Reactions of Thiyl Radicals. IX. Sensitized Photolysis of Methyl Sulfide. Pressure Dependence of Methylthiyl Radical Disproportionation–Combination[1]

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Abstract: The triplet mercury photosensitized decomposition of methyl sulfide vapor has been investigated to determine the effect of reactant and deactivating gas pressure on products from thiyl radical reactions. The ratio of yields of CH_3SH and CH_3SSCH_3 is found to be remarkably pressure sensitive, particularly at low-sulfide concentrations. With 68 μ of CH_3SCH_3, the ratio passes through a maximum at about 20 Torr of added N_2 or CF_4 or increases to a constant, pressure independent, value at 20 Torr of He pressure. The maximum results from the competing effect of diffusion of CH_3S to the wall, favoring recombination, which rate decreases with pressure, and collisional stabilization of $CH_3SSCH_3^*$ molecules in the vapor phase, favored by higher pressure. The results show that observed $\Phi(CH_3SH)/\Phi(CH_3SSCH_3)$ values are indicative of the actual disproportionation–combination ratio only at pressures sufficiently large for complete deactivation of hot-combination products and negligible wall reactions. The limiting value for k_{disp}/k_{comb} determined for CH_3S radicals here is 0.04. Ethane yields follow the same trends as those of CH_3SSCH_3 indicating the pressure effects may be characteristic of other radicals whose combination product requires stabilization. Kinetic analysis yields a number of rate constant values and indicates a lifetime of 10^{-9} sec for $CH_3SSCH_3^*$ in agreement with an RRK calculation. The quantum yields of products from the photosensitized decomposition at 200 Torr of pressure are C_2H_6, 0.47; CH_3SSCH_3, 0.37; CH_4, 0.07; and CH_3SH, 0.01.

Significantly different values have been reported for the disproportionation–combination ratio of alkyl thiyl radicals. The rate-constant ratio may be calculated directly from the relative yields of thiol and disulfide from the photolysis of sulfides, while for RSSR and RSH type reactants the yield of the product from either reaction 1 or 2 is compared to the total rate of RS radical production.

$$CH_3S + CH_3S \longrightarrow CH_3SH + CH_2S \quad (1)$$

$$CH_3S + CH_3S \longrightarrow CH_3SSCH_3 \quad (2)$$

When CH_3S radicals are produced by Hg photosensitization of CH_3SCH_3 at low pressures in a mass spectrometer coupled flow reactor,[2] the data yield a value of 0.4 ± 0.1 for k_1/k_2. In this laboratory, on the other hand, values of 0.05 or less have been found for alkylthiyl radicals from the direct photolysis of thiols,[3] disulfides,[4] and sulfides.[5]

The desire to resolve the apparent disagreement over a fundamental characteristic of these sulfur-containing radicals that play an enormously important role in biological systems has prompted us to carry out a detailed investigation, focusing particularly on pressure effects that have not been investigated to date, of the photolysis of methyl sulfide vapor sensitized by $Hg(^3P_1)$ atoms. This substrate is particularly suitable since unlike thiols and disulfides its decomposition gives rise to analyzable products from both the disproportionation reaction (CH_3SH) and the combination process (CH_3SSCH_3).

Lossing[2] has established that the primary process is cleavage of the C–S bond in reaction 3. The absence

$$CH_3SCH_3 + Hg(^3P_1) \longrightarrow CH_3 + CH_3S + Hg(^1S_0) \quad (3)$$

of H_2 as a product indicates that the sensitizer interaction site is the sulfur atom, rather than an attack that results in the rupture of the C–H bond as is characteristic of ethers.[6] The formation of the observed products can readily be rationalized on the basis of subsequent reactions of the primary fragments. The important question that must be examined is how the importance of the various possible processes is influenced by both the nature of the system and the experimental conditions under which it is examined.

As reported in this paper, we have found a unique pressure dependence of thiol and disulfide quantum yields that indicates the origin of the difference between rate-constant ratios reported in the literature, and whose interpretation provides useful insights into the reactions of thiyl radicals at the extremes of the normally investigated pressure range and, by implication, about their reactions in condensed phase.

Experimental Section

Methyl sulfide (Eastman) was purified by low-pressure fractionation between −45 and −117° in the vacuum line. The material used showed an impurity level less than 0.01%. Carbon tetrafluoride (Matheson) was distilled in the line between −196 and −183°. Reagent N_2 and He (Canadian Liquid Air) were passed from cylinders through a trap at −196° directly into the system.

At the conclusion of each experiment the photolysate was fractionated by low-temperature distillation. Methane was determined in a gas burette, while other products were measured by gas chromatography. Ethane was eluted on a 6-ft Poropac Q column, while a 12-ft column packed with 15% tricresyl phosphate

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(1) Part VIII: *Can. J. Chem.*, 50, 1734 (1972). From the Ph.D. thesis of D. R. Tycholiz, University of Saskatchewan, Saskatoon, Canada, 1972.

(2) A. Jones, S. Yamashita, and F. P. Lossing, *Can. J. Chem.*, 46, 833 (1968).

(3) (a) R. P. Steer and A. R. Knight, *J. Phys. Chem.*, 72, 2145 (1968); (b) *Can. J. Chem.*, 47, 1335 (1969).

(4) (a) P. M. Rao, J. A. Copeck, and A. R. Knight, *ibid.*, 45, 1369 (1967); (b) K. Sayamol and A. R. Knight, *ibid.*, 46, 999 (1968).

(5) (a) P. M. Rao and A. R. Knight, *ibid.*, 50, 844 (1972); (b) D. R. Tycholiz and A. R. Knight, *ibid.*, 50, 1734 (1972).

(6) R. Payette, M. Bertrand, and Y. Rousseau, *ibid.*, 46, 2693 (1968).

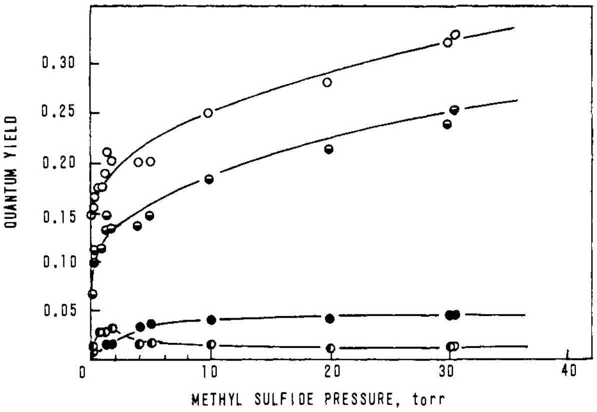

Figure 1. Quantum yield of C_2H_6 (○), CH_3SSCH_3 (◒), CH_4 (●), and CH_3SH (◐); as a function of methyl sulfide pressure in cell I and cell II.

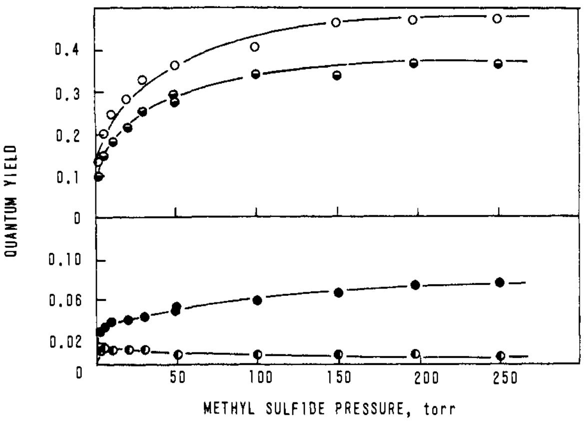

Figure 2. Quantum yield of C_2H_6 (○), CH_3SSCH_3 (◒), CH_4 (●), and CH_3SH (◐) as a function of methyl sulfide pressure in cell I.

on Chromosorb W was used for methanethiol, the substrate, and methyl disulfide. Products were identified by mass spectrometric analysis of the gc effluent or of the product separated in the line for methane.

A conventional grease-free vacuum system was used in conjunction with two reaction cells. Cell I was a quartz cylinder 4.5 cm in diameter with a total volume of 0.178 l., while cell II was a Pyrex cylinder, 9.8 cm in diameter and 120 cm in length fitted with a Vycor 7910 window, 5.7 cm in diameter at one end. This cell was fitted with a mercury saturator and gas circulating pump and had a total volume of 9.3 l. The large cell permitted examination of small substrate pressures at per cent decompositions below 1%. The light source for both cells was a modified Hanovia 687A45 low-pressure mercury resonance lamp. The light intensity was determined using Matheson propane, purified by low-temperature distillation, and preirradiated to attain a steady-state concentration of propylene, taking $\Phi(H_2) = 0.58$.[7] The measured values of I_a were 2.02 and 2.23 μEinsteins min^{-1} in cell I and 5.35 μEinsteins min^{-1} in cell II.

Results

The 2537-Å mercury photosensitized decomposition of methyl sulfide vapor at 25° yields four products that could be analyzed in our system, C_2H_6, CH_3SSCH_3, CH_4, and CH_3SH. There is some stoichiometric evidence that CH_2S may be a reaction product but the thioformaldehyde cannot be isolated in the monomeric form.

Figure 1 gives the quantum yields of product formation as a function of sulfide pressure up to 30 Torr. Data up to 1.5 Torr of pressure were obtained in cell II, while the quantum yields at higher pressures were observed in cell I. Data obtained in the latter cell for pressures to 250 Torr of CH_3SCH_3 are given in Figure 2.

The sharp rise in quantum yields at low pressures is due to increasing quenching of the sensitizer, while at higher sulfide pressures the more gradual increase arises primarily from pressure broadening of the Hg absorption line in the cell. The quenching cross section of CH_3SCH_3 for triplet mercury atoms[8] is 49.2 Å^2, and thus quenching should be complete at pressures in excess of 25–30 Torr.

A series of experiments with 50 Torr of CH_3SCH_3 in cell I at exposure times from 10 to 1.0 min demonstrated that although there is a slight increase in the amount of decomposition reducing the length of the irradiation period does not alter significantly the product distribution ratio. Thus $\Phi_{C_2H_6}:\Phi_{CH_3SSCH_3}:\Phi_{CH_3SH} = 1.0:0.76:0.03$ at 10 min and $1:0.74:0.04$ at 1.5 min.

A mass balance in carbon and sulfur among the products can be evaluated on the following basis. A yield for carbon-containing products, Φ_c, defined by eq 4

$$\Phi_c = \Phi_{CH_4} + 2\Phi_{C_2H_6} + \Phi_{CH_3SH} + 2\Phi_{CH_3SSCH_3} \qquad (4)$$

and a yield for sulfur-containing product, Φ_s, defined by eq 5

$$\Phi_s = \Phi_{CH_3SH} + 2\Phi_{CH_3SSCH_3} \qquad (5)$$

may be compared considering that the stoichiometry of the CH_3SCH_3 decomposition requires that $\Phi_c = 2\Phi_s$. Both equations are derived on the basis that CH_4 and CH_3SH arise *via* abstraction reactions. Using the appropriate values from Figure 2 at $P(CH_3SCH_3) =$ 50 Torr, $\Phi_c = 1.37 \pm 0.04$, and $2\Phi_s = 1.20 \pm 0.04$ while at 250 Torr of sulfide, $\Phi_c = 1.77 \pm 0.04$ and $2\Phi_s = 1.49 \pm 0.04$. The deficiency in sulfur indicates the likely formation of other sulfur-containing products that were not detected. Products arising from combination or disproportionation of "substrate radicals," $CH_3S\dot{C}H_2$, would not affect the mass valance calculated on this basis. If methane is formed predominantly by disproportionation, recalculation of the mass balance, including CH_2S as a product in the evaluation of Φ_s, assuming $\Phi_{CH_2S} = \Phi_{CH_4}$, gives $2\Phi_s = 1.30 \pm 0.04$ at $P(CH_3SCH_3) = 50$ Torr and $2\Phi_s = 1.65 \pm 0.04$ at 250 Torr. Although inclusion of the disproportionation reaction in the stoichiometry improves the mass balance, the data nevertheless indicate additional S-containing products. The revised calculations suggest that such a process is involved but do not provide conclusive evidence for its occurrence.

Thioformaldehyde can also be formed in the disproportionation of two CH_3S radicals. Although the participation of that process is mechanistically of considerable importance, the yield of CH_3SH is sufficiently small that its inclusion, either as in eq 4 and 5 or in a modified computation to account for simultaneous CH_2S production, does not affect the lack of identity between Φ_c and $2\Phi_s$ appreciably.

The absence[9] of products such as $CH_3SC_2H_5$ and

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(7) (a) R. A. Back, *Can. J. Chem.*, 37, 183 (1959); (b) T. Pollock, Ph.D. Thesis, University of Alberta, 1971.

(8) R. J. Cvetanovic, *Progr. Reaction. Kinet.*, 2, 69 (1964).

(9) Such compounds are involved in the methyl ethyl sulfide system and were analyzed for quantitatively in that case with the apparatus and techniques employed in the present study.

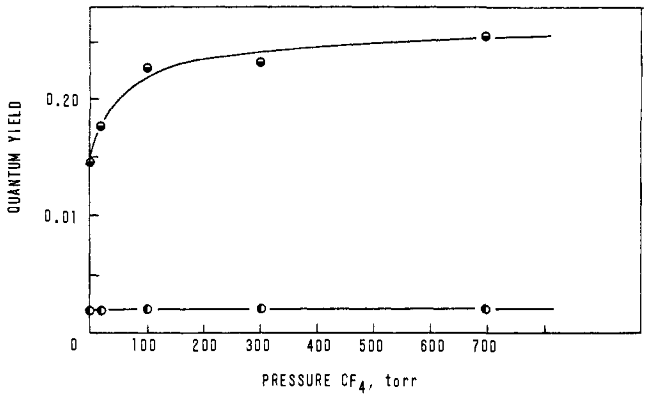

Figure 3. Quantum yield of CH_3SSCH_3 (◒) and CH_3SH (◐) as a function of CF_4 pressure for 1.46 Torr of methyl sulfide in cell I.

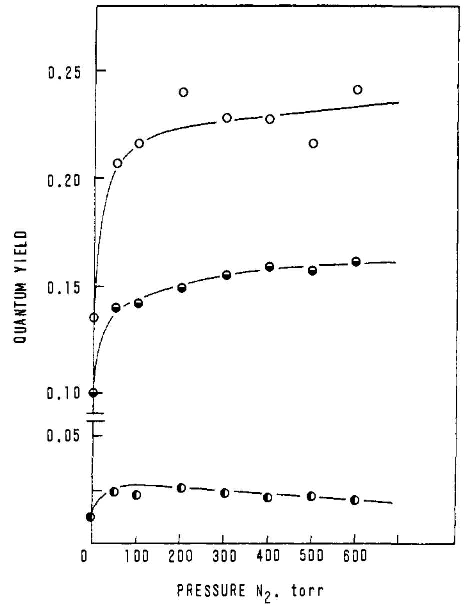

Figure 4. Quantum yield of C_2H_6 (○), CH_3SSCH_3 (◒), and CH_3SH (◐) as a function of N_2 pressure for 1.46 Torr of methyl sulfide in cell I.

$CH_3SCH_2SCH_3$ that would result if abstraction of H atoms from the substrate by CH_3 or CH_3S radicals occurred is additional evidence that the abstractive route to CH_4 and CH_3SH is not the major one in this system.

The quantum yield of substrate decomposition is given by $\Phi_c/2$ and the value at 250 Torr of CH_3SCH_3 is 0.88. Considering the uncertainty in the absolute value of the quantum yield for the actinometer, it is likely that the primary quantum yield in this system is unity.

Two series of experiments were carried out in which 1.46 Torr of the sulfide was photolyzed in the presence of CF_4 and of N_2. The results are given in Figures 3 and 4. The alterations in rate with added CF_4 should be due solely to the effects of collisional deactivation and pressure broadening of the Hg absorption line in the cell, since the quenching cross section of CF_4 for Hg($^3P_1$) atoms is essentially zero,[8] while with N_2, σ^2 = 0.274 Å^2, there will be significant quenching of excited mercury atoms to the $^3P_0$ level. Because of the relatively long lifetime of the latter state the formation of $^3P_0$ atoms will have the effect of increasing the amount of decomposition since the 1.46 Torr of substrate pressure will not result in complete quenching of Hg($^3P_1$) atoms. For each addend, then, the amount of sulfide decomposition should increase as the addend concentration is increased because of pressure broadening by both CF_4 and N_2, and in the case of nitrogen by Hg($^3P_0$) atom formation as well.

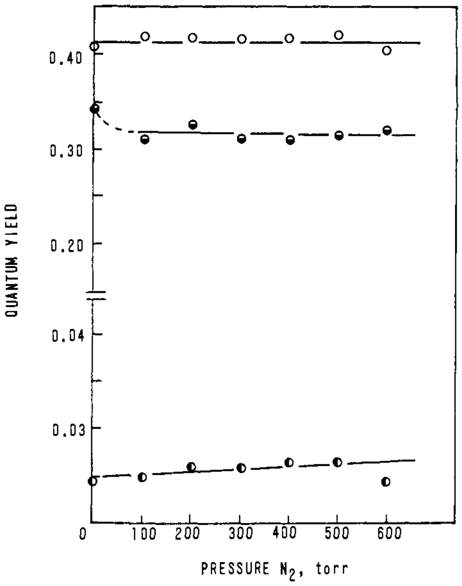

Figure 5. Quantum yield of C_2H_6 (○), CH_3SSCH_3 (◒), and CH_3SH (◐), as a function of N_2 pressure for 100 Torr of methyl sulfide in cell I.

As in the direct photolysis,[5a] increasing the total pressure increases the fraction of thiyl radicals terminating as CH_3SSCH_3, with a concomitant decline in CH_3SH yields. Here, this effect will be superimposed on the increase in total decomposition.

Figure 3 shows that while the disulfide quantum yield rises, the effects of increased decomposition and reduced proportion of CH_3SH formation evidently counterbalance and result in the pressure independence of Φ_{CH_3SH}. With nitrogen as the addend the two possible mechanisms for increased decomposition result in the much more rapid rise in quantum yields, including that of CH_3SH, shown in Figure 4. At pressures beyond about 100 Torr deactivation effects evidently predominate and Φ_{CH_3SH} declines as $\Phi_{CH_3SSCH_3}$ increases.

When the effects of added nitrogen are examined at 100 Torr of substrate pressure, the situation is significantly different. Under these conditions there is complete quenching by the substrate and pressure broadening effects due to additional pressure increases are minor. The results in Figure 5 show that apart from the initial drop in $\Phi_{CH_3SSCH_3}$ and the small gradual increase in Φ_{CH_3SH}, quantum yields are essentially unchanged when the system is increased by the addition of up to 600 Torr of N_2. Thus deactivational effects have evidently been maximized already by the 100 Torr of substrate. Furthermore, the absence of a decline in $\Phi_{CH_3SSCH_3}$ under these conditions shows that the triplet state that must be the intermediate in the primary process, eq 3, is not of sufficient longevity to undergo collisional deactivation (methyl sulfide is not characterized by a so-called "excited molecule mechanism" as is the case in Hg($^3P_1$)–olefin systems).

The results obtained with nitrogen also indicate that

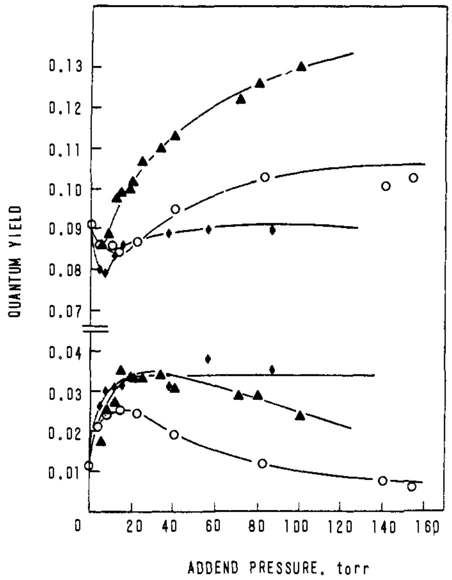

Figure 6. Quantum yield of CH_3SCH_3 (upper curves) and CH_3SH (lower curves) as a function of pressure of added N_2 (▲), He (◆), and CF_4 (○) for 68 μ of methyl sulfide in cell II.

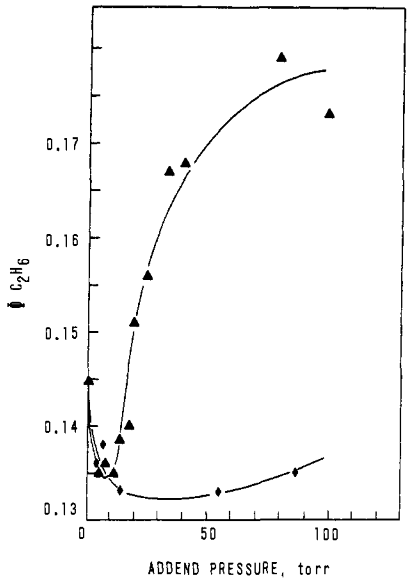

Figure 7. Quantum yield of C_2H_6 as a function of pressure of added N_2 (▲) and He (◆) for 68 μ of methyl sulfide in cell II.

there is no difference in the *chemical* effects of $Hg(^3P_1)$ and $(^3P_0)$ atoms. No new products are formed by the latter species and the product distribution changes that occur when it is involved can readily be explained solely on the basis of pressure effects.

To investigate further the effects of pressure on this system and to examine the reaction under conditions approaching those employed in Lossing's work[2] we carried out the sensitized photolysis of 68 μ of CH_3SCH_3 in cell II and measured the rates of thiol and disulfide formation as a function of pressure of added He, CF_4, and N_2. The results are shown in Figure 6. Ethane yields were also determined in the helium and nitrogen experiments and these are given in Figure 7. In these experiments intermittent exposure with continuous circulation of the photolysate was used to diminish possible effects of product accumulation near the cell window. Ten 0.1-min exposures, with intervening dark periods of 1 min, gave a total irradiation time of 1 min in each experiment.

With each addend the disulfide shows a characteristic minimum at pressures less than 20 Torr. This is followed by a gradual increase at higher pressures, except for helium where the yields are insensitive to further pressure increases. The opposite behavior is observed for Φ_{CH_3SH} which passes through a maximum with CF_4 and N_2 and rises to a pressure independent value with helium. The ethane quantum yield exhibits the same trends as that of the disulfide.

Discussion

A reaction mechanism comprising reaction 3 as the primary process, and the sequence of steps

$$2CH_3S \rightleftarrows CH_3SSCH_3^* \qquad (6)$$

$$2CH_3S \xrightarrow{\text{wall}} CH_3SSCH_3 \qquad (7)$$

$$M + CH_3SSCH_3^* \longrightarrow CH_3SSCH_3 + M \qquad (8)$$

$$2CH_3S \longrightarrow CH_3SH + CH_2S \qquad (9)$$

$$CH_3 + CH_3S \longrightarrow CH_4 + CH_2S \qquad (10)$$

(where M can be the substrate or added gas), along with a sequence analogous to reactions 6–8 involving CH_3 and C_2H_6, can be utilized to interpret the results and facilitate their kinetic analysis.

The formation of $C_2H_6^*$ and $CH_3SSCH_3^*$ molecules is indicated by the increase in the yields of these products, and the concomitant reduction in the fraction of the total decomposition giving CH_3SH when either CF_4 or N_2 is present in the photolysis of 1.46 Torr of sulfide (Figures 3,4), and from the more pronounced effects when more than 20 Torr is present in the photolysis of 68 μ of CH_3SCH_3 (Figures 6 and 7). Reaction 6 and its analog for CH_3 radicals are exothermic to the extent of the S–S and C–C bond energies, 67[10] and 84[11] kcal mol^{-1}, respectively. Removal of $CH_3SSCH_3^*$ molecules through reaction 8 reduces the stationary-state concentration of thiyl radicals with a resultant decrease in thiol production. The substrate itself would be expected to be efficient in this role as is substantiated by the absence of further disulfide rate increases when N_2 is added to 100 Torr of CH_3SCH_3 (Figure 5). In addition, Figure 1 shows that the yield of CH_3SH passes through a maximum at around 2 Torr of CH_3SCH_3 (the result of the opposite effects of increasing quenching of the sensitizer and disulfide deactivation). The expected inefficiency of helium as a deactivator is consistent with the apparent lack of significant alteration in $\Phi_{CH_3SCH_3}$ or Φ_{CH_3SH}, at helium pressures above 20 Torr.

The interpretation of the data in Figure 6 is complicated by the increase in total decomposition, by an amount evidently different for each addend, resulting from pressure broadening or $Hg(^3P_1)$ atom formation or both. The behavior of the system is more readily visualized through the plot of the ratio of thiol to disulfide yields presented in Figure 8.

In this form the data clearly show the almost identical behavior of the three addends up to a pressure in the 10–20-Torr range, characteristic of each addend, and the similarity of the decline in the disulfide–thiol ratio

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(10) H. Mackle, *Tetrahedron*, **19**, 1159 (1963).

(11) E. E. Smissman and J. R. J. Sorenson, *J. Org. Chem.*, 30, 4008 (1965).

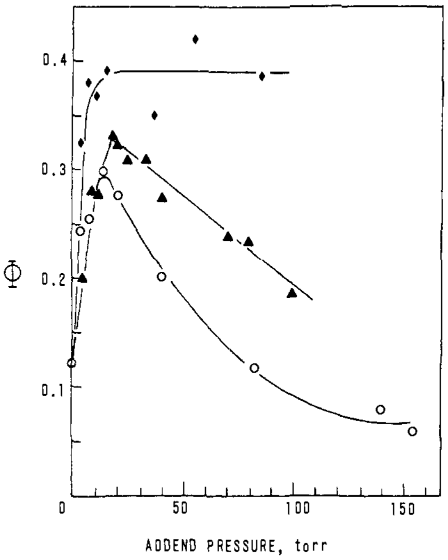

Figure 8. Variation in $\Phi = \Phi_{CH_3SH}/\Phi_{CH_3SSCH_3}$ as a function of added He (◆), N_2 (▲), and CF_4 (○) for 68 μ in cell II. Data from Figure 6.

with N_2 and CF_4 pressures greater than 20 Torr. The shift in the sulfur-containing product distribution toward the disulfide observed here is again consistent with the role of collisional deactivation proposed in the mechanism. There is some scatter in the calculated ratios beyond 15 Torr in the case of helium as addend, but there is evidently no pronounced effect over the limited pressure range studied.

The pressure dependence of the ethane yield beyond 20 Torr (Figure 7) is the same as that for the disulfide, and indicates that the formation of $C_2H_6^*$ and its collisional deactivation are governed by analogous considerations. The methane quantum yields could not be measured with He and N_2 as addends but would be expected to follow the trends shown by Φ_{CH_3SH}.

Two aspects of the conditions of these experiments suggest that the alteration in product distribution at pressures below 20 Torr is due to radical diffusion effects. Because of the large absorption coefficient of mercury for its own resonance radiation, over 90% of the excited mercury atoms are concentrated in the first 1 cm of path length.[12] Thus, despite the large cell volume involved in these experiments, initial thiyl radical formation is confined to a small region near the incident window. Wall reactions would therefore be expected to be more important than in the case where the concentration of radicals is homogeneous throughout the reactor volume. Thus when the substrate pressure is 68 μ, CH_3S radicals formed in the reaction zone may diffuse to the wall. As the addend pressure is increased the rate of diffusion declines and wall reactions become progressively less important. Of the two processes involving CH_3S radicals, combination requires stabilization and it will be favored at the wall. Thus the inclusion of reaction 7 in the mechanism is consistent with the observed decreasing fraction of thiyl radicals terminating as the disulfide, manifested by the initial rise in $\Phi_{CH_3SH}/\Phi_{CH_3SSCH_3}$, with addend pressure.

The second effect that results from increasing addend concentration is collisional deactivation in the gas phase of $CH_3SSCH_3^*$ molecules formed in reaction 6. As the collision frequency increases the equilibrium represented by eq 6 is shifted away from CH_3S, thereby reducing CH_3SH formation in the disproportionation process, eq 9.

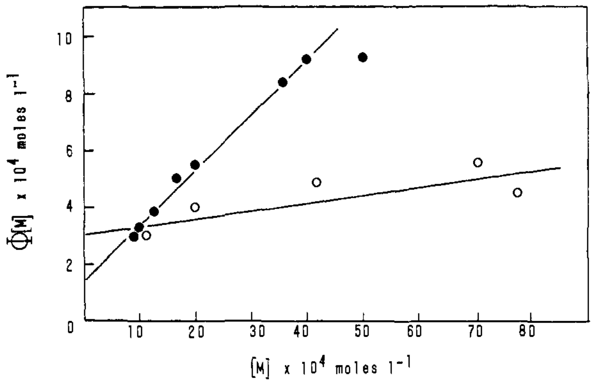

Figure 9. Plot of eq 14 for 68 μ of methyl sulfide in cell II, for N_2 pressures (●) greater than 18 Torr and CF_4 pressures (○) greater than 22 Torr.

The two opposite effects of increasing addend pressure would be expected to influence ethane production in the same way as they alter $\Phi_{CH_3SSCH_3}$, since ethane is also formed in an exothermic combination process. In the absence of addend CH_3 wall recombination is favored. As the deactivator concentration is increased $\Phi_{C_2H_6}$ initially declines because of the reduction in the diffusion rate and then increases as deactivation of $C_2H_6^*$ molecules formed in the gas phase becomes more important. With added helium the counter-diffusion effect is again important, but there is only a small increase in $\Phi(C_2H_6)$ through deactivation.

Some useful quantitative data on the reactions occurring in this system can be obtained from a limited kinetic analysis of the mechanism using the quantum yield data in Figure 8 in the pressure region where the wall reaction, eq 7, can be neglected. Under those conditions, the thiol:disulfide quantum yield ratio, Φ, equivalent to the observed value of $R(CH_3SH)/R(CH_3SSCH_3)$ can be determined *via*

$$\Phi = k_9[CH_3S]^2/k_8[M][CH_3SSCH_3^*] \qquad (11)$$

The steady-state concentration of excited disulfide molecules is given by

$$[CH_3SSCH_3^*] = k_6[CH_3S]^2/(k_{-6} + k_8[M]) \qquad (12)$$

where [M] is the addend concentration in mol l.$^{-1}$. These two relations give the following expression for Φ as a function of addend concentration

$$\Phi[M] = \frac{k_9k_{-6}}{k_8k_6} + \frac{k_9}{k_6}[M] \qquad (13)$$

The dependence of Φ[M] on [M] for N_2 pressures from 18 to 100 Torr and CF_4 pressures from 22 to 155 Torr is shown in Figure 9. The slope gives the value of k_9/k_6, the CH_3S radical disproportionation–combination ratio, and the value observed should be the same for all addends. The fact that the slope is 0.20 for $M \equiv N_2$ and 0.03 for $M \equiv CF_4$ likely arises because wall recombination is neglected in this analysis. The inaccuracy of this assumption would be expected to be

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(12) A. R. Knight, Ph.D. Thesis, University of Alberta, 1962.

more pronounced with N_2 as compared to the more effective deactivator CF_4 for which reaction 8 would be more important, and thus the ratio value of 0.03 should be more representative of the actual k_9/k_6 value. Indeed, there are indications of curvature in the kinetic plot of the data obtained with nitrogen and at the higher N_2 concentrations, the slope may be approaching that of the CF_4 plot.

A value of the k_9/k_6 ratio can also be obtained directly from the experimental data at high pressures where there is complete deactivation of $CH_3SSCH_3^*$ and thus where the rate of disulfide formation is identical to that of reaction 6. Under these conditions $\Phi = k_9/k_6$. Making use of the data in Figure 5 for the photolysis of 100 Torr of substrate, average values for the thiol and disulfide quantum yields over the range $P(N_2) =$ 300–600 Torr give $k_9/k_6 = 0.04$ in reasonable agreement with the value obtained from the kinetic analysis using data for CF_4 as deactivator.

The total rate of disappearance by combination and disproportionation of CH_3S radicals in the gas phase has been measured[13] utilizing the rotating sector technique and gives $k_9 + k_6 = 2.5 \times 10^{10}$ l. mol^{-1} sec^{-1}. Thus from $k_9/k_6 = 0.04$ determined here, the rate constants for combination and disproportionation of CH_3S radicals are $k_9 = 2.4 \times 10^{10}$ l. mol^{-1} sec^{-1} and $k_6 = 9.8 \times 10^8$ l. mol^{-1} sec^{-1}.

Values of the other rate constants can also be extracted from the graphical analysis. The intercept divided by the slope gives k_{-6}/k_8. The value of k_8 can be calculated, assuming an activation energy of zero, from the gas-kinetic collision frequency. With $d_{CH_3SSCH_3-M} = 6.0$ Å for $M \equiv N_2$ and 7.0 Å for $M \equiv CF_4$, the resulting k_8 values, in l. mol^{-1} sec^{-1}, are 3.1×10^{11} and 3.5×10^{11}, respectively. Together with the intercept values from Figure 9, this gives finally $k_{-6} = 2.2 \times 10^8$ sec^{-1} and 3.5×10^9 sec^{-1}. This indication of a lifetime of the excited disulfide molecule of *ca.* 10^{-9} sec can be compared with the rate constant for the unimolecular decomposition of the species computed from the RRK equation. Taking $E_a = \epsilon^* = 45$ kcal mol^{-1} and $A = k^* = 2 \times 10^{13}$ for the reaction from data on the thermal decomposition of methyl disulfide[14] and the excitation energy[15] as 77 kcal mol^{-1}, the RRK equation with $s = 12$, one-half the degrees of freedom in CH_3SSCH_3, yields 0.8×10^9 sec^{-1}. The agreement between this value and the rate constant obtained from the kinetic analysis indicates that the proposed mechanism is an adequate description of the system and the rate constant values obtained therefrom are meaningful.

One other possible reaction giving rise to thiol production

$$CH_3SSCH_3^* \longrightarrow CH_3SH + CH_2S \qquad (14)$$

must be considered. This process, following eq 6 is equivalent to a so-called "heat-to-head" disproportionation, as opposed to the "head-to-toe" mechanism represented by eq 9. If the kinetic treatment is expanded to include this process, the resulting equation again gives $\Phi[M]$ as a linear function of $[M]$ and thus the kinetic analysis of the type represented in Figure 9 does not indicate whether reaction 14 does actually occur. It is quite important to note, however, that if this process is involved it would be an additional not an alternative source of CH_3SH, since the observation of thiol formation under "infinite pressure" conditions shows that reaction 9 does occur.

The data obtained in this study elucidate the nature and origin of the wide discrepancy in values for k_9/k_6 reported in the literature. The relative yields of thiol and disulfide can be taken as being indicative of the disproportionation/combination ratio only under conditions where the pressure is sufficiently high that wall recombination can be neglected and that collisional deactivation of the excited disulfide molecule formed in the exothermic combination process is complete. The fact that the yield of ethane follows the same trend as that of the disulfide at low substrate pressure indicates that the pressure dependence resulting from the interplay of diffusion and deactivation effects may also be important with other radicals whose recombination product requires collisional stabilization.

The small values for the disproportionation–combination ratio of thiyl radicals found here are further examples of the growing body of evidence indicating that organo-sulfur compounds do not readily undergo transformations in which C—S bonds are converted to C=S, unlike the well established tendency of their oxygen analogs. The effect evidently arises from the relative exothermicities of the process for S- and O-containing species. The generally smaller exothermicities for such reactions with sulfur compounds result from the relatively small difference in CS single and double bonds.

For example, Heicklen and Johnson[16] report that $k_d/k_c = 9.3 \pm 0.6$ for CH_3O radicals. The combination process in that case has $\Delta H = -36.1$ kcal mol^{-1} and disproportionation, -78 ± 2 kcal mol^{-1}; the corresponding values for the same reactions with CH_3S are[17] -67 ± 7 and -42 ± 8 kcal mol^{-1}. Similarly, episulfides formed by the addition of S atoms to olefins are stable, whereas the corresponding epoxides from O-atom–olefin reactions usually undergo unimolecular decomposition. In the case of ethylene as olefin, thermochemical data indicate that the isomerization reaction to the thiocarbonyl product is 30 kcal mol^{-1} less exothermic than the corresponding reaction for the oxygen analog.[18]

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