis of DMSO in water, and methane and methanesulfenic acid to be the primary stable products of DMSO photolysis in acetonitrile (see subsequent paper, ref. 4) according to reactions 1) and 6) (see below), the products and material balances can be accounted for by the following reaction sequences. With the exception of reactions 1) and 6) the reactions are known from the literature (5-10). The material balances below the reaction equations are given in 10^{-6} mole units.

Photolysis of DMSO in Water:

$$\begin{array}{llclcllclcl}
1) & CH_3SOCH_3 & + & H_2O & \xrightarrow{+h\nu} & CH_4 & + & CH_3SO_2H & & & \\
 & 190 & & & & 190 & & 190 & & & \\
2) & 2\ CH_3SOCH_3 & & & \xrightarrow{+h\nu} & CH_3SO_2CH_3 & + & CH_3SCH_3 & & & \\
 & 120 & & & & 60 & & 60 & & & \\
3) & CH_3SO_2H & + & CH_3SOCH_3 & \longrightarrow & CH_3SO_3H & + & CH_3SCH_3 & & & \\
 & 30 & & 30 & & 30 & & 30 & & & \\
4) & 5\ CH_3SO_2H & & & \longrightarrow & 3\ CH_3SO_3H & + & CH_3SSCH_3 & + & H_2O \\
 & 130 & & & & 80 & & 26 & & & \\
5) & 3\ CH_3SO_2H & & & \longrightarrow & CH_3SO_3H & + & CH_3SO_2SCH_3 & + & H_2O \\
 & 30 & & & & 10 & & 10 & & &
\end{array}$$

with reaction 4) being the overall reaction of the sequence

$$\begin{array}{llclcllclcl}
4a) & 3\ CH_3SO_2H & & & \longrightarrow & CH_3SO_2SCH_3 & + & CH_3SO_3H & + & H_2O \\
4b) & 5\ CH_3SO_2SCH_3 & + & 2\ H_2O & \longrightarrow & 3\ CH_3SSCH_3 & + & 4\ CH_3SO_3H & & &
\end{array}$$

and assuming that most of the methyl methanethiolsulfonate is hydrolyzed under the conditions employed.

Photolysis of DMSO in Acetonitrile:

Since the material balance does not allow to decide whether the methanesulfenic acid is more easily oxidized or decomposed according to reaction 9), two alternatives are given below with reactions 8a) - 10a) in case that CH_3SOH is more easily oxidized, and with reactions 8b) - 10b) in case that methanesulfenic acid decomposes more easily.

6) $\underset{170}{CH_3SOCH_3} \xrightarrow[CH_3CN]{+\,h\nu} \underset{170}{CH_4} + \underset{170}{CH_3SOH}$

7) $2\ \underset{40}{CH_3SOCH_3} \xrightarrow{+\,h\nu} \underset{20}{CH_3SO_2CH_3} + \underset{20}{CH_3SCH_3}$

8a) $\underset{90}{CH_3SOH} + \underset{90}{CH_3SOCH_3} \longrightarrow \underset{90}{CH_3SO_2H} + \underset{90}{CH_3SCH_3}$

9a) $5\ \underset{80}{CH_3SOH} \longrightarrow \underset{16}{CH_3SO_3H} + 2\ \underset{32}{CH_3SSCH_3} + 2\ H_2O$

10a) $5\ \underset{90}{CH_3SO_2H} \longrightarrow 3\ \underset{54}{CH_3SO_3H} + \underset{18}{CH_3SSCH_3} + H_2O$

or

8b) $\underset{45}{CH_3SOH} + \underset{45}{CH_3SOCH_3} \longrightarrow \underset{45}{CH_3SO_2H} + \underset{45}{CH_3SCH_3}$

9b) $5\ \underset{125}{CH_3SOH} \longrightarrow \underset{25}{CH_3SO_3H} + 2\ \underset{50}{CH_3SSCH_3} + H_2O$

10b) $\underset{45}{CH_3SO_2H} + \underset{45}{CH_3SOCH_3} \longrightarrow \underset{45}{CH_3SO_3H} + \underset{45}{CH_3SCH_3}$

with reaction 9) being the overall reaction of the sequence

9c) $2\ CH_3SOH \longrightarrow CH_3SOSCH_3 + H_2O$

9d) $2\ CH_3SOSCH_3 \longrightarrow CH_3SO_2SCH_3 + CH_3SSCH_3$

9e) $5\ CH_3SO_2SCH_3 + 2\ H_2O \longrightarrow 4\ CH_3SO_3H + 3\ CH_3SSCH_3$

and again assuming that the methyl methanethiolsulfonate produced in the overall reactions 9) and 10a) (= reaction 4)) is hydrolyzed under the reaction conditions.

Preliminary quantum yield determinations of methane and dimethyl sulfone formation resulted in $\Phi(CH_4) \approx 0.2$ and $\Phi(CH_3SO_2CH_3) \approx 0.02 - 0.06$, respectively, for both solvents. The similarity (or even equality) of $\Phi(CH_4)$ for both solvents seems to be noteworthy, since the primary photochemical processes involved in reactions 1) and 6) occur with all probability via different pathways (4).

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). Product analysis was achieved gas chromatographically in the case of dimethyl sulfide, dimethyl sulfone, dimethyl disulfide, and methane; in the latter case methane was pumped off by a Toepler-pump at 77°K before analysis. Methyl methanethiolsulfonate was identified by IR-analysis after preparative thin layer chromatography on silica gel. Methanesulfonic acid was determined by potentiometric titration against 0,01 N sodium hydroxide after identification as p-toluidinium salt. When water is used as solvent, dimethyl sulfide, dimethyl sulfone, dimethyl disulfide, and methyl methanethiolsulfonate were extracted by carbon tetrachloride before analysis. Uranyl oxalate actinometry was performed for quantum yield determinations.

References

1. E. Block, The Photochemistry of Organic Sulfur Compounds, Quart.Rep.Sulfur Chem., 4, 237 (1969).
2. L. Horner and J. Dorges, Tetrahedron Letters, 1963, 757.
3. N. Kharasch and G.O. Lowe, reported by ref. 1.
4. K. Gollnick and H.U. Stracke, Tetrahedron Letters, subsequent paper.
5. R.A. Archer and B.S. Kitchell, J.Am.Chem.Soc., 88, 3462 (1966).
6. C.T. Chen and S.J. Yan, Tetrahedron Letters, 1969, 3855.
7. L. Bauer and J. Cymerman, J.Chem.Soc. (London), 1959, 109.
8. J.L. Kice and K.W. Bowers, J.Am.Chem.Soc., 84, 2384 (1962).
9. N. Kharasch, Sulfenium Ions and Sulfenyl Compounds, in N. Kharasch, Ed., Organic Sulfur Compounds, Pergamon Press, Oxford, 1961, Vol. 1, chapter 32.
10. W.E. Savige and J.A. Maclaren, Oxidation of Disulfides, with Special Reference to Cystine, in N. Kharasch and C.Y. Meyers, The Chemistry of Organic Sulfur Compounds, Pergamon Press, Oxford, 1966, Vol. 2, chapter 15.