

ISOTOPE EFFECTS IN THE PHOTOLYSIS OF METHANETHIOL

DEEPIKA KAMRA* and J. M. WHITE

Department of Chemistry, University of Texas, Austin, Texas 78712 (U.S.A.)

(Received December 17, 1976; in revised form February 18, 1977)

Summary

Quantum yields for the formation of hydrogen and methane in the photolysis of partially deuterated methanethiol (CH_3SD) have been measured at 185 and 254 nm. The sum of the quantum yields of these two products is unity, independent of thiol pressure, at both wavelengths. Adding n-butane or perfluorodimethylcyclobutane causes an increase in the hydrogen quantum yield, a decrease in the methane quantum yield, but no change in the sum of the two. These results are interpreted in terms of a hot atom mechanism involving cleavage of the C—S and S—D bonds in the parent molecule. Compared with earlier work using CH_3SH , replacing H by D causes a significant increase in the probability of C—S cleavage suggesting that the photodissociation process is strongly influenced by the masses of the two species attached to the central sulfur atom.

Introduction

As an extension of our previous work [1 - 3] on the photochemistry of CH_3SH , we report here studies of the primary photodissociation processes which occur in a partially deuterated methanethiol, CH_3SD . Our goal has been to examine the product distribution and compare it with that obtained from the photolysis of CH_3SH .

Our earlier work has emphasized the importance of hot atoms produced by photodissociation and variations in product distribution with excitation wavelength. These same features are explored in this paper by examining data at two excitation wavelengths and data taken in the presence of thermalizing gases. Quantum yields of hydrogen and methane are reported for all these conditions. In earlier work Inaba and Darwent [4] studied the isotopic distribution of hydrogens and methanes obtained by photolysis of CH_3SD and concluded that H atoms in CH_3 were not involved in abstraction reactions.

*Present address: Jarvis Christian College, Hawkins, Texas, U.S.A.

Experimental

All experiments were performed at room temperature (298 ± 3 K) using gas phase materials. The mercury-free high vacuum system and the reaction vessel have been described earlier [1].

The light source for both 185 and 254 nm light was a low pressure Hg resonance lamp. The 185 line was isolated with the use of gamma irradiated LiF discs as described earlier [1]. The 254 nm line was isolated with the use of a Corning 7910 Vycor filter which has an effective cut-off at about 220 nm. Photolysis times were chosen so that less than 1% of the reactant was decomposed. The reagents, CH_3SD , HBr, HI, H_2S , n-butane and perfluorodimethylcyclobutane (PFDMCB), were all thoroughly degassed before use by a number of thaw-freeze-pump cycles. An IR spectrum of CH_3SD showed the sample to be 90% labelled.

After photolysis the total hydrogen and methane quantum yields were determined using mass spectrometry and both HBr (185 nm) and HI (254 nm) actinometry [1, 2]. The extinction coefficients for H_2S , HBr, HI and CH_3SD were determined using a Cary Model-14 spectrophotometer. The values used are listed in Table 1. The values reported for H_2S , HBr and HI are in good agreement with the literature [5 - 7].

Since extinction coefficients at 185 nm were difficult to determine on our spectrophotometer, the extinction of CH_3SD at 185 nm was determined in an alternative manner. Assuming the extinction coefficient of HBr at 185 nm, CH_3SD was used as a filter in the first compartment of a two compartment cell, while HBr was used in the second compartment. Yields of H_2 in the second compartment (HBr) were determined with and without CH_3SD in the first compartment. From these data the extinction coefficient can be determined once the cell pressure and length are known. The result, in good agreement with the value determined using the spectrophotometer, is given in Table 1. The extinction coefficient of H_2S was determined in the same way.

Results

Figure 1 summarizes the quantum yields for hydrogen components ($\text{H}_2 + \text{HD} + \text{D}_2$) and methane components ($\text{CH}_4 + \text{CH}_3\text{D}$) over a range of methanethiol-d pressures at 185 and 254 nm respectively. At both wavelengths the quantum yields of hydrogen and methane show no dependence on the substrate pressure. The sum of the quantum yields of hydrogen and methane components add to unity within experimental error at both wavelengths: 0.96 ± 0.04 at 254 nm and 1.03 ± 0.07 at 185 nm. Comparing the present results for the quantum yields of hydrogen and methane at 185 nm ($\phi(\text{H}_2) = 0.507 \pm 0.025$, $\phi(\text{CH}_4) = 0.523 \pm 0.060$) with those reported earlier for CH_3SH at 185 nm [1] ($\phi(\text{CH}_2) = 0.70 \pm 0.03$, $\phi(\text{CH}_4) = 0.28 \pm 0.02$), it is observed that the yield of hydrogen drops by about 0.2 while the yield of

TABLE 1
Extinction coefficients

Molecule	ϵ (Torr ⁻¹ cm ⁻¹) at 185 nm		ϵ (Torr ⁻¹ cm ⁻¹) at 254 nm
	From absorption spectrum	From photolysis data	
CH ₃ SD	$6.18 \pm 0.04 \times 10^{-2}$	6.13×10^{-2}	$1.97 \pm 0.03 \times 10^{-3}$
HBr	$3.37 \pm 0.02 \times 10^{-2}$	—	—
HI	—	—	$5.82 \pm 0.02 \times 10^{-3}$
H ₂ S	3.76×10^{-2} *	3.60×10^{-2}	—

*Reference 5.

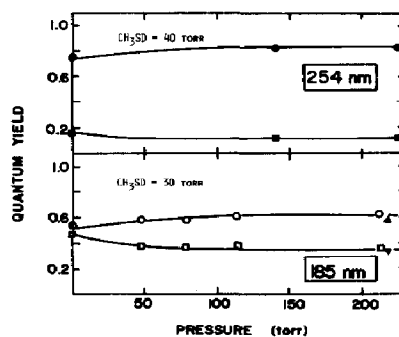
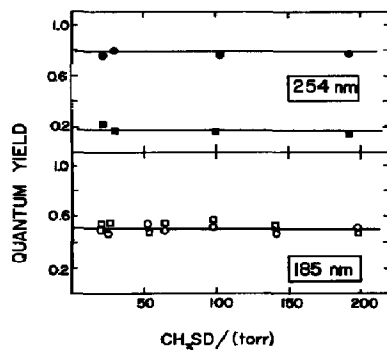


Fig. 1. Quantum yields of hydrogen and methane produced in the photolysis of CH₃SD at 254 and 185 nm. Circles denote hydrogen and squares denote methane.

Fig. 2. Quantum yields of hydrogen and methane as a function of thermalizer pressure. At 254 nm the CH₃SD pressure was fixed at 40 Torr and PFDMCB was used as the thermalizer. At 185 nm the CH₃SD pressure was fixed at 30 Torr and n-butane was used as the thermalizer except for one experiment, denoted by triangles, which was done with PFDMCB. Circles denote hydrogen and squares denote methane.

methane goes up by a similar amount. Comparing the present results at 254 nm ($\phi(\text{CH}_2) = 0.78 \pm 0.019$, $\phi(\text{CH}_4) = 0.18 \pm 0.018$) with those for CH₃SH reported by Bridges and White [3] ($\phi(\text{CH}_2) = 0.83 \pm 0.03$, $\phi(\text{CH}_4) = 0.16 \pm 0.03$) the yield of hydrogen is again noticed to drop, though only by 0.05, while the yield of methane goes up by only 0.02.

Two long-time photolyses were done for CH₃SD at 60 and 55 Torr of initial thiol pressure for 16 and 45 h respectively. Here, as noted earlier [1], a pale yellow residue was noticed which reacts with oxygen to form SO₂. These deposits are believed to be condensed thioformaldehyde as discussed below.

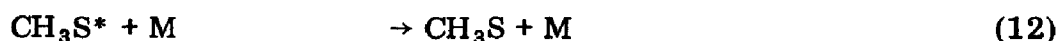
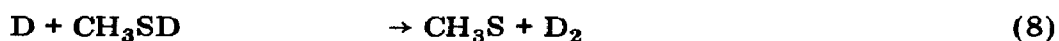
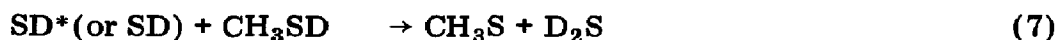
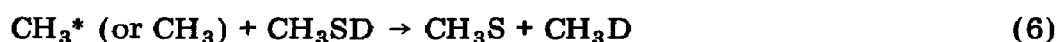
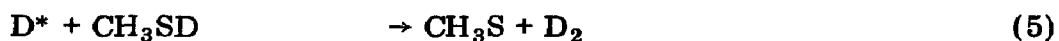
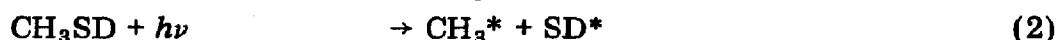
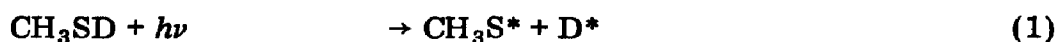
In order to evaluate the role played by translationally excited atoms and other free radicals CH₃SD was photolyzed with different pressures of added n-butane as a thermalizer. Figure 2 summarizes the results obtained from the photolysis of CH₃SD–n-butane mixtures at 185 nm. Per cent decomposition of the thiol was kept below 1%. A blank run at 185 nm using

182 Torr of n-butane gave no products and ruled out the possibility that any extra hydrogen was produced by the direct photolysis of butane. Bridges and White [2] have shown that the quantum yield of H_2 produced in the photolysis of a 5:1 mixture of n-butane and HI was not different from $\phi(H_2)$ for pure HI, which rules out the possibility that extra hydrogen was produced as the result of the reactions of butyl radicals which arise upon abstraction of H by hot hydrogen atoms. Our results show that upon butane addition the yield of hydrogen goes up with an accompanying decrease in the methane yield. One photolysis with added PFDMCB at high pressure was also done and is shown in Fig. 2. It is noticed that here, as in the case of the CH_3SH results [1], PFDMCB is apparently not quite as effective a thermalizer as n-butane. An important observation from these data is that the total quantum yield remains constant as the pressure of the thermalizer is increased.

Figure 2 also summarizes the results from the photolysis of CH_3SD -PFDMCB mixtures at 254 nm. The observations are similar to the 185 nm results given above.

Discussion

Comparing the above results with those of CH_3SH photolysis at 185 nm [1] and 254 nm [3], it is observed that the products of CH_3SD photolysis, hydrogen and methane, have qualitatively similar characteristics. This suggests that basically similar mechanisms are involved. Considering all the above observations, the following mechanism is suggested for CH_3SD photolysis at 185 and 254 nm.



M is taken to be CH_3SD , C_4H_{10} and/or PFDMCB. The species bearing asterisks represent energetic non-Boltzmann species. A steady state analysis of the proposed mechanism furnishes the following relations:

TABLE 2
Quantum efficiencies of primary processes

Molecule	λ (nm)	ϕ_1	ϕ_2
CH ₃ SH	185	0.79	0.21
CH ₃ SH	254	0.93	0.07
CH ₃ SD	185	0.62	0.38
CH ₃ SD	254	0.81	0.19

$$\phi(\text{D}_2) = \frac{k_5[\text{CH}_3\text{SD}] + k_9[\text{M}]}{(k_4 + k_5)[\text{CH}_3\text{SD}] + k_9[\text{M}]} \phi_1 \quad (14)$$

$$\phi(\text{CH}_3\text{D}) = \phi_2 + \frac{k_9[\text{CH}_3\text{SD}]}{(k_4 + k_5)[\text{CH}_3\text{SD}] + k_9[\text{M}]} \phi_1 \quad (15)$$

$$\phi(\text{D}_2) + \phi(\text{CH}_3\text{D}) = \phi_1 + \phi_2 = 1 \quad (16)$$

where the subscripted symbols refer to the reactions in the mechanism and ϕ denotes quantum yields.

In these expressions ϕ_1 and ϕ_2 are the quantum efficiencies of reactions (1) and (2) respectively. The values for ϕ_1 and ϕ_2 can be estimated by using eqns. (14) and (16) and the data from Fig. 2. Equation (14) predicts that the hydrogen quantum yield approaches ϕ_1 when M is large (M other than CH₃SD). Figure 2 suggests that ϕ_1 is 0.62 and 0.81 for 185 and 254 nm respectively. Using these values and eqn. (16), by difference we can estimate that ϕ_2 is 0.38 and 0.19 at 185 and 254 nm respectively. These values and the values of ϕ_1 and ϕ_2 for CH₃SH photolysis at 185 nm [1] and 254 nm [3] are given in Table 2.

When samples were photolyzed for extended periods, a yellow deposit appeared at the walls of the reaction vessel. This material is believed to be polymeric thioformaldehyde formed by the photolysis of dimethyl disulfide which is known to have a large extinction coefficient [8] and which produces CH₂S when photolyzed [9]. The decomposition of excited CH₃S radicals to form thioformaldehyde and a hydrogen atom may also occur to some extent in our system. However, the quantum yield must not be very high, otherwise we should observe a total quantum yield (methane plus hydrogen) greater than unity. The concerted photoelimination of H₂ and CH₂S is not significant according to the flash photolysis work of Collear and Dickson [9].

The most interesting feature of the results reported here is the large change, at 185 nm, in the ratio of C—S to S—H bond cleavage which occurs when CH₃SH is replaced by CH₃SD in the photolysis. The shift can be understood in terms of a model which focuses on the repulsive character of the excited state that is populated upon photon absorption and along which photodissociation occurs. The absorption spectrum of methanethiol [1] shows

no structure in the range 185 - 254 nm which is attributable to bound states. It is also clear that different excited states are involved at these two wavelengths [10].

Excitation of either CH_3SH or CH_3SD will lead to very nearly the same region of the excited state potential energy surface. Significant repulsive character must exist along both the C—S and S—H directions of this surface in order for both cleavages to occur with significant probability. On such a surface the effect of replacing SH with SD is to be found by considering the dynamics of the dissociative trajectories, since the shape of the surface does not change. In simplest terms, an H atom can be accelerated much more readily than either a D or CH_3 group. The determining features in such dynamical arguments are the masses of the particles being accelerated and the steepness of the potential energy surface in the region of the excitation. A dissociation involving a steep surface and a light atom will predominate over a steep surface and a heavy fragment because the light fragment can move to regions of lower potential energy more rapidly. Doubling the mass of the light atom will make the heavy fragment more competitive. This model will account for our observations at 185 nm.

As the repulsiveness of the surface decreases in the region populated by absorption, the relative importance of the masses of the particles involved may be overshadowed by differences in the slope of the surface along the S—H and C—S directions. This is apparently the case at 254 nm.

Acknowledgment

This work was supported by the Robert A. Welch Foundation.

References

- 1 D. Kamra and J. M. White, *J. Photochem.*, 4 (1975) 361.
- 2 L. Bridges, G. L. Hemphill and J. M. White, *J. Phys. Chem.*, 76 (1972) 2668.
- 3 L. Bridges and J. M. White, *J. Phys. Chem.*, 77 (1973) 295.
- 4 T. Inaba and B. deB. Darwent, *J. Phys. Chem.*, 64 (1960) 1413.
- 5 L. E. Compton, J. L. Gole and R. M. Martin, *J. Phys. Chem.*, 73 (1969) 1158.
- 6 C. F. Goodeve and N. O. Stein, *Trans. Faraday Soc.*, 27 (1931) 393.
- 7 B. J. Huebert and R. M. Martin, *J. Phys. Chem.*, 72 (1968) 3046.
- 8 J. G. Calvert and J. N. Pitts, Jr., *Photochemistry*, Wiley-Interscience, New York, 1966, p. 491.
- 9 A. B. Callear and D. R. Dickson, *Trans. Faraday Soc.*, 66 (1970) 1987.
- 10 L. B. Clark and W. T. Simpson, *J. Chem. Phys.*, 43 (1965) 3666.