pare C-terminal methyl esters and permethylated derivatives. The peptides included RVYVHPF; YGGFLK and HLGLAR; RYLPT, VHLTP, YPFPG, YGGFM, FFFFF, *t*-Boc-YAG[*N*-Me]FG-ol, YGGFL, YGGFL-NH₂, FLEEI, and FLEEL; ALAL, ALAL-OCH₃, FFFF, GPRP, *N*-acetyl-GPRP-OCH₃, GPGG, VAAF, VAAF-OCH₃, AGFL, GGFL, AGFM, VIHN, GGFM, and GGFM-NH₂; ALG, GLY, MLF, GLF, GGV, GGV-OCH₃, FFF, IPI, *N*-benzoyl-GGG, *N*-benzoyl-GHL, *p*-OH-*N*-benzoyl-GHL, and AAA-OCH₃; IN, AL, LG, LG-OCH₃, FF, LL, LL-OCH₃, GH, *N*-benzoyl-GK, *N*-benzoyl-GF, and GL-NH₂; and permethylated *N*-benzoyl-GF, *N*-acetyl-LG, *N*-acetyl-GGV, *N*-acetyl-YGGFL-NH₂, and *N*-acetyl-GGFM-NH₂.

Matrices used for fast atom bombardment (FAB) were 3-nitrobenzyl alcohol, 5:1 dithiothreitol/dithioerythritol, and 2:1 thioglycerol/glycerol and were obtained from Aldrich. The (M + Cat)⁺ complexes were prepared by mixing small amounts (micrograms) of the peptides with one of the FAB matrices, which had been previously saturated with an alkali iodide.

Mass spectrometric experiments were performed by using a VG 70-S, normal-geometry mass spectrometer. The mass spectrometer is equipped

with an Ion Tech saddle-field FAB gun and a commercial FAB ion source. Precursor ions were produced by bombarding the sample with 7-keV Ar atoms at an atom gun current of 2 mA. Ions produced were accelerated to 8-keV translational energy.

Fragment ions that were formed by collision-induced decomposition (CID) in the first field-free region between the ion source and the ESA were observed by using B/E linked scans. Helium was used as collision gas at a pressure of 1 × 10⁻⁶ Torr (∼50% beam reduction), as measured by the ion gauge in the first field-free region. Experiments were performed at a fragment ion resolution of approximately 1500 (10% valley), and magnet calibration was performed from a mixture of LiI, NaI, RbI, and CsI in H₂O. All spectra were acquired by using VG software, and CID spectra are the result of averaging 10–20 scans. Background spectra were acquired for all experiments to eliminate artifact fragment ions that might arise from chemical noise.

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Evidence for Facile and Selective Desulfurization: The Reactions of 2,5-Dihydrothiophene on Mo(110)

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Abstract: The reactions of 2,5-dihydrothiophene (2,5-DHT) on Mo(110) have been studied under ultrahigh vacuum conditions by using temperature-programmed reaction and X-ray photoelectron spectroscopies and found to be similar to those observed in organometallic complexes. Following adsorption of a saturation exposure of 2,5-DHT at 120 K, approximately 75% of the reactant molecules remain intact, while the remaining 25% immediately undergo sulfur elimination, yielding atomic sulfur and either weakly adsorbed butadiene (∼12%) or an unidentified strongly bound hydrocarbon intermediate (∼12%). During temperature-programmed reaction, the weakly adsorbed butadiene is desorbed above 140 K, while the strongly bound hydrocarbon nonselectively decomposes to gaseous dihydrogen and surface carbon. Surface sulfur is produced from both reactions. The primary reaction pathway for initially intact adsorbed 2,5-DHT is gaseous butadiene elimination. Molecular desorption near 200 K, and nonselective, irreversible decomposition beginning below 300 K are relatively minor competing pathways. Roughly two-thirds of the irreversibly adsorbed 2,5-DHT yields gas-phase butadiene and surface S in an intramolecular process, while one-third decomposes completely to H₂, surface carbon, and surface sulfur. The reactivity of 2,5-DHT is qualitatively different from the other four-carbon sulfur cycles studied under similar conditions, tetrahydrothiophene and thiophene. This is rationalized in terms of the degree of reorganization required in the transition state for intramolecular elimination, which makes such a process kinetically favorable for 2,5-DHT.

Introduction

A large number of studies aimed at advancing the understanding of industrially significant HDS reactions have employed thiophene (*c*-C₄H₄S) as a model substrate. Despite these efforts, the mechanism for thiophene desulfurization is not yet understood in detail, and a considerable amount of debate has been engendered over the principal reaction models. In one scheme, partial or full hydrogenation of the thiophene ring precedes desulfurization.[1] Alternatively, hydrogenolysis of the carbon–sulfur bonds may directly occur, forming 1,3-butadiene.[2] In a third model, best described as dehydrosulfurization, surface hydrogen is not required at all for thiophene desulfurization, as β-hydrogen elimination can produce diacetylene as the initial hydrocarbon product.[3]

On the basis of a recent series of organometallic studies, the mechanistic pathway for thiophene hydrodesulfurization processes has been proposed to proceed via nuclephilic attack at the 2-

position by hydride species, followed by protonation at the 3-position to give an η³-2,3-dihydrothiophene intermediate,[4,5] This intermediate isomerizes to a more thermodynamically favorable sulfur-bound 2,5-dihydrothiophene (2,5-DHT), which can then eliminate butadiene.[6,7]

Previous ultrahigh vacuum studies in our laboratory have examined the reactions of thiophene (*c*-C₄H₄S)[8,9] and tetrahydro-

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thiophene (c-C_4H_8S)[10] on Mo(110), Thiophene does not produce volatile hydrocarbon products during temperature-programmed reaction but instead completely decomposes to gaseous dihydrogen, surface carbon, and surface sulfur. Some molecular desorption is also observed at high coverages,[8] Indeed, we have recently found that sulfur is removed from thiophene upon adsorption on Mo(110) at 120 K, producing atomic sulfur and an unidentified hydrocarbon intermediate.[9] In contrast, tetrahydrothiophene produces gaseous hydrocarbon products, butane and butene, with approximately 25% selectivity.[10] The hydrocarbon products are formed via reaction of an adsorbed butyl thiolate (C_4H_9S-) produced from hydrogenolysis of a C–S bond in tetrahydrothiophene.

To further extend our understanding of desulfurization reactions, we have studied the reactions of 2,5-dihydrothiophene (2,5-DHT) on Mo(110). Although no previous ultrahigh vacuum studies of the surface chemistry of 2,5-DHT have been reported, microreactor studies over supported Re and Mo catalysts have shown that butadiene is the principal desulfurization product.[6] Reactor experiments in the presence of D_2 have suggested that the observed butadiene is directly eliminated from 2,5-DHT. Similarly, thermal reaction of the ($CO)_4Fe(2,5$-DHT) complex yields butadiene as the exclusive hydrocarbon product.[7] In our ultrahigh vacuum work, as in the cited catalytic and organometallic studies, we find that 2,5-dihydrothiophene forms butadiene as the principal desulfurization product. Unlike tetrahydrothiophene, 2,5-DHT does not undergo ring opening to form a surface thiolate during temperature-programmed reaction.

Experimental Section

All experiments were performed in an ultrahigh vacuum chamber with a base pressure of 2×10^{-10} Torr. This apparatus has been described in detail elsewhere.[11,12] Temperature-programmed reaction data were obtained by using a quadrupole mass spectrometer interfaced to an IBM PC for data collection. Under a multiplexing arrangement, up to 10 masses could be monitored during a single experiment. The mass spectrometer was housed in a differentially pumped cryoshield equipped with a rotatable aperture which served to minimize detection of desorption products not originating from the crystal face. Unless otherwise specified, all reactant exposures were made at a crystal temperature of 120 K. Because the Mo(110) crystal was radiatively heated without a temperature controller, the sample heating rate during temperature-programmed reaction was nonconstant, dropping reproducibly from ~14 to 10 K/s between 120 and 200 K, and decreasing more slowly to 6 K/s between 200 and 750 K.

X-ray photoelectron spectroscopy experiments were performed by using 1253.6-eV Mg $K\alpha$ illumination (15 kV, 300 W). Spectra were accumulated at an analyzer pass energy of 17.9 eV for 20 min in each experiment. Data were typically recorded in a multiplexed fashion at the $S(2p)$, $C(1s)$, $O(1s)$, and $Mo(3d)$ emission regions. Absolute binding energies were calibrated against the $Mo(3d_{5/2})$ photoemission peak at 227.7 eV[13] and are believed to be accurate to within ±0.2 eV. In annealing experiments, following reactant exposure at 120 K, the sample was briefly heated to the desired temperature and allowed to recool to 120 K prior to data collection. This method allowed observation of any irreversible reactions taking place as a result of heating.

A nonlinear background due to substrate photoemission was removed from each photoelectron spectrum by subtracting a smoothed spectrum recorded for clean Mo(110). In each case, spectra were fit with the minimum number of photoemission features required to reasonably reproduce the original data. Unless otherwise specified, an 80% Gaussian/20% Lorentzian composition was assumed for each peak, with a full width at half-maximum (fwhm) of 1.10 eV. Because of spin–orbit coupling in the $S(2p)$ final state, two peaks with a binding energy difference of 1.2 eV and a relative intensity of 1.8:1 are associated with each chemical state for sulfur. Due to the presence of a large background photoemission peak at ~161 eV from $Mo(3p_{3/2})$ electrons produced by stray Al $K\alpha$ radiation, the reported intensities for binding energies less than 163 eV in the $S(2p)$ spectra are estimated to have as much as ±10% variation from experiment to experiment.

2,5-Dihydrothiophene was provided by Prof. R. J. Angelici of Iowa State University and synthesized there by Moon-Gun Choi. Small
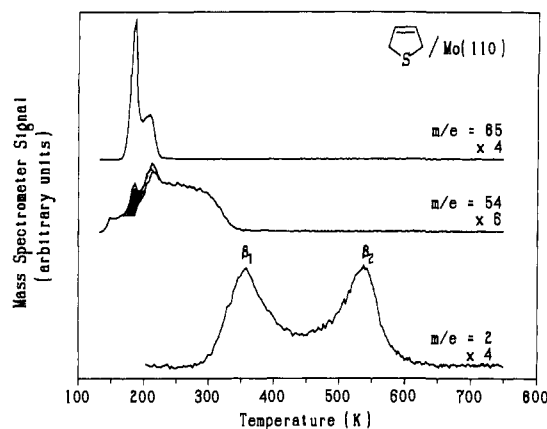
Figure 1. Temperature-programmed reaction spectra for a 35-s exposure of 2,5-dihydrothiophene made onto Mo(110). The 85 amu signal is the most intense fragment for 2,5-DHT, while the 54 amu signal is due both to the parent ion for 1,3-butadiene and to cracking of 2,5-DHT. The shaded region represents the estimated contribution of 2,5-DHT to the 54 amu data on the basis of its recorded fragmentation pattern.

amounts of pentane and butadiene in the 2,5-DHT sample were removed by using multiple freeze–pump–thaw cycles in a dry ice/acetone bath. The sample was degassed daily prior to use. X-ray photoelectron spectra of 2,5-DHT multilayers condensed on Mo(110) at 120 K exhibited a carbon-to-sulfur atomic ratio of 4.0 ± 0.2, as determined by the integrated $C(1s)$ and $S(2p)$ peak areas after correction for the relative atomic sensitivity factors.[13] This indicates that any butadiene contamination arising from 2,5-DHT reaction within the sample bottle or the dosing lines is, at most, ~5% of the adsorbed species. 1,3-Butadiene (Matheson, 99.5%), hydrogen sulfide (Matheson, 99.5%), hydrogen (Matheson, 99.9995%), deuterium (Matheson, 99.5%), and oxygen (Matheson, 99.98%) were used as received. All reactant exposures for temperature-programmed reaction and X-ray photoelectron spectroscopy experiments were made through a leak valve and directed doser with constant valve settings and backing pressures and are therefore reported only in terms of the exposure times.

Details of the preparation and cleaning procedures for the Mo(110) crystal have been given elsewhere.[10] The Mo(110)–p(2×2)–S surface was prepared by annealing multilayer exposures of hydrogen sulfide to 1400 K.[8] A 0.33 monolayer oxygen overlayer was prepared on Mo(110) by dosing controlled amounts of O_2 onto the clean crystal at a temperature of 1200 K.[14]

In the Auger electron spectroscopy experiments described below, peak height measurements were made following temperature-programmed reaction to 750 K. The C/S Auger peak height ratio ($R_{C/S}$) is defined in terms of the following derivative spectrum peak-to-peak heights:

$$R_{C/S} = C(272 \text{ eV})/[S(152 \text{ eV}) + Mo(148 \text{ eV})]$$

Similarly, the S/Mo Auger peak height ratio ($R_{S/Mo}$) is defined as

$$R_{S/Mo} = [S(152 \text{ eV}) + Mo(148 \text{ eV})]/[Mo(186 \text{ eV}) + Mo(221 \text{ eV})]$$

The S peak at 152 eV overlaps with a Mo peak at 148 eV. However, because the intensity of the Mo peak is small, it does not significantly affect the measured peak height for sulfur except at very low sulfur coverages. Accordingly, no effort was made to decompose the two features.

Results

Temperature-Programmed Reaction Spectroscopy. Gaseous 1,3-butadiene and dihydrogen are produced during temperature-programmed reaction of 2,5-dihydrothiophene on Mo(110) (Figure 1). For large exposures, 2,5-DHT desorption is also observed in two peaks at 185 and 210 K. The 185 K desorption increases indefinitely with increasing exposure and is therefore attributed to the sublimation of 2,5-dihydrothiophene multilayers. Dihydrogen is evolved in two broad features at 350 and 540 K, labeled β_1 and β_2, respectively. Evolution of 1,3-butadiene (54 amu) is observed over a broad temperature range, 140–330 K. A small portion of the signal at 54 amu is attributable to 2,5-DHT fragmentation within the mass spectrometer, and the estimated

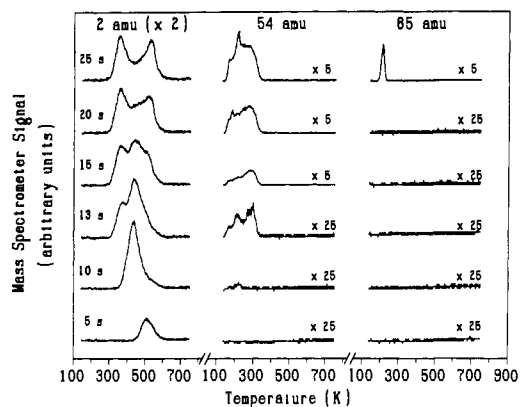(10) Roberts, J. T.; Friend, C. M. *J. Am. Chem. Soc.* **1986**, *108*, 7204.
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Figure 2. Temperature-programmed reaction spectra recorded as a function of 2,5-dihydrothiophene exposure onto Mo(110). The 85 amu signal is the most intense fragment for 2,5-DHT, while the 54 amu signal in these experiments is primarily due to 1,3-butadiene. A small amount of intensity arising from 2,5-DHT fragmentation has been subtracted from the 54 amu data for the 25-s exposure.

contribution from this source to the total 54 amu signal has been shaded in Figure 1. The identification of this product as 1,3-butadiene is based on the fragmentation pattern observed above 220 K for this desorption feature, which matches that recorded for an authentic sample of 1,3-butadiene.[15] No other gaseous hydrocarbon products are detected. Specifically, the absence of 1,2-butadiene and 2-butene production strongly argues against the possibility of 2,5-DHT reaction via a thiolate intermediate.[16]

There are three distinct regimes of reactivity as a function of 2,5-dihydrothiophene exposure (Figures 2 and 3). A relative exposure of 1.0 is defined herein as an exposure of 25 s, the dose above which desorption of 2,5-DHT multilayers is observed at 185 K during temperature-programmed reaction. At low exposures (relative exposure < 0.4), complete decomposition of 2,5-DHT to its atomic constituents is the predominant reaction. A small amount of butadiene formation near 200 K is also observed. In this exposure range, the postreaction C/S Auger ratio, $R_{C/S}$, remains reasonably constant at a value of ~0.23. Given the minimal amount of butadiene production, a value for $R_{C/S}$ of 0.23 is therefore taken as a reference for C$_4$S surface stoichiometry.

For greater relative exposures (0.4–0.8), the amount of butadiene produced increases sharply, while the dihydrogen yield is approximately constant. At the highest exposures (0.8–1.0), the amount of butadiene formed increases slightly and 2,5-DHT desorption is observed at 210 K. The normalized integrated desorption intensities of dihydrogen and 1,3-butadiene during temperature-programmed reaction are shown in Figure 3. In postreaction Auger spectra, $R_{C/S}$ drops steadily for initial relative exposures between 0.4 and 1.0 since carbon is leaving the surface during reaction in the form of butadiene. At reaction saturation, $R_{C/S}$ attains a value of 0.075, indicating a surface stoichiometry of roughly C$_{1.3}$S. On the basis of this figure, the branching ratio at saturation is estimated to be two-thirds butadiene formation and one-third irreversible decomposition.[17] From this ratio, the normalized dihydrogen and butadiene desorption yields shown above can be rescaled and summed to obtain the total product yield from irreversibly adsorbed 2,5-DHT as a function of initial reactant exposure (Figure 3).

The maximum amount of sulfur deposited from 2,5-DHT reaction on Mo(110) is roughly 0.23 monolayer. This coverage is estimated through comparison of the saturation value of $R_{S/Mo}$
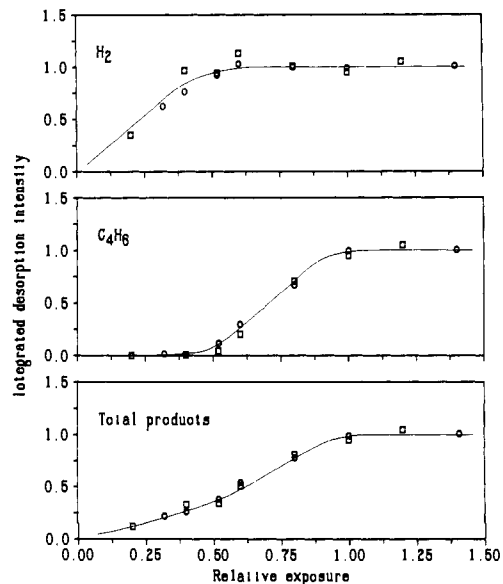
Figure 3. Integrated desorption intensity for dihydrogen and 1,3-butadiene as a function of initial 2,5-dihydrothiophene exposure onto Mo-(110). The integrated values have been normalized to the values at reaction saturation. A relative exposure of 1.0 corresponds to a 2,5-DHT dose of 25 s. Also shown is the total product yield obtained by assuming that 33% of the 2,5-DHT at reaction saturation decomposes to H$_2$ and adsorbed carbon and sulfur during temperature-programmed reaction, while 67% reacts to form butadiene and adsorbed S. The different symbols represent experiments performed on different days.

from 2,5-DHT reaction (0.84 ± 0.03), to the S/Mo Auger peak height ratio measured for Mo(110)-p(2×2)-S (0.90 ± 0.01), which has a sulfur coverage of 0.25 monolayer. Because no sulfur-containing products other than the parent molecule are desorbed during reaction, the ratio $R_{S/Mo}$ reflects the amount of 2,5-DHT that reacts on the surface, either nonselectively to afford atomic S, atomic C, and gaseous H$_2$ or selectively to yield atomic S and gaseous butadiene. $R_{S/Mo}$ does not account for any reversibly adsorbed 2,5-DHT. Consistent with the total temperature-programmed reaction yields (Figure 3), $R_{S/Mo}$ increases as a function of exposure up to a relative exposure of 1.0 (data not shown).

The rate of gaseous butadiene production above 180 K during temperature-programmed reaction of 2,5-DHT is limited by the rate of a surface reaction, whereas simple desorption kinetics also contribute to the rate at lower temperatures. This is evident from experiments using butadiene itself. On clean Mo(110), low coverages of 1,3-butadiene completely decompose during temperature-programmed reaction, producing H$_2$ and adsorbed carbon in the range 250–550 K. For high 1,3-butadiene coverages on Mo(110) and all coverages on Mo(110)-p(2×2)-S, butadiene desorbs in the range 140–180 K, with a maximum at 160 K.[18]

Temperature-programmed reaction of 2,5-dihydrothiophene in the presence of preadsorbed deuterium atoms provides evidence that 2,5-dihydrothiophene does not react via a thiolate intermediate. In these experiments, no incorporation of deuterium into the butadiene product was observed (data not shown). Similarly, no deuterium was incorporated into butadiene produced in experiments where D$_2$ was adsorbed *following* 2,5-DHT exposure. As the lack of butene evolution has already suggested, the failure of the butadiene product to incorporate surface deuterium excludes the possibility of surface 2-butene thiolate (CH$_3$CH=CHCH$_2$S−) formation from adsorbed 2,5-DHT, as C—H(D) bond formation is required for this process. Indeed, the lack of deuterium incorporation suggests that direct intramolecular elimination is the most likely route for producing butadiene from adsorbed 2,5-DHT.

(15) The fragmentation patterns of the other 54 amu hydrocarbons, 1,2-butadiene, 1-butyne, and 2-butyne, differ substantially from that of 1,3-butadiene: Heller, S. R.; Milne, G. W. A. *EPA/NIH Mass Spectral Database*; U.S. Government Printing Office: Washington, DC, 1978.

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(17) Only sulfur is deposited from the butadiene formation reaction, whereas carbon and sulfur in a ratio of 4:1 are deposited from nonselective decomposition. The branching ratio was thus calculated by using the relationship: C/S = 1.3 = 4x, where x is the fraction of 2,5-DHT that reacts nonselectively. The fraction that forms butadiene is then 1 − x.

(18) Very small amounts of propene evolution from butadiene in the ranges 200–270 K on clean Mo(110) and 240–320 K on Mo(110)-p(2×2)-S indicate that some selective C–C bond scission accompanied by C–H bond formation must also take place.
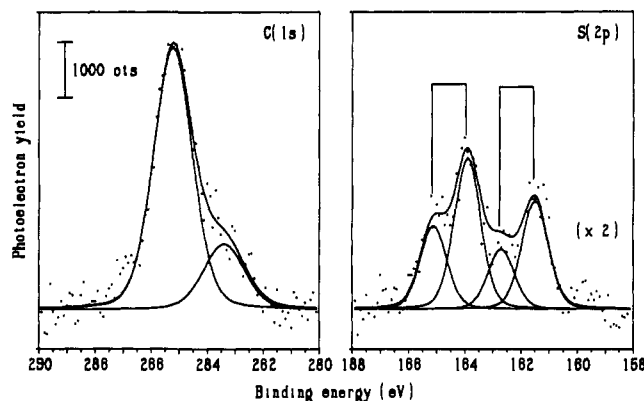
Figure 4. C(1s) and S(2p) X-ray photoelectron spectra for an unannealed relative 2,5-DHT exposure of 0.76 made at a crystal temperature of 120 K. Because of spin–orbit coupling in the S(2p) final state, two peaks with a binding energy difference of 1.2 eV and a relative intensity of 1.8:1 are associated with each chemical state for sulfur.

Table I. Curve-Fit Parameters for S(2p) and C(1s) X-ray Photoelectron Spectra of Unannealed 2,5-DHT (Relative Exposure = 0.76) at 120 K (Figure 4)[a]

S(2p)				
binding energy, eV	161.5	162.7	163.9	165.1
fwhm, eV	1.10	1.10	1.10	1.10
area, (counts·eV)/s	422	233	590	324
C(1s)				
binding energy, eV	283.4	285.2		
fwhm, eV	1.60	1.70		
area, (counts·eV)/s	2387	9056		

[a] All features are 80% Gaussian/20% Lorentzian.

X-ray Photoelectron Spectroscopy. The S(2p) X-ray photoelectron spectrum in Figure 4 shows that atomic sulfur and intact 2,5-DHT are present on the surface following 2,5-DHT adsorption at 120 K (relative exposure 0.76). Four peaks associated with two distinct chemical states for sulfur are clearly observed. One set of peaks, accounting for roughly 40% of the total peak area, has binding energies of 161.5 and 162.7 eV (Table I). Because the S(2p) binding energies reported for Mo(110)-p(2×2)–S are 161.3 and 162.5 eV,[19] we attribute this state to surface atomic sulfur. Another pair of peaks with about 60% of the total area lies at 163.9 and 165.1 eV. This state must arise from covalently bound sulfur and, on the basis of comparison with several reference molecules, is assigned to intact 2,5-DHT. S(2p) binding energies for thiolates on Mo(110) have considerably lower binding energies than those observed after 2,5-DHT adsorption, e.g., 162.6 and 163.8 eV for ethyl thiolate (C_2H_5S-).[20] Conversely, the S(2p) binding energies here are quite similar to those reported for cyclic sulfides such as pentamethylene sulfide ($c-C_5H_{10}S$) on Mo(110): 164.0 and 165.2 eV.[21] On the basis of this close agreement, the higher binding energy peaks are assigned to sulfur in intact 2,5-DHT.

The corresponding C(1s) X-ray photoelectron data are consistent with the presence of intact 2,5-DHT and one or more hydrocarbon fragments following 2,5-DHT adsorption at 120 K (Figure 4 and Table I). The C(1s) spectrum can be reasonably fit with two peaks at 283.4 (fwhm = 1.60 eV) and 285.2 eV (fwhm = 1.60 eV). On the basis of the presence of atomic sulfur in the S(2p) spectrum discussed above, the smaller peak at 283.4 eV in the C(1s) spectrum is assigned to one or more desulfurized hydrocarbons of unknown stoichiometry. The peak at 285.2 eV is at least partially assigned to intact 2,5-DHT on the basis of good agreement between this binding energy and those measured both for intact cyclic sulfides on Mo(110) and for 2,5-DHT itself adsorbed on an inert, oxygen-precovered Mo(110) surface (Θ_O

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~ 0.33).[14] For example, the C(1s) spectrum for 2,5-DHT on the oxygen-precovered surface is best fit with a single slightly broadened peak at 285.2 eV (fwhm = 1.30 eV), while the C(1s) binding energies previously reported for ethylene sulfide and pentamethylene sulfide adsorbed on Mo(110) are 285.2 (fwhm = 1.25 eV)[22] and 285.5 eV (fwhm = 1.5 eV),[21] respectively. The rather large half-width in the cases of 2,5-DHT and pentamethylene sulfide are attributed to unresolved chemical shifts between the inequivalent carbons,

Quantitative comparison of the C(1s) and S(2p) X-ray photoelectron spectra presented in Figure 4 shows that the C(1s) peak at 285.2 eV is not entirely derived from intact 2,5-DHT but must also be partially due to a desulfurization product. Specifically, while the S(2p) spectrum indicates that roughly 40% of the total sulfur is atomic in nature, only 20% of the total signal in the C(1s) spectrum has thus far been assigned to desulfurization products. As the experimentally determined ratio of carbon to sulfur on the surface is 4.1 ± 0.2, this discrepancy cannot be due to hydrocarbon desorption following desulfurization but prior to analysis.

X-ray photoelectron spectra recorded for 1,3-butadiene on Mo(110) suggest that the 285.2 eV peak in the spectrum for 2,5-DHT contains a contribution from adsorbed butadiene. At high 1,3-butadiene exposures, butadiene desorption with a maximum at 160 K is observed during temperature-programmed reaction, while C(1s) spectra recorded for these coverages following adsorption at 120 K show four peaks with equal intensities at 283.1, 283.8, 284.5, and 285.2 eV (fwhm = 1.10 eV) (data not shown). The two higher binding energy peaks at 284.5 and 285.2 eV are assigned to weakly adsorbed 1,3-butadiene, which eventually desorbs below 200 K. The two low binding energy peaks are attributed to decomposition products since they alone are observed at low 1,3-butadiene exposures for which only nonselective decomposition occurs.

Following a relative 2,5-DHT exposure of 0.76 at 120 K, a relative surface population of ~60% intact 2,5-DHT, ~20% weakly adsorbed butadiene, and ~20% adsorbed hydrocarbon fragments is estimated on the basis of the assumptions that all of the high binding energy S(2p) photoemission at 163.9 and 165.1 eV is attributable to molecularly adsorbed 2,5-DHT, while all of the low binding energy C(1s) photoemission at 283.4 eV is attributable to desulfurized hydrocarbon fragments. The amount of intact 2,5-DHT is easily seen to be ~60% from the S(2p) spectrum, and if 60% of the total C(1s) intensity is thereby assigned to intact 2,5-DHT, all in the broad peak at 285.2 eV, then the photoemission attributable to hydrocarbons is evenly divided between the low binding energy peak at 283.4 eV (desulfurized hydrocarbon fragments) and the remaining intensity near 285 eV (weakly adsorbed butadiene). Because C/S Auger measurements show that roughly 30–40% of the adsorbed 2,5-DHT for a relative exposure of 0.76 ultimately decomposes to H_2, atomic S, and atomic C, it appears that in addition to the hydrocarbon fragments formed at 120 K, further nonselective decomposition of initially intact 2,5-DHT must also occur during temperature-programmed reaction.

From X-ray photoelectron spectra recorded for an unannealed relative 2,5-dihydrothiophene exposure of 1.0 made at 120 K and the assumptions and arguments developed in the preceding discussion, the surface composition *at saturation coverage* is estimated to be 75% intact 2,5-DHT and 25% desulfurization products, with weakly bound butadiene and strongly adsorbed hydrocarbons present in roughly equal amounts (data not shown). The atomic ratio of carbon to sulfur measured in these spectra is also 4.0 ± 0.2,

In Figure 5, S(2p) spectra are shown for multilayer exposures of 2,5-DHT (relative exposure = 1.4) that have been briefly annealed to 190, 220, 260, 300, 450, and 750 K. The corresponding curve-fitting parameters are given in Table II. Up to 300 K, all of the spectra contain the same two sets of S(2p) features: a low binding energy state attributed to surface atomic sulfur and a high binding energy state assigned to intact 2,5-DHT.

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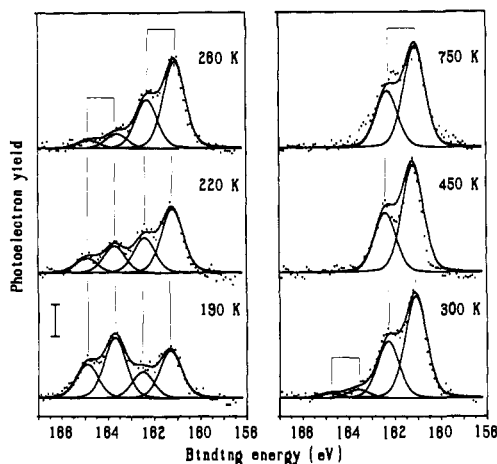
Figure 5. S($2p$) X-ray photoelectron spectra for annealed multilayer exposures of 2,5-DHT on Mo(110) (relative exposure = 1.4). Because of spin–orbit coupling in the S($2p$) final state, two peaks with a binding energy difference of 1.2 eV and a relative intensity of 1.8:1 are associated with each chemical state for sulfur. The intensity scale shown is equivalent to 1000 counts.

Table II. Curve-Fit Parameters for S($2p$) X-ray Photoelectron Spectra of 2,5-DHT (Relative Exposure = 1.4) After Annealing to the Indicated Temperatures (Figure 5)[a]

	S($2p_{3/2}$)	S($2p_{1/2}$)	S($2p_{3/2}$)	S($2p_{1/2}$)
190 K				
binding energy, eV	161.3	162.5	163.7	164.9
fwhm, eV	1.10	1.10	1.10	1.10
area, (counts·eV)/s	710	392	905	505
220 K				
binding energy, eV	161.2	162.4	163.7	164.9
fwhm, eV	1.10	1.10	1.10	1.10
area, (counts·eV)/s	962	527	404	224
260 K				
binding energy, eV	161.1	162.3	163.6	164.8
fwhm, eV	1.10	1.10	1.10	1.10
area, (counts·eV)/s	1308	728	220	121
300 K				
binding energy, eV	161.1	162.3	163.6	164.8
fwhm, eV	1.10	1.10	1.10	1.10
area, (counts·eV)/s	1517	844	128	69
450 K				
binding energy, eV	161.2	162.4		
fwhm, eV	1.10	1.10		
area, (counts·eV)/s	1612	897		
750 K				
binding energy, eV	161.2	162.4		
fwhm, eV	1.10	1.10		
area, (counts·eV)/s	1531	855		

[a] All features are 80% Gaussian/20% Lorentzian.

Above 300 K, only atomic sulfur is present. On the basis of the decrease in S($2p$) intensity between 190 and 220 K, we estimate that no more than 15% of an initial saturation coverage of 2,5-DHT is desorbed at 220 K during temperature-programmed reaction.

As the annealing temperature is raised from 220 through 300 K, the amount of intact 2,5-DHT observed in the S($2p$) X-ray photoelectron spectra steadily decreases, with a concomitant increase in the amount of atomic sulfur. While a small portion of this conversion is apparently due to nonselective 2,5-DHT decomposition, the major reaction producing atomic sulfur in this temperature range must be selective desulfurization yielding gaseous butadiene. This is consistent with the conclusion formed on the basis of 1,3-butadiene desorption temperatures that desulfurization most likely occurs throughout the temperature range from 200 to 300 K, resulting in the immediate desorption of butadiene.
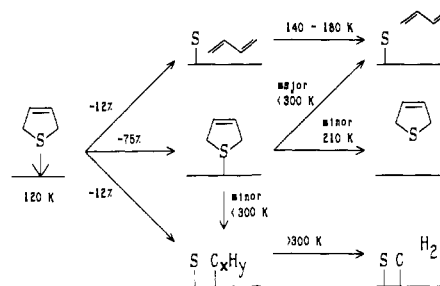
Figure 6. Proposed reaction scheme for 2,5-dihydrothiophene adsorbed to saturation on Mo(110). The mode of adsorption for intact 2,5-DHT is unknown, but only S-bonding has been observed in transition-metal complexes.

Corresponding C($1s$) X-ray photoelectron spectra confirm that the major reaction above 200 K is the selective desulfurization of 2,5-DHT accompanied by immediate butadiene desorption.[23] After annealing to temperatures as high as 300 K, at least two features are plainly evident in the C($1s$) spectra. Following the assignments made for unannealed 2,5-DHT exposures, a broad peak at ~285 eV is attributed to intact 2,5-DHT and, in the 190 K spectrum, also to weakly adsorbed butadiene. Between 190 and 300 K, this peak decreases steadily in intensity until it essentially vanishes. Near 283.5 eV, a peak assigned to one or more adsorbed hydrocarbons produced from 2,5-DHT desulfurization is observed. This feature increases slightly in intensity between 190 and 300 K. However, the total integrated C($1s$) intensity decreases in this temperature range as butadiene leaves the surface. The fact that the peak near 285 eV becomes weaker in parallel with the S($2p$) peaks assigned to intact 2,5-DHT while the low binding energy C($1s$) peak assigned to adsorbed desulfurization products grows only slightly clearly shows that the major reaction above 200 K is selective desulfurization with immediate butadiene evolution. Between 300 and 450 K, the spectra show that further reaction of the surface-bound hydrocarbon(s) takes place. This corresponds to the temperature range in which β_1 dihydrogen evolution is observed. Following annealing to 750 K, above the β_2–H$_2$ desorption, nonselective decomposition is complete, with a single peak attributed to surface atomic carbon at 282.7 eV in the C($1s$) spectrum.

Discussion

On the basis of the data presented above, we propose the scheme shown in Figure 6 for the reaction of 2,5-dihydrothiophene on Mo(110). For a saturation exposure, ~75% of the 2,5-DHT is molecularly adsorbed, while the remaining ~25% undergoes sulfur elimination following adsorption. The 2,5-dihydrothiophene that reacts at 120 K forms either weakly bound butadiene, which desorbs below 200 K, or a more strongly adsorbed hydrocarbon fragment which nonselectively decomposes to gaseous dihydrogen and surface carbon. The major reaction pathway for the 2,5-DHT that remains intact upon adsorption is the elimination of gaseous butadiene. Minor reaction pathways for the initially intact 2,5-DHT are molecular desorption near 210 K and nonselective decomposition to form gaseous dihydrogen, surface sulfur, and surface carbon. In total, roughly two-thirds of the irreversibly adsorbed 2,5-dihydrothiophene ultimately yields gaseous butadiene, while one-third is completely dissociated. The reactions of 2,5-dihydrothiophene on Mo(110) are quite similar to those reported for transition-metal complexes, which likewise induce the elimination of butadiene from the ligated 2,5-DHT.[24-26] While our experiments do not define the mode(s) of adsorption for intact

(23) Because the spectra are not well resolved, with photoemission from multiple species at ~285 eV, curve fitting was not performed on these data. However, in conjunction with the S($2p$) spectra discussed above, conclusions of a qualitative nature may still be formed.

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2,5-DHT on Mo(110), only sulfur-bound 2,5-DHT has been observed in transition-metal complexes.[24–26] We note also that determining the orientation of adsorbed 2,5-DHT on Mo(110) using near-edge X-ray absorption fine structure measurements[27] is expected to be reasonably difficult because intact 2,5-DHT is clearly not isolable on this surface at 120 K.

The reactivity of 2,5-dihydrothiophene on Mo(110) is substantially different from that of thiophene. Thiophene only undergoes complete decomposition to H_2, surface S, and surface C, with all desulfurization occurring upon adsorption at 120 K.[8,9] In contrast, although a significant amount of 2,5-dihydrothiophene also undergoes desulfurization upon adsorption, approximately two-thirds of the irreversibly adsorbed 2,5-DHT ultimately reacts to selectively form gaseous butadiene. In addition, approximately twice as much sulfur is deposited during the reaction of 2,5-dihydrothiophene as for thiophene (0.23 vs ~0.1 monolayer).

The high selectivity for gaseous butadiene formation from 2,5-DHT arises at least in part from the fact that it can desulfurize to form a product hydrocarbon in a direct intramolecular elimination reaction, whereas thiophene cannot. A minimum of two C–H bonds must be formed to make butadiene from thiophene, for example. The reasons for the complete absence of gaseous hydrocarbon formation from thiophene reaction on Mo(110) are not clear, although there is clearly a relative deficiency of surface hydrogen under the conditions of our experiments. On the other hand, this is most likely not the only contributing factor, as thiophene reaction on hydrogen-saturated Mo(110) also does not produce any gaseous hydrocarbons.[8]

Interestingly, gaseous butadiene evolution from 2,5-DHT is first observed for a total sulfur coverage of ~0.1 monolayer, essentially the same as the maximum sulfur coverage from thiophene reaction on Mo(110). These data suggest that at a sulfur coverage near 0.1 monolayer nonselective decomposition becomes kinetically less favored, thereby opening up other reaction channels. In the case of 2,5-dihydrothiophene, butadiene elimination is promoted, whereas thiophene simply desorbs under these conditions. Indeed, nonselective decomposition of thiophene is suppressed in favor of desorption on the sulfided Mo(110)–(2×2)–S surface.[8] This then suggests why thiophene desorption is preferred over hydrogenation or hydrogenolysis under ultrahigh vacuum conditions: Under catalytic conditions, the hydrogen pressure is higher, thereby allowing hydrogenation and hydrogenolysis to take place on a sulfided surface.

The reaction of 2,5-dihydrothiophene is also significantly different from that of the fully hydrogenated analogue, tetrahydrothiophene. As with thiophene, only half as much sulfur is deposited from the reaction of tetrahydrothiophene as compared to 2,5-dihydrothiophene. Although tetrahydrothiophene also readily desulfurizes, forming gaseous butane and butene, it is considerably less selective: ~25% C_4 products compared to 60% for 2,5-DHT.[10] Tetrahydrothiophene desulfurization proceeds via hydrogenolysis of a C–S bond to form adsorbed *n*-butyl thiolate, which then yields butane and butene. In marked contrast to tetrahydrothiophene, 2,5-dihydrothiophene clearly does not form hydrocarbon products via a surface thiolate.

The qualitative difference in the reactivities of tetrahydrothiophene and 2,5-DHT can be rationalized in terms of the degree of reorganization required for a direct elimination process for the two reactants. The absence of thiolate formation in the reaction of 2,5-dihydrothiophene suggests that direct elimination to form butadiene and atomic sulfur is kinetically more favorable than C–S bond hydrogenolysis. This is also supported experimentally by the fact that the kinetics for butadiene elimination from 2,5-DHT are considerably more rapid than those for hydrogenolysis of tetrahydrothiophene on Mo(110).[10] Indeed, intramolecular elimination reactions are known to compete favorably with thiolate formation for the strained cyclic sulfides, trimethylene sulfide and ethylene sulfide.[22,28] The kinetics for intramolecular elimination from the cyclic sulfides have been proposed to be controlled both by the enthalpy for ring opening (relief of ring strain) and by the degree of reorganization in the transition state for a concerted process.[29] However, both tetrahydrothiophene and 2,5-DHT have minimal ring strain, 1.7 kcal/mol,[30] so that their differing reactivities cannot arise from this factor.

The degree of reorganization of 2,5-DHT along the pathway for intramolecular elimination of butadiene is expected to be comparable to that for ethylene elimination from ethylene sulfide, since in both cases only C–C π bonds are formed. Recent theoretical work suggests that the barrier for concerted C–S bond breaking and C–C π bond formation is <0.1 eV for ethylene sulfide.[29] Indeed, experimentally, the selectivity and kinetics for ethylene elimination from ethylene sulfide are similar to those for butadiene formation from 2,5-DHT.[22] Ethylene is directly eliminated from ethylene sulfide with ~75% selectivity on Mo(110) at surface temperatures as low as 100 K, and, like 2,5-DHT, reaction via a thiolate intermediate is *not* observed.

In contrast to butadiene formation from 2,5-DHT, the formation of cyclobutane as a direct elimination product from tetrahydrothiophene is not expected to be kinetically favored.[16,28] The degree of reorganization required in forming cyclobutane from tetrahydrothiophene is likely to be similar to that for forming cyclopropane from trimethylene sulfide, which requires displacement of the carbons originally bound to sulfur by ~1.1 Å.[28] However, the substantially greater ring strain in trimethylene sulfide (19.4 kcal/mol) compared to that in tetrahydrothiophene (1.7 kcal/mol) is expected to result in a lower barrier for both elimination and ring-opening processes in the case of trimethylene sulfide,[16,30] and, indeed, both elimination of cyclopropane and hydrogenolysis to form propyl thiolate occur during its reaction on Mo(110), albeit with slower kinetics than for the analogous ethylene sulfide reactions. Theoretical studies show that for a concerted transition state the barrier for cyclopropane elimination from trimethylene sulfide is ~0.4 eV, substantially higher than the barrier for ethylene elimination from ethylene sulfide and in good agreement with experiment.[29] Taken together, the absence of ring strain in tetrahydrothiophene and the substantial amount of reorganization required in the transition state for a concerted elimination appear to render this pathway kinetically unfavorable.

Since direct elimination processes are relatively unfavorable for tetrahydrothiophene, other reaction pathways become important, such as nonselective decomposition or C–S bond hydrogenolysis. The relatively low selectivity for hydrocarbon formation during tetrahydrothiophene reaction is likely to be related to the need for surface hydrogen in both the ring-opening step to form the thiolate and thiolate hydrogenolysis to form butane. In the absence of preadsorbed hydrogen, thiolate formation and subsequent hydrocarbon production cannot take place without some preceding nonselective C–H bond activation in adsorbed tetrahydrothiophene. In fact, experimentally, the presence of preadsorbed hydrogen on Mo(110) increases the yield of butane from tetrahydrothiophene reaction by approximately a factor of 6 compared to the clean surface.[10] Furthermore, temperature-programmed reaction of 1-butanethiol (C_4H_9SH) on Mo(110) produces butane and butene with 70% selectivity via a thiolate intermediate formed by S–H bond cleavage upon adsorption.[10] Not only is nonselective C–H activation not needed for thiolate formation in the case of butanethiol, but S–H bond cleavage yields a stoichiometric amount of surface H.

The greater amount of sulfur deposition from 2,5-DHT compared to tetrahydrothiophene or thiophene is tentatively attributed to its ability to displace the butadiene product into a physisorbed state, thereby freeing adsorption sites for more reactant. Indeed, very small amounts of gaseous butadiene are evolved during isothermal 2,5-DHT reaction at low temperature,[31] and the X-ray

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(31) The amount of displaced butadiene is not quantitatively significant inasmuch as the surface C/S ratio determined by X-ray photoelectron spectroscopy is 4.0 ± 0.2.

photoelectron data suggest that the weakly bound butadiene state does not interact significantly with the molybdenum surface since it has a rather high C(1s) binding energy (~285 eV). Butadiene directly bound to the surface is expected to have a lower C(1s) binding energy due to final state screening. Interestingly, ethylene sulfide deposits 0.32 monolayer of sulfur during reaction, compared to 0.23 for 2,5-DHT and ~0.1 for tetrahydrothiophene and thiophene. Consistent with this explanation, in the case of ethylene sulfide, ethylene is directly evolved into the gas phase at 100 K so that the product does not occupy surface sites. In contrast, both tetrahydrothiophene and thiophene initially form strongly bound products.

The marked dependence of the reaction selectivity on the initial exposure of 2,5-dihydrothiophene (Figure 3) may be caused by a modification of the surface activity as the coverage of reaction products, such as sulfur and/or hydrocarbon fragments, increases. In experiments explicitly examining the effects of surface sulfur on desulfurization reactions, the presence of adsorbed sulfur was found to slow the kinetics for nonselective reaction of both sulfur-containing and hydrocarbon reaction intermediates on Mo(110).[32] A similar effect is proposed here since we have shown experimentally that some nonselective reaction occurs upon adsorption at 120 K. Since this process is apparently not reversible, postulated changes in adsorbate structure induced by intermolecular interactions at high coverage, thought to be important in the reactions of large thiols on Mo(110),[19] are not necessary for explaining coverage-dependent selectivities in the case of 2,5-dihydrothiophene.

The presence of *molecular* 2,5-dihydrothiophene on the surface also appears to modify the kinetics for butadiene elimination. A

pronounced maximum in the rate of butadiene evolution is observed just above the 2,5-DHT desorption peak near 210 K for large initial 2,5-DHT exposures (relative exposure > 0.8) (Figure 1). The coincidence of a maximum in the rate of butadiene elimination with the trailing edge of 2,5-DHT desorption suggests that 2,5-dihydrothiophene modifies its own reaction kinetics either through effects on the local electronic structure or by site blocking.

Conclusions. 2,5-Dihydrothiophene readily eliminates butadiene during temperature-programmed reaction on Mo(110). Approximately two-thirds of the irreversibly adsorbed 2,5-DHT yields gaseous butadiene and adsorbed sulfur via an intramolecular elimination process, while one-third is nonselectively decomposed on the surface without producing any gas-phase hydrocarbons. Selective desulfurization to form gaseous butadiene is favored at high initial 2,5-DHT coverages, possibly because of a moderation of the surface activity as decomposition products, such as sulfur, are deposited during reaction. The differences between the reactivity of 2,5-DHT and those of thiophene and tetrahydrothiophene are attributed largely to the fact that intramolecular elimination is kinetically more favorable for 2,5-DHT. Only minimal reorganization is required along the path for butadiene formation from 2,5-DHT, while thiophene has no stable gaseous elimination product and cyclobutane formation from tetrahydrothiophene would require substantial displacement of the carbons bound to the sulfur. These findings are generally consistent with previous studies of 2,5-DHT reactivity on high surface area catalysts and in organometallic complexes.

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Solvent and Secondary Kinetic Isotope Effects for the Microhydrated S_N2 Reaction of $Cl^-(H_2O)_n$ with CH_3Cl

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Abstract: We have calculated gas-phase rate coefficients and deuterium kinetic isotope effects (KIEs) for isotopic substitution in either the methyl group or the water of the title reaction with $n = 1$ and 2. The calculations are carried out by variational transition-state theory with semiclassical transmission coefficients, and they are based on 27- and 36-dimensional reaction-path potentials presented previously. A critical aspect of the potentials is that the solute part is based on high-level ab initio calculations. We also analyze the effect of deuterium substitution at methyl for the case of $n = 0$. We calculate an inverse effect for substitution at methyl both for bare solute ($n = 0$) and for microhydrated solute with $n = 1$ or 2. A detailed mode analysis shows that the inverse effect for the unhydrated reaction is dominated by C–H stretch contributions rather than by CH_3 deformations as is usually assumed in analyzing experimental data on solution-phase reactions. Furthermore, the C–H stretch contribution to the inverse α-deuterium KIE is essentially unaffected by microhydration. We find that for $n = 1$ the secondary KIE for substitution at methyl is larger than the solvent KIE, but for $n = 2$ the trend is reversed. The solvent KIEs are also interpreted in terms of the contributions of individual vibrational modes; in the $n = 2$ case the KIE is attributable to the breaking of a water–water hydrogen bond and the weakening of a water–chloride hydrogen bond.

Introduction

Gas-phase reactions of microhydrated ions provide opportunities for exploring fundamental concepts of condensed-phase kinetics

using the techniques, both experimental and theoretical, of few-body gas-phase dynamics.[1-12] In previous work[12] we have cal-

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