ON THE PHOTOLYSIS OF METHANETHIOL AND ETHANETHIOL AT 185 nm*

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Summary

Quantum yields for the formation of hydrogen and methane in the photolysis of methanethiol at 185 nm are 0.70 ± 0.03 and 0.26 ± 0.02, respectively. At the same wavelength ethanethiol gives quantum yields of 0.62 ± 0.01, 0.30 ± 0.01, and 0.07 ± 0.01 for hydrogen, ethane, and ethylene respectively. In both cases the sum of these quantum yields is unity, independent of thiol pressure. The data are treated in terms of a mechanism which also accounts for earlier work at 254 and 214 nm. Hot hydrogen atom reactions are invoked as a result of thermalization effects observed when n-butane or perfluorodimethylcyclobutane is mixed with the thiol. Decreases, with increasing photon energy, in the ratio of S–H to C–S bond cleavage are noted and correlated with earlier work on the spectra and molecular orbitals of the parent compounds. Satisfactory correlations are also noted between the average energy of the photochemically produced hydrogen atoms and the fraction of these atoms which undergo energy sensitive reactions.

Introduction

In conjunction with investigations of energy partition in the photo-dissociation of thiols [1] and the photochemistry of thiols [2, 3] we have studied in detail the photolysis of methanethiol and ethanethiol at 185 nm. This wavelength was selected because: (1) it was used in energy partition experiments; (2) the absorption spectrum of CH_3SH suggests that a different electronic state may be involved than at longer wavelengths [2, 3]; (3) the effect of higher energy radiation may lead to interesting kinetics not observed at lower energies; and (4) no quantum yield data are yet available at 185 nm.

Steer and Knight [4] have reported a detailed investigation of the photolysis of CH_3SH at 254 nm. They reported a pressure dependent

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quantum yield of hydrogen with a value of 1.0 ± 0.05 when extrapolated to zero pressure of methanethiol. They concluded that the only important primary process was the scission of the S–H bond. However, later Bridges and White [3] studied the photolysis at 254 and 214 nm and showed that the quantum yield of hydrogen was pressure independent, wavelength dependent, and less than unity. They based their interpretation on both C–S and S–H bond ruptures in the primary photolysis step. Callear and Dickson [5] in a flash photolysis study at ~ 195 nm reported the same two primary processes with the ratio of C–S to S–H bond cleavage being 1:1.7. The wavelength dependence on quantum yields is further demonstrated by Sturm [6] who, in a short set of photolysis at various wavelengths, showed that the ratio $[CH_4]/[H_2]$ increases sharply from 254 to 185 nm.

Steer and Knight [7] have also studied the photochemistry of ethane-thiol at 254 nm concluding that S–H bond rupture is the major primary process with a quantum yield near unity. In a comparable study Dzantiev *et al.* [8] found C–S bond rupture occurred with a quantum yield of about 0.1. Bridges *et al.* [2] have reported hydrogen, ethane, hydrogen sulfide, and ethylene quantum yields occurring in the photolysis of C_2H_5SH at 254 and 214 nm. On the basis of these measurements, they concluded that both C–S and S–H bond rupture were significant primary processes which were wavelength dependent as in the case of CH_3SH.

In this paper we report experimentally determined product quantum yields arising from the photolysis of CH_3SH and C_2H_5SH at 185 nm. The pressure dependence and thermalizer dependence of these quantum yields is examined and the data are discussed in terms of a mechanism which includes both hot atom and thermal atom reactions. The important primary processes include C–S and S–H cleavage; in addition there is some evidence that molecular elimination of H_2 occurs.

Experimental

All experiments were performed at room temperature (298 ± 3 K) using gas phase materials. The reaction cell (5 cm diameter and 15 cm long) was constructed of fused quartz with Suprasil windows. The cell was filled on a standard mercury-free vacuum line pumped by an oil diffusion pump to base pressures near 1×10^{-6} Torr. This vacuum line was separated from a mercury manometer by means of a magnetic reluctance pressure trans-ducer. Reagent pressures were measured with the manometer by nulling the transducer. The light source was a low-pressure Hg resonance lamp. ^{60}Co gamma-irradiated lithium fluoride discs [9] (25 mm diameter by 2 mm thick) were used with the Hg lamp to filter the 2537 Å line or 254 nm. Considerable care must be exercised in the use of these filters because the radiation-induced color centers which filter 254 nm are bleached by expo-sure to ultra-violet light. Regular monitoring of the optical density is there-fore necessary in order to avoid systematic quantum yield errors.

Methanethiol was purified by degassing and distilling twice under

vacuum from −98 °C (methanol slush) to −117 °C (ethanol slush). The middle third was retained and stored in a U-tube at −196 °C. Ethanethiol was purified in a similar way except the distillation was from −84 °C (ethyl acetate slush) to −117 °C (ethanol slush). Thiol purity was monitored with a residual gas analyzer. Reagent grade hydrogen bromide, butane, and perfluorodimethylcyclobutane (PFDMCB) were thoroughly degassed before use.

After photolysis the reaction vessel was immersed in liquid nitrogen, connected to a Toepler pump, and the non-condensable gases were pumped into a calibrated volume ($V = 5.14 \pm 0.06$ cm^3). The pressure was measured on a mercury manometer with a cathetometer (uncertainty ± 0.04 Torr). This sample was then analyzed on a calibrated CEC 21-614 residual gas analyzer. A trap at −78 °C was placed between the reaction vessel and the Toepler pump to eliminate any mercury transfer. Only these non-condensables were analyzed in the case of methanethiol since H_2 and CH_4 were the products of interest. In the case of ethanethiol, however, it was necessary to replace the liquid nitrogen bath with an ethanol slush (−117 °C) in order to remove the ethane from the parent material. In this distillation ethylene and most of the hydrogen sulfide were also removed and analyzed.

The actinometry using the production of H_2 from the photolysis of HBr was done as by Bridges and White [3]. Extinction coefficients for CH_3SH, C_2H_5SH and HBr were determined using a Cary-14 spectrometer. The values used are listed in Table 1. The values reported are in good agreement with the literature [10]. The photolysis times were chosen so that the decomposition of thiol was less than 1% in order to minimize errors in the quantum yield of the products.

TABLE 1

Extinction coefficients (Torr^{-1} cm^{-1})

Molecule	ϵ (Torr^{-1} cm^{-1}) at 185 nm
CH_3SH	5.60×10^{-2}
C_2H_5SH	1.25×10^{-1}
HBr	3.37×10^{-2}

Results

Photolysis of pure methanethiol

The products non-condensable at −196 °C, hydrogen and methane, were measured mass spectrometrically. Figure 1 gives the yields of hydrogen and methane over a range of methanethiol pressures and shows that the quantum yields of hydrogen (0.70 ± 0.03) and methane (0.26 ± 0.02) are independent of substrate pressure. The sum of quantum yields of hydrogen and methane is unity, within experimental error. Compared to the results [3]
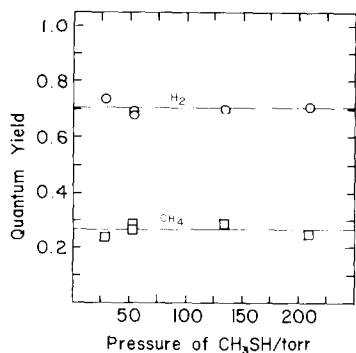
Fig. 1. Hydrogen (○) and methane (□) quantum yields as a function of CH_3SH pressure for photolysis at 185 nm.

TABLE 2

Effect of time of exposure on the quantum yields of products

P_{CH_3SH} (Torr)	t (s)	Φ_{H_2}	Φ_{CH_4}
47	600	0.71	0.26
47	1200	0.72	0.25
46	1800	0.69	0.26
44	3600	0.68	0.26

TABLE 3

Quantum yields for methanethiol photolysis

λ (nm)	Φ_{H_2}	Φ_{CH_4}
254	0.83 ± 0.03	0.16 ± 0.03
214	0.66 ± 0.03	0.35 ± 0.03
185	0.70 ± 0.03	0.26 ± 0.02

of photolyses at 254 nm (Φ_{H_2} = 0.83 ± 0.03, Φ_{CH_4} = 0.16 ± 0.3) we note that Φ_{H_2} is lower by about 0.1 while the quantum yield of methane is higher by a similar amount. These 185 nm results are similar to the 214 nm results of Bridges and White [3] which gave Φ_{H_2} = 0.66 ± 0.03 and Φ_{CH_4} = 0.35 ± 0.03. Table 3 summarizes these data.

In order to test for the possible influence of products on the quantum yields, CH_3SH was photolyzed at 185 nm for varying times from 600 to 3600 s. The results are given in Table 2 and clearly show that there is no effect on the final quantum yield by any of the products formed. A typical time for the photolyses reported in Fig. 1 was 1500 s.

A photolysis of 60 Torr of CH_3SH at 185 nm was done for 20 h and a pale yellow residue was formed around the face and sides of the cell. The

deposit was heaviest on the face and decreased along the length of the cell. The cell was evacuated, filled with about 200 Torr of O_2 and heated until all the residue disappeared. The condensable products were frozen to -196 °C and the cell evacuated. The mass spectrum and the u.v. spectrum of the products showed that SO_2 was present. It is well known [11] that sulfur readily oxidizes in the presence of oxygen to give SO_2. We take this deposit to be either elemental sulfur and/or thioformaldehyde [12]. A similar experiment was performed using 254 nm light. To get an equivalent number of absorbed photons, as for the above case at 185 nm, a time of 2 h was required. In fact, our photolysis at 254 nm was done for 3 h (thus a larger percentage decomposition than at 185 nm) and no deposits were noticed. The deposit is thus characteristic for the 185 nm radiation only. While this experiment offers some guidance in constructing a suitable mechanism for the reaction, caution must be exercised in its interpretation since photolysis of product molecules contribute to the observed residue. This is discussed in detail later.

Photolysis of methanethiol–thermalizer mixtures
    To evaluate the role played by excited atoms and other free radicals, we conducted a series of photolyses with n-butane as an added thermalizer. A blank run at 185 nm using 182 Torr of n-butane gave no products and ruled out the possibility of any extra hydrogen being produced by the direct photolysis of butane. Bridges and White [2] have also 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 Φ_{H_2} for pure HI, which rules out the possibility of extra hydrogen produced by reactions of hot hydrogen atoms with the butane. Figure 2 summarizes the results obtained using CH_3SH at 32 ± 2 Torr. As previously noted [3] there is an enhancement of the hydrogen yield and a compensating decline in the methane yield such that the total yield of methane and hydrogen remains unity independent of butane pressure.
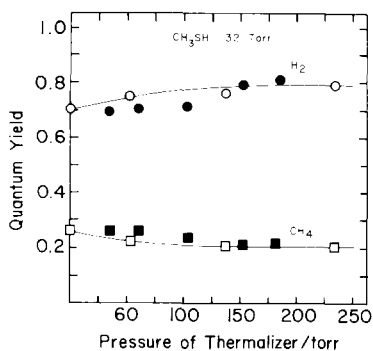

Fig. 2. The effect of n-butane (open symbols) and perfluorodimethylcyclobutane (filled symbols) on the hydrogen (circles) and methane (squares) quantum yields. The photolysis was at 185 nm and 32 ± 2 Torr of methanethiol was used.

As further check, we conducted a series of photolyses using perfluoro-dimethylcyclobutane (PFDMCB) as a thermalizer. Here the possibility of any H_2 production *via* the thermalizer is completely ruled out. Figure 2 summarizes the results obtained with PFDMCB as the thermalizer. In this case also we notice an increase in the quantum yield of hydrogen and a decrease in the quantum yield of methane. Comparing PFDMCB with n-butane we note that the former is not as effective. This point is considered in the discussion.

The significant feature of the results from both thermalizers is that the sum, $\Phi_{H_2} + \Phi_{CH_4}$ remains constant (1.00 ± 0.1) as the pressure of thermalizer is increased. The individual yields change by as much as 20% and show systematic trends with thermalizer pressure but the sum remains invariant to within less than 10%. This suggests two things: (1) hot atom reactions are important; and (2) secondary decomposition of excited radicals or molecules is not an important contributor to Φ_{CH_4} and Φ_{H_2} since these should be quenched by added thermalizer and thus reduce the total quantum yield.

Photolysis of ethanethiol
As expected the results with C_2H_5SH follow very closely the data for CH_3SH. Figures 3 and 4 summarize the quantum yields as a function of thiol pressure and as a function of thermalizer pressure. Ethylene, which is not a product of CH_3SH photolysis, appears in low yield in the C_2H_5SH case. It was also possible to measure H_2S yields from ethanethiol. Again, for the pure thiol case, the quantum yields are pressure independent suggesting that secondary reactions producing H and C_2H_5 are not important unless they themselves involve either H or C_2H_5 as a reactant. Averages of the quantum yields reported in Fig. 3 are: $H_2 = 0.62 \pm 0.01$, $C_2H_6 = 0.30 \pm 0.01$, $C_2H_4 = 0.07 \pm 0.01$, and $H_2S = 0.16 \pm 0.17$. The large uncertainty associated with the H_2S is attributed to the difficulty of separating it from large quantities of C_2H_5SH in the distillation described in the experimental section and the fact that some parent compound transferred into the sample used for analysis.

The thermalizing effect of n-butane is plotted in Fig. 4. The yields of ethane and ethylene both decline, while the yield of hydrogen increases, as n-butane is added. The sum of the yields of hydrogen and ethane is systematically slightly less than unity over the full range of these pressures while the sum of the hydrogen, ethane, and ethylene quantum yields is nearer unity. However, the experimental uncertainties which we associate with these measurements do not permit an unambiguous decision on the matter.

The quantum yield of disulfide was estimated at 185 nm by photolyzing a sample of 90 Torr of C_2H_5SH and attributing the increased optical density in the 270 to 290 nm region to $C_2H_5SSC_2H_5$ [15]. The hydrogen pressure was measured and taken as $\Phi_{H_2} = 0.62$. The resulting ethanethiol quantum yield was 0.98.

Compared with earlier work at 254 and 214 nm [2] the present work shows a lower hydrogen quantum yield and higher ethane and ethylene yields. Table 4 summarizes the results for C_2H_5SH at all three wavelengths.
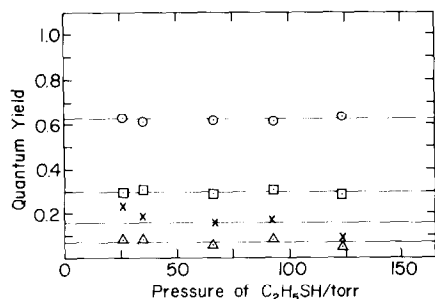
Fig. 3. Hydrogen ($\circ$), ethane ($\square$), hydrogen sulfide ($\times$), and ethylene ($\triangle$) quantum yields as a function of ethanethiol pressure for photolysis at 185 nm.
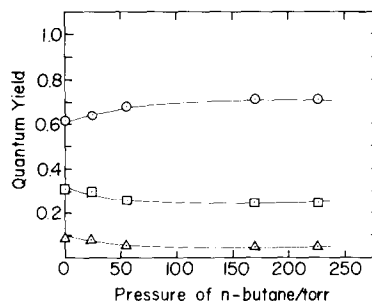
Fig. 4. Effect of n-butane pressure on hydrogen ($\circ$), ethane ($\square$), and ethylene ($\triangle$) quantum yields. The photolysis wavelength was 185 nm and the ethanethiol pressure was 35 ± 1 Torr.

TABLE 4

Quantum yields for ethanethiol photolysis

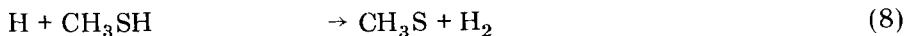| λ (nm)	Φ_{H_2}	$\Phi_{C_2H_6}$	$\Phi_{C_2H_4}$	Φ_{H_2S}
254	0.82 ± 0.02	0.16 ± 0.02	0.025 ± 0.006	0.19 ± 0.03
214	0.75 ± 0.03	0.28 ± 0.03	0.038 ± 0.004	0.28 ± 0.02
185	0.62 ± 0.01	0.30 ± 0.01	0.07 ± 0.01	0.16 ± 0.17

Other photolyses
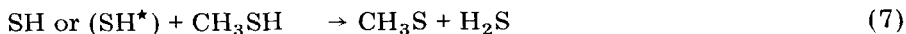
A photolysis of 90 Torr of H_2S was done at 185 nm to check our operational technique. The result for Φ_{H_2} was 0.93 in agreement with the literature values (1.00 ± 0.1) [13]. A photolysis of 25 Torr of CH_3SH was done at 254 nm and the value for the quantum yields of hydrogen and methane agreed with the result obtained previously in this laboratory [3]. In addition two photolyses of C_2H_5SH at 254 nm gave results in excellent agreement with earlier work [2].

Discussion

Methanethiol

The following mechanism is proposed as an explanation of the above results for methanethiol:

$$CH_3SH + h\nu \rightarrow CH_3S^\star + H^\star \tag{1}$$

$$CH_3SH + h\nu \rightarrow CH_3^\star + SH^\star \tag{2}$$

$$CH_3SH + h\nu \rightarrow CH_2S + H_2 \tag{3}$$

$$H^\star + CH_3SH \quad \rightarrow CH_3 + H_2S \text{ and/or}$$

$$(H^\star + CH_3SH \rightarrow CH_4 + SH) \tag{4}$$

$$H^* + CH_3SH \qquad\qquad \rightarrow CH_3S^* + H_2 \tag{5}$$

$$CH_3^* \text{ (or } CH_3) + CH_3SH \quad \rightarrow CH_3S + CH_4 \tag{6}$$

$$SH \text{ or } (SH^*) + CH_3SH \quad \rightarrow CH_3S + H_2S \tag{7}$$

$$H + CH_3SH \qquad\qquad \rightarrow CH_3S + H_2 \tag{8}$$

$$H^* + M \qquad\qquad \rightarrow H + M \tag{9}$$

$$CH_3^* + M \qquad\qquad \rightarrow CH_3 + M \tag{10}$$

$$CH_3S^* + M \qquad\qquad \rightarrow CH_3S + M \tag{11}$$

$$SH^* + M \qquad\qquad \rightarrow SH + M \tag{12}$$

$$CH_3S + CH_3S \qquad\qquad \rightarrow CH_3SSCH_3 \tag{13}$$
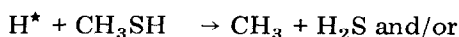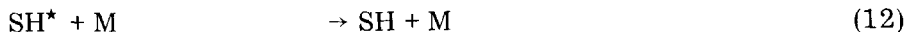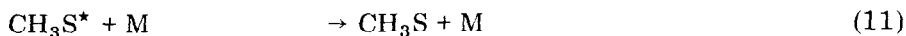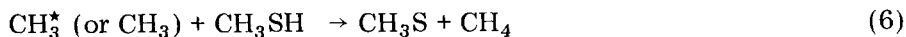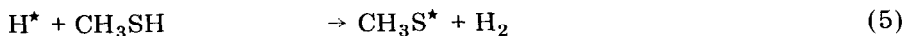
In this mechanism M is taken to include CH_3SH, C_4H_{10}, and/or PFDMCB. The symbols bearing asterisks represent energetic non-Boltzmann species.

The mechanism proposed for the photolysis at 185 nm is the same as that at 254 and 214 nm except for the addition of the primary step (3) [2, 3]. This step is included because it may account for the pale yellow deposit noticed after extended irradiation of CH_3SH and the observation of HD in the photolysis of CH_3SD [12]. There are, however, several pieces of experimental evidence suggesting that this process plays at most only a minor role. One of the most compelling is the observation of Callear and Dickson [5] that CH_2S appeared late in the period following the flash photolysis of CH_3SH with radiation, in the 180 - 200 nm region, which had an average wavelength of 195 nm. This means that thioformaldehyde is not an important primary product but arises as the result of secondary processes involving CH_3S radical–radical reactions. The production of CH_2S *via* recombination–disproportionation is supported by the work of Tycholiz and Knight [14] who investigated the mercury photosensitized photolysis of methyl sulfide, CH_3SCH_3, found low yields of CH_3SH and CH_3SSCH_3, and inferred that CH_3SH and CH_2S were formed by the disproportionation of CH_3S radicals. This disproportionation process has such a low yield (~ 0.04 of the recombination to form the disulfide) that it cannot account for the production of the pale yellow deposit at 185 nm in our long-term experiments. The photolysis of the disulfide product appears to be a more plausible explanation. Callear and Dickson [5] observed both S_2 and CH_2S spectra when they flashed CH_3SSCH_3. We find no evidence for sulfur or thioformaldehyde in our photolyses of CH_3SH at 254 nm but this is not inconsistent with our interpretation when account is taken of the much larger extinction of CH_3SSCH_3 at 185 nm than at 254 nm [15].

A second argument suggesting the relatively small contribution of process (3) comes from our experimental observation that no deposit built up at 185 nm during a series of short photolyses, each of which was followed by evacuation and refilling with CH_3SH. Any thioformaldehyde formed should have polymerized during the course of any given photolysis [16, 17], remained in the reaction vessel during the evacuation period, and built up to a visible amount after several hours of net photolysis time.

Finally, the observations of Bridges and White [3] at 214 nm, which are much like the 185 nm data insofar as quantum yields are concerned, suggest that process (3) is not predominant because the quantum yield of CH_3SSCH_3 is unity and a material balance requires $[H_2] + [CH_4] = [CH_3SSCH_3] + [CH_2S]$ if we use the above mechanism. Thus, since $\Phi_{H_2} + \Phi_{CH_4} = 1$, Φ_{CH_2S} must be quite small. A note of caution must be exercised, however, because the scatter in the disulfide yields is relatively large ($\pm$ 0.1).

In this context it should be pointed out that at 254 nm where the quantum yields of H_2 and CH_4 are considerably different, the yield of disulfide is also near unity [3]. Inaba and Darwent [18] found that D_2 was the only detectable product formed in the photolysis of CH_3SD at 254 nm which supports the notion that process (3) is unimportant. While our preliminary results with CH_3SD [12] suggest that some HD may be formed, the qualitative conclusions are the same.

The hydrogen atoms produced in reaction (1) are hot [1], and in the proposed mechanism can undergo reactions (4), (5) or (9). The reactions (4), (8) and (9) offer an explanation of the observed increase in $\Phi(H_2)$ and the decrease in $\Phi(CH_4)$ with added thermalizer, i.e., reaction (4) for thermal H atoms is insignificant compared with reaction (8), but becomes significant for hot H atoms. Bridges and White [19] also give evidence from the photolysis of $HI-CH_3SH$ mixtures that reaction (4) occurs. The abstraction of H from the methyl group by hot hydrogen atoms does not seem to be important although it cannot definitely be ruled out on the basis of our experiments. The work of Inaba and Darwent [18] on CH_3SD at 254 nm tends to support this conclusion. However, we have preliminary evidence which indicates that the situation at 185 nm may be somewhat different [12].

Since ethane was not observed as a product, the only fate of CH_3 radicals seems to be the abstraction of hydrogen atoms from the thiol. Inaba and Darwent [18] observed CH_3D as the only methane species when they photolyzed CH_3SD at 254 nm, indicating abstraction of only the sulfhydral hydrogen by CH_3 radicals.

Any role played by excited dimethyl disulfide molecules, formed by the combination of CH_3S radicals was ruled out based on the experiment done by Bridges and White [3]. They photolyzed a mixture of dimethyldisulfide and methanethiol at 300 nm, where the thiol is transparent and the disulfide absorbs strongly, and observed no hydrogen or methane.

A steady-state treatment of the proposed mechanism furnishes the following relations:

$$\Phi_{H_2} = \Phi_3 + \frac{k_5[CH_3SH] + k_9[M]}{(k_4 + k_5)[CH_3SH] + k_9[M]} \Phi_1 \tag{14}$$

$$\Phi_{CH_4} = \Phi_2 + \frac{k_4[CH_3SH]}{(k_4 + k_5)[CH_3SH] + k_9[M]} \Phi_1 \tag{15}$$

$$\Phi_{H_2} + \Phi_{CH_4} = \Phi_1 + \Phi_2 + \Phi_3 \tag{16}$$

$$\Phi_1 + \Phi_2 + \Phi_3 = 1.0 \tag{17}$$

In these expressions Φ_1, Φ_2, and Φ_3 are the quantum efficiencies of reactions (1), (2) and (3) of the mechanism. Equations (14) and (15) predict that when [M] is large (M other than CH_3SH in this case) the quantum yield of hydrogen approaches $\Phi_1 + \Phi_3$ while the quantum yield of methane approaches Φ_2. Using this information along with data from Figs. 1 and 2 we estimate $\Phi_1 + \Phi_3 = 0.79$, and Φ_2 to be about 0.21.

Using the above estimate along with equation (15) and assuming $\Phi_3 \ll \Phi_1$ an estimate for the fraction X of hot hydrogen atoms undergoing reaction (4) in the photolysis of pure methanethiol ([M] = [CH_3SH]) can be obtained:

$$X = \frac{k_4}{k_4 + k_5 + k_9} = \frac{\Phi_{CH_4} - \Phi_2}{\Phi_1} \tag{18}$$

The value for X is found to be 0.063, which may be compared with 0.133 at 214 nm and 0.098 at 254 nm [3]. This suggests that the hot H atoms formed in primary process (1) have about the same energy at 185 and 254 nm and that the energy of atoms formed at 214 nm is significantly higher. It is interesting to compare this result with the data obtained by Sturm and White [1] on the energy partition process in CH_3SH. They found a marked apparent decrease in average H atom energy between 214 and 185 nm which is confirmed by the results of these experiments. However, they found the energy of H atoms formed at 185 nm (1.13 ± 0.08) was larger than the energy of atoms formed at 254 nm (0.89 ± 0.04). This apparent discrepancy may possibly arise from one or both of the following sources. First, the assumption that Φ_3 is negligibly small may be incorrect and second, some adjustment of the energies obtained by Sturm and White [1] needs to be made in the light of recent data [20]. Both of these corrections will tend to improve the correlation between the fraction of atoms which react by process (4) and the average energy of those atoms [21].

Assuming Φ_3 is negligible we get $\Phi_1/\Phi_2 = 3.76$ which is about a factor of 2 higher than Callear and Dickson find [5] and which appears to be somewhat larger than the experimental uncertainties for reasons which are not clear.

Our data indicate that PFDMCB is a less efficient thermalizer for hot hydrogen atoms than is n-butane. The reason may be that the rapidly moving hydrogen atoms can transfer their energy more readily to the vibrational modes of n-butane, especially those modes which are related primarily to motion of the light molecular hydrogen atoms. In the PFDMCB the fluorines are not only heavier but very tightly bound to the carbon skeleton.

Ethanethiol

The photolysis of ethanethiol can be understood in terms of the

mechanism proposed above for methanethiol with only a few additional elementary steps. These additions are necessary in order to account for the formation of ethylene:

$$C_2H_5SH + h\nu \quad \rightarrow C_2H_4 + H_2S \tag{19}$$

$$C_2H_5^* + C_2H_5SH \rightarrow C_2H_4 + C_2H_6 + SH \tag{20}$$
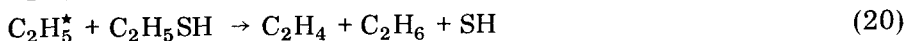
Otherwise the reaction scheme is the same as for methanethiol with C_2H_5 substituted for CH_3 in appropriate places. The evidence for reaction (19) is not particularly strong. It was proposed [2] to account for the small ethylene yield which persists even at very large thermalizer pressures. Reaction (20), in competition with reaction (10), accounts for the decline of the ethylene yield as the thermalizer pressure increases.

Other primary processes involving molecular elimination of hydrogen do not appear to be important. Possibilities include ethylene episulfide and vinyl mercaptan [22] but we find no direct evidence for their formation in our experiments. There are independent measurements which tend to confirm this conclusion. Callear and Dickson [5] postulated only C–S and S–H bond cleavage as being important in their flash photolysis. However, they suggest that CH_2S and CH_3 arise as a result of the dissociation of highly excited C_2H_5S radicals. These radicals are stabilized by the addition of large amounts of nitrogen. In our experiments where there is a large excess of parent compound any excited radicals which decomposed to give CH_3 would eventually lead to methane which we do not find in our photolyses. The reason may be that in our system the radicals are stabilized by reactive encounters with CH_3SH in which the sulfhydryl hydrogen atom is exchanged. This kind of reaction which results in no net chemical change can be a very effective means of energy transfer [23]. As with CH_3SH [2], the quantum yield of diethyldisulfide is equal to unity at 185 nm as shown by the measurements reported earlier. Thus, molecular elimination reactions cannot be very important.

Following the procedure used for methanethiol the fraction of hot hydrogen atoms that react by process (4) is estimated to be 0.14 ± 0.05 which is in qualitative agreement with earlier work at 254 and 214 nm [2]. While the rather large experimental uncertainty associated with these numbers makes quantitative assessment impossible, it is interesting to note that earlier work on energy partitioning in C_2H_5SH [24] is in qualitative agreement with this work. For the three wavelengths 254, 214 and 185 nm, the fraction of hot atoms which react by process (4) have been estimated as 0.09 ± 0.04, 0.10 ± 0.05 and 0.14 ± 0.05 while the average translational energy of H atoms produced in reaction (1) have been estimated as 1.0 ± 0.04, 1.48 ± 0.04, and 1.08 ± 0.05 eV respectively. Qualitatively we conclude from these data that for energies above 1 eV there appears to be very little variation with translational energy of the rate coefficient ratio k_4/k_9.

Reasoning as in the methanethiol case, we note that the quantum yield of reaction (1), Φ_1, should correspond to the asymptotic H_2 quantum

yield at high pressure of thermalizer. From Fig. 4 we estimate $\Phi_1 = 0.72$ compared to 0.8 and 0.9 at 214 and 254 nm, respectively [2]. The asymptotic yield of ethylene at high thermalizer pressure is about 0.05 which we take as an upper bound for Φ_{19}, the molecular elimination process which leads to ethylene. By requiring the sum of the yields of hydrogen, ethane, and ethylene to be unity we estimate Φ_2, the C–S cleavage, to be 0.23 ± 0.03 compared to 0.19 and 0.09 at 254 and 214 nm, respectively [2].

We can relate our results for the relative amounts of C–S and S–H bond cleavage as a function of wavelength with the spectral considerations of Clark and Simpson [10b]. On the basis of the spectra of several small divalent sulfur compounds and simple molecular orbital models, they suggest that absorption at 254 nm promotes an electron to an antibonding orbital which is analogous to the $n\pi^*$ transitions in carbonyl compounds. This transition is not strongly localized in either the C–S or S–H regions of the spectrum. Repulsion in this region can thus account for the observed preference for S–H cleavage. If about equal force is applied to the CH_3 and H fragments, the low mass of H guarantees its relatively rapid acceleration and thus preferential cleavage. At 185 nm Clark and Simpson [10b] suggest that absorption is due to an orbital localized to a greater degree in the C–S region thus accounting in a qualitative way for the increase in C–S cleavage at the shorter wavelengths. Of course, one must keep in mind that absorption is only one part of the overall primary part; the details of the subsequent dissociative trajectory, and thus the details of the potential energy surface, are also important. This is apparent when consideration is given to the 214 nm results which are more like 185 than 254 nm but which, in the analysis of Clark and Simpson, involve a transition to an antibonding S–H type molecular orbital.

Conclusion

Quantum yields of products formed in the photolysis of methanethiol and ethanethiol at 185 nm are presented and compared with earlier work done at 254 and 214 nm. Both substrates show quantum yields which are independent of substrate pressure but which are influenced by thermalizing species. A single mechanism is adequate to account for the observed data at all three wavelengths but the relative amounts of various processes depends on the photon energy. In particular the ratio of C–S to S–H bond cleavage increases as one passes from 254 to 185 nm for both CH_3SH and C_2H_5SH. Satisfactory correlations can be made between the average energy of the hot hydrogen atoms produced at these wavelengths and the fraction which undergoes energy sensitive reactions.

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