

the varying concentration of **4** crosses its cmc, the Benesi-Hildebrand<sup>16</sup> graph shows a clear break at the cmc. The monomeric complexation constants for **4** are extraordinarily high; there is precedent for electrostatic enhancement of binding to cyclodextrins,<sup>17</sup> especially in DMSO,<sup>18</sup> and neutral guests fail to bind to **4**. However, **3** exhibits only a modest affinity for anionic guests in water. The alkyl chain of **4** may create a more hydrophobic microenvironment<sup>19</sup> for the guests, thus augmenting the hydrophobic binding and magnifying the electrostatic attraction between host and guest.

A provisional model to account for positive cooperativity is depicted schematically in Figure 2. Guest binds to the cyclodextrin cavity and expels the resident alkyl chain into the micelle interior. This renders the micelle more lipophilic, causing other alkyl chains to partition out of cyclodextrin. As a result, affinity of cyclodextrin for guest is enhanced since the alkyl chains compete less effectively for the same sites. Clearly it is the aggregate that is the allosteric entity rather than any single host. We are currently investigating the generality of this novel mechanism for cooperative binding.

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- (16) Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703.  
 (17) (a) Matsui, Y.; Ogawa, K.; Mikami, K.; Yoshimoto, M.; Mochida, K. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1219. (b) Tabushi, I.; Kuroda, Y.; Mizutani, T. *J. Am. Chem. Soc.* **1986**, *108*, 4514. (c) Tabushi, I.; Shimizu, N.; Sugimoto, T.; Shiozuka, M.; Yamamura, K. *J. Am. Chem. Soc.* **1977**, *99*, 7100.  
 (18) Siegel, B.; Breslow, R. *J. Am. Chem. Soc.* **1975**, *97*, 6869.  
 (19) Emert, J.; Breslow, R. *J. Am. Chem. Soc.* **1975**, *97*, 670.

### Ring Size and Strain as a Control of Reaction Selectivity: Ethylene Sulfide on Mo(110)

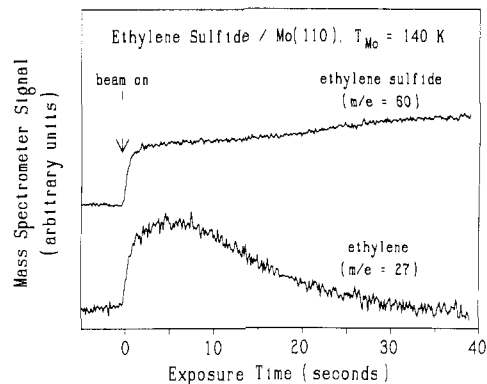
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The adsorption and reaction of sulfur-containing organic molecules on single-crystal transition-metal surfaces form a subject of current interest to us<sup>1</sup> and others.<sup>2</sup> The primary focus of our work is an investigation of how thermodynamic properties of adsorbate molecules affect the mechanism(s) by which they react. To this end, we have studied the reactions of two saturated cyclic sulfides—trimethylene sulfide (*c*-C<sub>3</sub>H<sub>6</sub>S) and tetrahydrothiophene (*c*-C<sub>4</sub>H<sub>8</sub>S)—on Mo(110).<sup>1a-c</sup> On the basis of these studies we proposed that ring strain in the cyclic sulfide controls reaction selectivity on Mo(110). This work concerns the reactions of a third cyclic sulfide, ethylene sulfide (*c*-C<sub>2</sub>H<sub>4</sub>S), on Mo(110). The results presented here demonstrate that ring size as well as ring strain determines the reaction selectivity of cyclic sulfides on Mo(110).

Salient features of the reactions of tetrahydrothiophene and trimethylene sulfide on Mo(110) are summarized as follows. Certain features of their temperature-programmed reactions are similar. Each undergoes ring opening to form a thiolate inter-



**Figure 1.** The mass spectrometrically determined partial pressures of ethylene and ethylene sulfide measured as a function of ethylene sulfide exposure to a Mo(110) surface held at 140 K. Ethylene sulfide impinged upon Mo(110) from an effusive source located approximately 0.5 in. from the crystal, the configuration resulting in optimal detection of ethylene. The ions detected— $m/e = 27$  for ethylene and  $m/e = 60$  for ethylene sulfide—were chosen for their optimal signal-to-noise ratios. The ethylene pressure curve has been corrected by subtracting the contribution of ethylene sulfide (approximately 50% of the total signal), which also cracks at  $m/e = 27$ . During the dose the ionization gauge measured pressure rise in the chamber was approximately  $1 \times 10^{-10}$  Torr.

mediate which then decomposes to surface sulfur and gaseous alkanes and alkenes between 300 and 375 K. Accompanying these similarities, however, are marked differences. Some trimethylene sulfide reacts by intramolecular elimination to form cyclopropane at 190 K. No cyclobutane formation pathway is observed for tetrahydrothiophene. Tetrahydrothiophene desorbs intact from Mo(110) at 310 K, but no reversibly chemisorbed state is detected for trimethylene sulfide. These differences were rationalized by proposing that thiolate formation and intramolecular elimination are kinetically driven by loss of ring strain in the cyclic sulfide. Hence, both processes are more favorable for trimethylene sulfide (ring strain = 19 kcal/mol<sup>3</sup>) than for tetrahydrothiophene (ring strain = 2 kcal/mol<sup>3</sup>). Chemisorbed trimethylene sulfide does not desorb, because it reacts to form cyclopropane and chemisorbed propyl thiolate at a surface temperature lower than that necessary to overcome the barrier to desorption. Similarly, tetrahydrothiophene does not undergo intramolecular elimination because the transition states leading to desorption and the thiolate intermediate are more accessible than that leading to cyclobutane formation.

Ethylene sulfide is nearly as strained as trimethylene sulfide (18 versus 19 kcal/mol<sup>3</sup>). Also, ethylene formation upon adsorption of ethylene sulfide on room temperature Cu(110) has been previously inferred.<sup>4</sup> We therefore expected that intramolecular elimination of ethylene from ethylene sulfide would be as favorable as intramolecular elimination of cyclopropane from trimethylene sulfide. We find that intramolecular elimination is the dominant observed reaction pathway, occurring upon adsorption for crystal temperatures as low as 100 K, with an activation energy of  $\leq 6$  kcal/mol.<sup>5</sup> In contrast to trimethylene sulfide, no competitive ring opening to a thiolate occurs, a fact which does not reflect any inherent instability of the C<sub>2</sub> thiolate.<sup>6</sup> Furthermore, as opposed to other cyclic sulfides, complete decomposition of ethylene sulfide to surface carbon and sulfur is a minor reaction pathway, accounting for approximately 15% of all irreversibly chemisorbed ethylene sulfide.

Exposure of a cold Mo(110) surface to an effusive source of room temperature ethylene sulfide<sup>7</sup> results in the immediate ev-

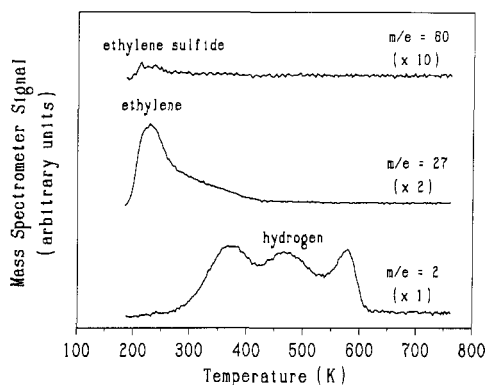
(1) (a) Roberts, J. T.; Friend, C. M. *J. Am. Chem. Soc.* **1986**, *108*, 7204-7210. (b) Roberts, J. T.; Friend, C. M. *J. Am. Chem. Soc.* **1987**, *109*, 3872-3882. (c) Roberts, J. T.; Friend, C. M. *J. Am. Chem. Soc.* **1987**, *109*, 4423-4424. (d) Roberts, J. T.; Friend, C. M. *Surf. Sci.* **1987**, *186*, 201-218.  
 (2) (a) Lang, J. F.; Masel, R. I. *Surf. Sci.* **1987**, *183*, 44-66. (b) Zaera, F.; Kollin, E. B.; Gland, J. L. *Surf. Sci.* **1987**, *184*, 75-89. (c) Gellman, A. J.; Farias, M. H.; Salmeron, M.; Somorjai, G. A. *Surf. Sci.* **1984**, *136*, 217-228. (d) Preston, R. E.; Benziger, J. B. *J. Phys. Chem.* **1985**, *89*, 5010-5017. (e) Richardson, N. V.; Campuzano, J. C. *Vacuum* **1981**, *31*, 449-451.

(3) Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279-324.

(4) Thomas, T. M.; Grimm, F. A.; Carlson, T. A.; Agron, P. A. *J. Electron Spectrosc. Relat. Phenom.* **1982**, *25*, 159-169.

(5) (a) Calculated by using Redhead's method<sup>5b</sup> and assuming a pre-exponential factor of  $10^{13}$ . (b) Redhead, P. A. *Vacuum* **1962**, *12*, 203-211.

(6) (a) The ethyl thiolate has been prepared by reaction of ethanethiol on Mo(110).<sup>7b</sup> (b) Roberts, J. T.; Friend, C. M., to be published.



**Figure 2.** Temperature-programmed reaction of ethylene sulfide on Mo(110). Adsorption occurred at 140 K, and the heating rate was approximately 15 K/s. The multiplication factors are referenced to hydrogen and are uncorrected for degree of fragmentation and ionization efficiency in the mass spectrometer. The intensity of the ethylene sulfide peak is so low that ethylene sulfide cracking at  $m/e = 27$  does not contribute to the ethylene peak.

olution of gaseous ethylene. In Figure 1 are shown the partial pressures of ethylene and ethylene sulfide (measured mass spectrometrically) in the ultrahigh vacuum chamber as a function of time during the ethylene sulfide dose for a crystal temperature of 140 K. The ethylene pressure rises immediately upon exposure of the surface to ethylene sulfide. Ethylene production reaches a maximum rate at an exposure of approximately 10 s. After 20 s, the rate of formation drops. Ethylene production stops after 60 s. Production of ethylene upon adsorption was evident for crystal temperatures as low as 100 K, the lowest temperature we could access. The ethylene yield was not dependent upon crystal temperature between 100 and 140 K, as measured by the ethylene pressure curves and by the sulfur Auger spectra after reaction. Ethylene sulfide and ethylene are the only species whose pressure was observed to change. Notably, no formation of ethane or displacement of water, dihydrogen, or carbon monoxide from the crystal or the chamber walls could be detected.

Temperature-programmed reaction after ethylene sulfide adsorption demonstrates that not all ethylene sulfide reacts to form gas-phase ethylene upon adsorption. Three products are detected at saturation exposures (60 s) during temperature-programmed reaction, as shown in Figure 2: ethylene at 220 K, small amounts of ethylene sulfide at 220 K, and dihydrogen at 375, 460, and 575 K. The nature of the ethylene peak is under investigation, principally by X-ray photoemission spectroscopy. The dihydrogen peaks at 375 and 460 K likely result from a combination of desorption and limited states, as discussed previously.<sup>1a,b</sup> The dihydrogen peak at 575 K is assigned to the decomposition of a surface hydrocarbon fragment. Auger electron spectra recorded after temperature-programmed reaction of ethylene sulfide reveal that approximately 15% of irreversibly chemisorbed ethylene sulfide decomposes to surface carbon, surface sulfur, and gaseous dihydrogen.

Preadsorbed hydrogen does not affect the yield of either ethylene peak nor does preadsorbed hydrogen result in formation of any new products such as ethane. Reaction of ethylene sulfide on a surface presaturated with deuterium reveals no deuterium incorporation into either the ethylene produced upon adsorption or that which evolves at 220 K, confirming that ethylene elimination is wholly intramolecular. Although deuterium-containing products (HD and D<sub>2</sub>) are evident in all regions of the dihydrogen temperature programmed reaction spectrum, deuterium is preferentially incorporated into the 375 K peak.

These experiments further illustrate the dramatic effect of ring strain in determining the reaction selectivity of cyclic sulfides on Mo(110). Intramolecular elimination is the dominant reaction

pathway for ethylene sulfide, with minor amounts (ca. 15%) of complete decomposition the only other detectable reaction. Importantly, these experiments also demonstrate that ring strain is not the sole determinant of reaction selectivity. No thiolate formation occurs despite the fact that ethylene sulfide is approximately as strained as trimethylene sulfide. The lack of thiolate formation may result from a more favorable entropy of activation for ethylene sulfide intramolecular elimination, an easily rationalized proposition if C-C bond formation is assumed to start early on the reaction coordinate(s) leading to intramolecular elimination. Ethylene sulfide and its derivatives are unique among cyclic sulfides because the carbons undergoing C-C bond formation during intramolecular elimination are already bonded to each other. Hence ethylene sulfide requires less structural reorganization (and activation entropy) for formation of the intramolecular elimination transition state(s). The size of the ethylene sulfide ring may therefore play a key role in the determination of its reaction selectivity.

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### Gas-Phase Coupling of Methyl Radicals during the Catalytic Partial Oxidation of Methane

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It is generally accepted that the initial step in the catalytic oxidative coupling of methane involves the homolytic cleavage of a C-H bond. This results in the formation of surface OH species and CH<sub>3</sub><sup>•</sup> radicals which may undergo coupling to form ethane. A question arises as to whether the methyl radical coupling occurs on the surface or in the gas phase. Keller and Bhasin<sup>1</sup> proposed a mechanism for the catalytic oxidative coupling of CH<sub>4</sub> in which the formation of C<sub>2</sub>H<sub>6</sub> resulted from the surface coupling of adsorbed CH<sub>3</sub><sup>•</sup> radicals. In contrast to this mechanism, Lunsford and co-workers<sup>2,3</sup> proposed that a homogeneous gas-phase coupling of CH<sub>3</sub><sup>•</sup> radicals, formed by the surface abstraction of H-atoms from CH<sub>4</sub>, was the primary pathway for C<sub>2</sub>H<sub>6</sub> formation. Evidence for the existence of gas-phase CH<sub>3</sub><sup>•</sup> radicals during the oxidative coupling of CH<sub>4</sub> has been obtained by Driscoll et al.<sup>3</sup> with use of a matrix isolation electron spin resonance (MIESR) technique and, more recently, by Jones et al.<sup>4</sup> with use of the Paneth lead mirror technique.<sup>5</sup> The modeling studies of Labinger and Ott<sup>6</sup> and of Kimble and Kolts<sup>7</sup> also support the role of gas-phase CH<sub>3</sub><sup>•</sup> radicals; however, the actual significance of these radicals in the formation of C<sub>2</sub>H<sub>6</sub> has not been experimentally proven. In this communication a lower limit for the rate of gas-phase CH<sub>3</sub><sup>•</sup> radical formation over a lithium-promoted MgO catalyst has been determined and this result is compared with the overall rate of C<sub>2</sub>H<sub>6</sub> formation.

The experiments were carried out by using a modification of the MIESR apparatus<sup>8</sup> which is designed to detect gas-phase radicals emanating from surfaces of catalytic interest. In this system reactant gases along with argon are passed over a heated catalyst bed, and the effluent gases pass through a leak into a

(1) Keller, G. E.; Bhasin, M. M. *J. Catal.* **1982**, *73*, 9-19.

(2) Ito, T.; Wang, J. X.; Lin, C. H.; Lunsford, J. H. *J. Am. Chem. Soc.* **1985**, *107*, 5062-5068.

(3) Driscoll, D. J.; Martir, W.; Wang, J. X.; Lunsford, J. H.; *J. Am. Chem. Soc.* **1985**, *107*, 58-63.

(4) Jones, C. A.; Leonard, J. J.; Sofranko, J. A. *J. Catal.* **1987**, *103*, 311-319.

(5) Paneth, F.; Hofeditz, W. *Ber. Dtsch. Chem. Ges.* **1929**, *B62*, 1335.

(6) Labinger, J. A.; Ott, K. C. *J. Phys. Chem.* **1987**, *97*, 2682.

(7) Kimble, J. B.; Kolts, J. H. *Energy Progr.* **1986**, *6*, 226.

(8) Martir, W.; Lunsford, J. H. *J. Am. Chem. Soc.* **1981**, *103*, 3728-3732.

(7) For a description of the apparatus used for this work see ref 1a. Ethylene sulfide was obtained from Aldrich and purified by distillation. Ethylene sulfide was degassed before use each day.