exclusive production of the non-silyl adducts **7** and **10**. Thus, the α-amino radical **20**, formed by SET to DCA followed by desilylation, does indeed add to enones.

Desilylation of the amine cation radical **18** represents the more typical behavior of α-silyl cation radicals.[1] Thus, it appears that desilylation is more efficient than deprotonation unless these species are in contact ion pairs with basic partners (e.g., enone radical anions).[14] In a general sense, the medium effects can be understood in terms of the base strength of the enone radical anions. Thus, while solvent polarity, protic nature, and ionic strength will govern efficiencies of CIP formation, they also influence the pK_b of the enone anion radicals.

In summary, we have uncovered interesting medium effects on silylamine-cyclohexenone SET photoaddition reactions. An interpretation in terms of differential reactivity of CIP and SSIP or free ion radical intermediates is proposed. It will be interesting to see if this phenomenon is general and if it can be used as a diagnostic tool in the study of other photoelectron-transfer processes.

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(13) Competitive light absorption occurs at high enone concentrations.

(14) Application of Arnold's method[14b] suggests that the enone radical anion is more basic than that of DCA, reflective mainly of the reduction potential differences for the neutral precursors (e.g., $E_{1/2}(-)$ values for enone are ca. −2.6 V while those for DCA are −0.89 V). (b) Wayner, D. D. M.; Arnold, D. R. *Can. J. Chem.* **1985**, *63*, 871.

Coadsorption as a Probe of Mechanism: Cyclic Sulfides and Straight Chain Thiols on Mo(110)

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We recently reported that tetrahydrothiophene and trimethylene sulfide undergo desulfurization on Mo(110) to form gaseous alkanes and alkenes in a temperature-programmed reaction experiment.[1,2] In both cases, straight chain alkane evolution preceded alkene evolution. We proposed that the intermediate leading to straight chain alkanes and alkenes from these two cyclic sulfides is a surface thiolate. The thiolate undergoes competitive C_1-hydrogenation to alkane and C_2-dehydrogenation to alkene, depending on the surface hydrogen concentration. The proposed mechanism of hydrocarbon formation from tetrahydrothiophene on Mo(110) is depicted in Figure 1.

Ethanethiol, 1-propanethiol, and 1-butanethiol also react on Mo(110) to form alkanes and alkenes with alkane production preceding alkene production.[1-3] Comparison to alcohols and thermodynamic considerations suggest that thiols almost certainly react on Mo(110) to form a stable thiolate intermediate which then decomposes to hydrocarbons. Although the temperatures of alkane production from the thiols were approximately 40 K lower than those from the cyclic sulfides, we suggested that the identical temperature *ordering* of the reaction products was strong experimental support for the formation and subsequent decomposition of a thiolate intermediate during the temperature-programmed reaction of trimethylene sulfide and tetrahydrothiophene. Also, adsorption of either of the cyclic sulfides on a hydrogen-presaturated surface resulted in alkane production temperatures virtually identical with those from the thiols. Finally, experiments measuring the extent of surface deuterium incorporation into all hydrocarbon products from the cyclic sulfides and thiols were consistent with the decomposition of cyclic sulfides and thiols by way of the thiolate intermediate. These results are described in detail in previous work.[1-3]

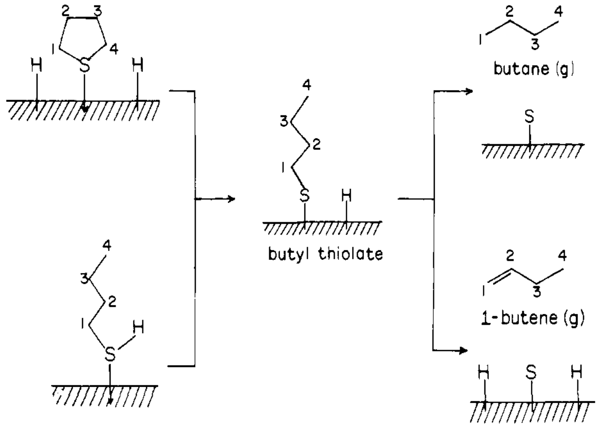

Figure 1. Proposed mechanism of hydrocarbon formation from tetrahydrothiophene on Mo(110).

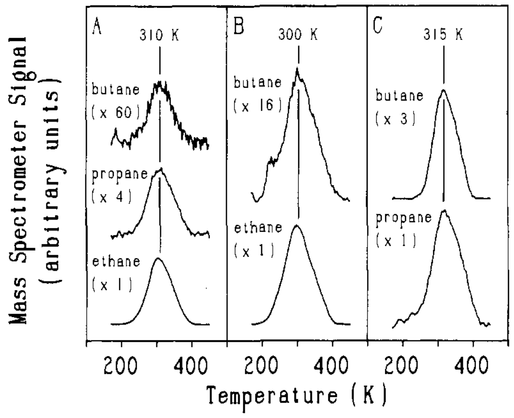

Figure 2. Temperature-programmed reaction spectra of the coadsorbed mixtures. Adsorption was performed at a surface temperature of 150 K. The heating rate during reaction was approximately 15 K/s. The ions detected were chosen so that only one alkane contributed to the signal. The multiplication factors are referenced to the most intense alkane signal from the coadsorbed mixture investigated and are uncorrected for degree of fragmentation and ionization efficiency in the mass spectrometer: (A) ethane (m/e = 30), propane (m/e = 44), and butane (m/e = 58) from multilayers of an ethanethiol/1-propanethiol/1-butanethiol mixture (ratio = 15:3:1) on Mo(110); (B) ethane (m/e = 30) and butane (m/e = 43) from multilayers of an ethanethiol/tetrahydrothiophene mixture (ratio = 6:11); (C) propane (m/e = 44) and butane (m/e = 58) from multilayers of a trimethylene sulfide/1-butanethiol mixture (ratio = 9:1).

We report here that coadsorbed cyclic sulfides $C_nH_{2n}S$ (n = 3, 4) and linear thiols $C_mH_{2m+1}SH$(m = 2, 3, 4) react during a temperature-programmed reaction experiment to form alkanes C_nH_{2n+2} and C_mH_{2m+2} at exactly the same temperature. These experiments lend powerful support to our proposal that cyclic sulfides and straight chain thiols react on Mo(110) by way of a thiolate intermediate.

If multilayers of an ethanethiol/1-propanethiol/1-butanethiol mixture (ratio = 15:3:1)[4] were adsorbed on Mo(110), the expected products were detected in a temperature-programmed reaction

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(1) Roberts, J. T.; Friend, C. M. *J. Am. Chem. Soc.* **1986**, *108*, 7204-7210.

(2) Roberts, J. T.; Friend, C. M. *J. Am. Chem. Soc.* **1987**, in press.

(3) Roberts, J. T.; Friend, C. M., in preparation.

(4) The coadsorbed mixtures described in this work were prepared by mixing the adsorbate molecules in the adsorbate reservoir, so that the molecules were simultaneously adsorbed on the crystal. The ratios are estimated from the mass spectra of the gaseous mixtures. In all cases the relative intensities of the multilayer desorptions were in agreement with the ratios of the gaseous mixtures.

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experiment. Molecular hydrogen, from total decomposition of some fraction of the adsorbate mixture, evolved in two peaks, at 370 and 580 K. Ethene, propene, and butene were detected at approximately 350 K. Because of overlapping mass spectral cracking fractions, the temperatures of the alkene peaks could not be accurately determined, but they were certainly very close and probably identical. Finally, ethane, propane, and butane evolved in peaks of identical line shape at 310 K (Figure 2A). The hydrocarbon yields were consistent with those previously measured for the individual thiols, based on the integrated mass spectral intensities.[1-3] Coadsorption of two different ethanethiol/1-propanethiol/1-butanethiol mixtures (ratios = 0:4:1, 15:3:1) resulted in alkane production at slightly different temperatures (315 and 320 K, respectively). However, for all of the thiol mixtures investigated, the ethane, propane, and butane temperatures were identical. Therefore, the kinetics of the process leading to alkane production from the three alkyl thiols are identical and are not affected by the length of the alkyl chain. The slight differences in the peak temperatures that are detected for different ratios of ethanethiol/1-propanethiol/1-butanethiol and when the thiols are reacted individually[1-3] are tentatively attributed to differences in the surface carbon, sulfur, and/or hydrogen stoichiometry, although the stoichiometries were not determined.

Similar coadsorption experiments were performed by coadsorbing one of the cyclic sulfides, tetrahydrothiophene, or trimethylene sulfide with a thiol. In Figure 2B are shown the temperature-programmed reaction spectra of ethane and butane from the coadsorption of ethanethiol and tetrahydrothiophene (ratio = 6:1) on Mo(110). The ethane and butane peak temperatures and line shapes were identical within experimental error. For the tetrahydrothiophene/ethanethiol ratio represented by Figure 2B, alkane evolution occurred at 300 K. The experiment was repeated for three different ethanethiol/tetrahydrothiophene ratios (6:1, 9:1, and 15:1), and in all cases the two alkanes evolved at the same temperature, although the peak temperature depended slightly on the adsorbate ratio. Figure 2C shows the temperature-programmed reaction of propane and butane from a 1:2 1-butanethiol/trimethylene sulfide mixture. Propane evolution from trimethylene sulfide proceeded at 315 K, as did butane evolution from 1-butanethiol. Again, the peak temperatures and line shapes were identical, regardless of the 1-butanethiol/trimethylene sulfide ratio in the coadsorbed mixture (1:9, 1:4, or 1:2). In both coadsorption experiments it was impossible to compare the temperatures of the alkene peaks because of overlapping mass spectral cracking products. Also, in the case of trimethylene sulfide, a cyclopropane peak at 190 K[5] partly overlapped with the propene peak, preventing accurate temperature determination. The relative yields in the coadsorption experiments are consistent with those measured for the individual reactants.[1-3]

These experiments are confirming evidence that tetrahydrothiophene and trimethylene sulfide decompose to alkanes and alkenes on Mo(110) by way of a common intermediate, proposed to be a surface thiolate. Furthermore, the coincidence of the alkane peak temperatures from the cyclic sulfides and the thiols suggests that the slow step in the desulfurization of trimethylene sulfide and tetrahydrothiophene to alkanes and alkenes is decomposition of the surface thiolate, not ring opening. Finally, the thiol coadsorption experiments demonstrate that the kinetics of alkane formation from the thiolate are independent of the number of carbon atoms in the thiolate. Differences in the hydrocarbon evolution temperatures observed when the individual thiols were adsorbed[1-3] are attributed to the effect of surface carbon, sulfur, and/or hydrogen coverage. Reaction of a coadsorbed mixture allows direct comparison of the reaction kinetics of the molecules in that mixture because coadsorbed molecules are by definition reacting on the same surface.

We are unaware of any instance where adsorbate coadsorption has been used to compare the relative kinetics of two related surface reactions. However, coadsorption experiments such as those described here may be of great use for that purpose when used with other surface chemical probes. The primary requirements for their success are that the coadsorbed molecules (a) not greatly affect each other's reaction kinetics and (b) not form islands of distinct phases.

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(5) Cyclopropane formation[2] occurs via a competing pathway at low temperature. Increased ring in trimethylene sulfide strain may account for the selectivity change observed.

Total Synthesis of (±)-2-Desoxystemodinone. A Novel Hydroxyl-Assisted, Intramolecular Ene Reaction†

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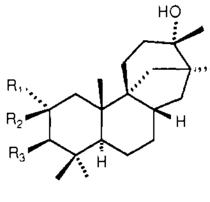
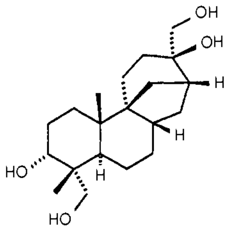
Structural elucidation in 1973 of a pair of novel tetracyclic diterpenes, stemodin (**1**) and stemodinone (**2**),[1] launched numerous synthetic ventures directed at these substances[2] and their congeners 2-desoxystemodinone (**3**)[3] and maritimol (**4**).[2b,4] A stereochemical variant of the stemodane ring system found in the antiviral, tumor inhibitory fungal metabolite aphidicolin (**5**)[5] has likewise provided a focus of intense synthetic interest.[6,7]



1, R_1 = OH, R_2 = R_3 = H
2, R_1 = R_2 = O, R_3 = H
3, R_1 = R_2 = R_3 = H
4, R_1 = R_2 = H, R_3 = OH



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The preparation of **6** in eight steps from geraniol was reported recently,[8] and we now describe an efficient conversion of this tricyclic ketone to (±)-**3**. The key transformation in this sequence is a unique hydroxyl-assisted ene reaction that establishes the stemodane framework from a conformationally restricted aldehyde precursor.

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† Dedicated to Professor George Büchi on the occasion of his sixty-fifth birthday.

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