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Thioacylium Ions. Gas-Phase Ion-Molecule Reactions of Thioic and Dithioic Acid Derivatives

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Abstract: Thioacylium ions CH_3CS^+ and $C_2H_5CS^+$ can be generated in the gas phase from acylium ions CH_3CO^+ and $C_2H_5CO^+$ and ethanethioic and propanethioic acids by using ion cyclotron resonance techniques. Similarly, CH_3CS^+ is formed in the ion chemistry of acetyl sulfide. Evidence to support the thioacylium structure for these ions was obtained from the nature of their reactions (proton transfer and thioacylation) and from the fact that they behave indistinguishably from thioacylium ions generated by EI cleavage of *O*-methyl ethanethioate and methyl ethanedithioate, $CH_3C(S)XCH_3$, X = O, S. The heat of formation of CH_3CS^+ is estimated to be 210 kcal mol^{-1} and the proton affinity of thioketene, $CH_2{=}C{=}S$, as 201.5 ± 1.0 kcal mol^{-1}. Mechanism studies with isotopically labeled reactants show that association of acylium ions with neutral *S*-acyl compounds leads to thioacylium ions by attack of RCO^+ at sulfur and to acylium ions ($R'CO^+$) by attack at carbonyl oxygen. Contrary to their behavior in condensed phase, protonated *O*-methyl ethanethioate and methyl ethanedithioate do not react with water or methanol in the gas phase under ICR conditions, although the esters do react with *tert*-butyl alcohol to produce ions of the type $CH_3C(S)XCH_3\text{-}t\text{-}Bu^+$. These results show that thioacyl compounds, like their acyl analogues, do not readily add nucleophiles to the carbonyl carbon in the gas phase.

In contrast to the well-documented chemistry of acylium ions (RCO^+),[1] thioacylium ions (RCS^+) are relatively unknown. The simplest member of the series, HCS^+, has been detected in interstellar clouds[2] and in mass spectral fragmentation,[3] but attempts to prepare HCS^+ and higher homologues in condensed phase have been largely unsuccessful. Ionization of alkanethioic acids and esters in super acid media failed to form RCS^+,[4] although aryl thioacylium cations ($ArCS^+$) have been generated from thiobenzoyl chlorides by silver metathesis reactions (eq 1).[4,5] The

$$ArC({=}S)Cl + Ag^+SbF_6^- \xrightarrow{SO_2(l)} Ar\overset{+}{C}{=}S + SbF_6^- + AgCl \qquad (1)$$

corresponding reactions applied to the generation of *alkyl* thioacylium ions have been thwarted by the fact that the precursor alkanethiocarbonyl chlorides are unknown. Even the formation of thioacylium ions by a simple proton-transfer reaction to thioketenes ($R_2C{=}C{=}S$) appears unfeasible because of the instability of thioketenes. Both aldothioketenes and ketothioketenes rapidly polymerize except at very low temperatures (−196 °C) or when the ketene is highly hindered.[6] In contrast, cumulated thiocarbonyl compounds such as $O{=}C{=}S$, $S{=}C{=}S$, and $RN{=}C{=}S$ are remarkably stable. Yet attempts to form thioacylium ions by methylation (of COS at oxygen) led instead to acylium ions by attack at sulfur.[7]

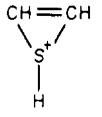
In general, thiocarbonyl compounds are thought to be less stable than carbonyl compounds because of relatively poor 2p–3p π overlap in multiple bonds between carbon and sulfur.[8] By this reasoning, ions of the type $RC{\equiv}S^+ \leftrightarrow RC^+{=}S$ are anticipated to be less stable than the oxygen analogues $RC{\equiv}O^+ \leftrightarrow RC^+{=}O$, and the limited thermodynamic data available bear this out, as will be discussed later. Certainly, the paucity of data on simple thioacylium ions such as 1-thioxoethylium, CH_3CS^+, and 1-thioxopropylium, $CH_3CH_2CS^+$, suggests that they are either thermodynamically unstable, highly reactive, or both. It was therefore surprising to discover that the major product ions in the gas-phase ion–molecule chemistry of ethanethioic acid (**1**) and propanethioic acid (**2**), as studied by ICR techniques, have the elemental composition of 1-thioxoethylium and 1-thioxopropylium ions, $C_2H_3S^+$ (*m/z* 59) and $C_3H_5S^+$ (*m/z* 73), respectively. The reactant ions were identified as the acylium ions CH_3CO^+ (*m/z* 43) and $C_2H_5CO^+$ (*m/z* 57), produced by electron-impact cleavage of the respective neutral thioic acid (eq 2). This reaction raises the

$$\begin{array}{llll} RC({=}O)SH & +\ RCO^+ & \rightarrow\ RCS^+ & +\ RC({=}O)OH \qquad (2) \\ \mathbf{1},\ R{=}Me & m/z\ 43 & m/z\ 59 & \\ \mathbf{2},\ R{=}Et & m/z\ 57 & m/z\ 73 & \end{array}$$

intriguing possibility that acylium ions can displace thioacylium ions from neutral *S*-acyl compounds.

Although the P/P + 2 abundance ratios for the product ions of *m/z* 59 and *m/z* 73 in reaction 2 confirm that they are sulfur-containing ions, this information alone cannot distinguish thioacylium ions from ions of isomeric structure. Several structures are conceivable for ions of composition $C_2H_3S^+$, such as **3**–**8**. Of

$CH_3C{\equiv}S^+$ **3** $CH_2{=}C{=}SH^+$ **4** $HC{\equiv}CSH_2^+$ **5** $CH_2{=}CHS^+$ **6**



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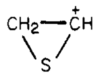

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these, structures **3** and **4**, representing 1-thioxoethylium and protonated thioketene, respectively, appear to be the most likely from the viewpoint that the formation would involve a minimum of bond reorganization.

The objective of the study we now report was to obtain evidence regarding the structures of ions produced in reaction 2 and to probe the possible pathways by which the ions are formed. In the course of this work, it was necessary to study the ion–molecule chemistry of various *S*-acyl compounds and esters of thioic and dithioic acids. The results are revealing as to the chemistry of thioacylium ions and the mechanisms of acyl and thioacyl transfer reactions in the gas phase.

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[1] Olah, G. A.; Germain, A.; White, A. M. In "Carbonium Ions"; G. A. Olah, P. v. R. Schleyer, Eds.; Wiley-Interscience: New York, 1976; Vol. 5, p 2049ff.

[2] (a) Prasad, S. S.; Huntress, W. T., Jr. *Astrophys. J.* **1982**, *260*, 590. (b) Thaddeus, P.; Guelin, M.; Linke, R. A. *Ibid.* **1981**, *246* (2), L41.

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[4] Olah, G. A.; Surya Prakash, G. K.; Nakajima, T. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 812.

[5] Lindner, E.; Karmann, H.-G. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 548.

[6] (a) Mayer, R.; Krober, H. *Z. Chem.* **1975**, *15*, 91. (b) Howard, E. G. U. S. Patent 3 035 030 1962; *Chem. Abstr.* **1962**, *57*, 13617. (c) Boonstra, H. J.; Arens, J. F. *Recl. Trav. Chim. Pays-Bas* **1960**, *79*, 866. (d) Wormsbaecher, D.; Edelmann, F.; Behrens, U. *Chem. Ber.* **1982** *115*, 1332.

[7] Olah, G. A.; Bruce, M. R.; Clouet, F. L. *J. Org. Chem.* **1981**, *46*, 438.

[8] Ohno, A. In "Organic Chemistry of Sulfur"; S. Oae, Ed.; Plenum Press: New York, 1977; Chapter 5.

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Table I. Major Primary and Product Ions from Thioic Acid Derivatives[a]

m/z	$CH_3C(O)SH$[b]	$C_2H_5C(O)SH$	$(CH_3CO)_2S$	$CH_3C(O)SCH_3$	$CH_3C(S)OCH_3$	$CD_3C(S)OCH_3$	$CH_3C(S)SCH_3$	$CD_3C(S)SCH_3$[e]
				Primary				
43	CH_3CO^+ (100)		CH_3CO^+ (100)	CH_3CO^+ (100)	CH_3CO^+ (5)			
46						CD_3CO^+ (6)		
57		$C_2H_5CO^+$ (100)						
59					CH_3CS^+ (22)		CH_3CS^+ (86)	
61								CD_2HCS^+ (7)
62						CD_3CS^+ (41)		CD_3CS^+ (60)
90				$M^{+\cdot}$ (50)	$M^{+\cdot}$ (100)			
93						$MH^{+\cdot}$ (100)		
106							$M^{+\cdot}$ (100)	
108								$CD_2HCS_2CH_3^{+\cdot}$ (13)
109								$M^{+\cdot}$ (100)
				Product				
59	CH_3CS^+, **43**[c]		CH_3CS^+, **43**					
73		$C_2H_5CS^+$, **57**						
77	MH^+, **43**							
91		MH^+, **57**		MH^+, **43**	MH^+, **43, 59**			
94						MH^+		
95						MD^+, **46, 62**		
107							MH^+, **86**[d]	
110								MH^+, **61**
111								MD^+, **61, 62**
119	MAc^+, **77**		MH^+, **43**					
135			$C_4H_7OS_2^+$, **59**					
147		MAc^+, **91**						
161			MAc^+, **119**					

[a] At 19 eV. Primary ions less abundant than 5% of the base peak are not listed. Pressure 10^{-6} torr. [b] Relative ion intensity in parenthesis, after 15 ms. [c] Precursor ions in boldface. [d] Minor formation of M_2H^+ m/z 213 after 400 ms. [e] 10% $CD_2HCS_2CH_3$.

Formation of Thioacylium Ions. A number of sulfur-containing carboxylic acid derivatives were screened as possible sources of thioacylium ions. In addition to ethanethioic acid (**1**), diacetyl sulfide (**9**) and *O*-methyl ethanethioate (**10**) were found to react with acetyl cations to give $C_2H_3S^+$ m/z 59, according to reactions 3 and 4. In the case of **10**, methyl acetate was added to provide a source of the acetyl cation. The isomeric ester *S*-methyl ethanethioate (**11**) did *not* react with acetyl ions to form m/z 59 (eq 5).

$$\underset{\mathbf{9}}{CH_3C({=}O)SC({=}O)CH_3} + \underset{m/z\ 43}{CH_3CO^+} \rightarrow \underset{m/z\ 59}{CH_3CS^+} + CH_3C({=}O)OC({=}O)CH_3 \qquad (3)$$

$$\underset{\mathbf{10}}{CH_3C({=}S)OCH_3} + \underset{m/z\ 43}{CH_3CO^+} \rightarrow \underset{m/z\ 59}{CH_3CS^+} + CH_3C({=}O)OCH_3 \qquad (4)$$

$$\underset{\mathbf{11}}{CH_3C({=}O)SCH_3} + \underset{m/z\ 43}{CH_3CO^+} \not\rightarrow \underset{m/z\ 59}{CH_3CS^+} + CH_3C({=}O)OCH_3 \qquad (5)$$

Our approach to the determination of the structure of ions m/z 59 formed in reactions 2–4 was to generate ions of the same composition in alternate ways but with less ambiguity as to ion structure. A reasonable premise is that ions of the same composition derived from different sources most likely have the same structure if they exhibit the same chemical behavior.[9] Conversely, different behavior is anticipated for ions of different structure. We sought to generate CH_3CS^+ by electron impact cleavage of thioacyl compounds *O*-methyl ethanethioate (**10**) and methyl ethanedithioate (**12**) and to compare the behavior of these ions with those generated in reactions 2 and 3. As anticipated, both **10** and **12** produced m/z 59 as the major fragment ion (Table I), although **10** also produced CH_3CO^+ m/z 43 indicative of internal rearrangement of the ester methyl group from oxygen to sulfur. The relative abundance of the two primary fragment ions CH_3CO^+ m/z 43 and CH_3CS^+ m/z 59 was 1:5. This rearrangement has been noted previously.[10] As expected, the deuterium-labeled ester **10**-d_3 led only to labeled fragment ions CD_3CS^+ m/z 62 and CD_3CO^+ m/z 46. No further label scrambling was evident in their formation or in their subsequent reactions.

EI Fragmentation

$$\underset{\mathbf{10}}{CH_3C(S)OCH_3} \xrightarrow{5} \underset{m/z\ 59}{CH_3\overset{+}{C}S} \qquad \xrightarrow{1} \underset{m/z\ 43}{CH_3\overset{+}{C}O}$$

$$\underset{\mathbf{10}\text{-}d_3}{CD_3C(S)OCH_3} \xrightarrow{5} \underset{m/z\ 62}{CD_3\overset{+}{C}S} \qquad \xrightarrow{1} \underset{m/z\ 46}{CD_3\overset{+}{C}O}$$

$$\underset{\mathbf{12}}{CH_3C(S)SCH_3} \rightarrow \underset{m/z\ 59}{CH_3\overset{+}{C}S}$$

$$\underset{\mathbf{12}d_3}{CD_3C(S)SCH_3} \rightarrow \underset{m/z\ 62}{CD_3\overset{+}{C}S}$$

Reactions of Thioacylium Ions. The most important primary fragment ions and product ions formed in the ICR ion-molecule reactions of the thiocarboxylic acid derivatives **1**, **2**, and **9–12** are summarized in Table I. It can be seen from this table and from the time plot of Figure 1 that the thioacylium ions m/z 59 and 73 are surprisingly unreactive. They exhibit only two types of reaction, proton transfer and thioacylation, and it is important to note that the same reactions were observed irrespective of the

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(9) See: Lehman, T. A.; Bursey, M. M. In "Ion Cyclotron Resonance Spectrometry"; Wiley: New York, 1976; 110–123.

(10) Thomson, J. B.; Brown, P.; Djerassi, C. *J. Am. Chem. Soc.* **1966**, *88*, 4049.

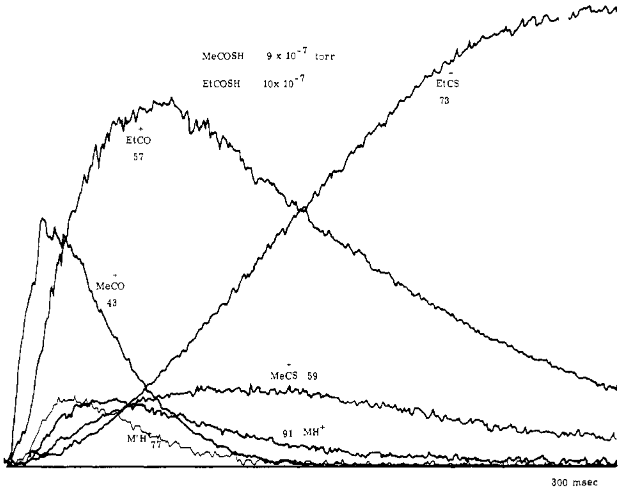

Figure 1. Plot of ion abundance with time in the ion chemistry of a mixture of ethanethioic and propanethioic acids under ICR conditions.

source of the reactant ion m/z 59. For example, diacetyl sulfide **9** led to a product ion of m/z 135 for which $C_2H_3S^+$ m/z 59 is the precursor (eq 6a). Double-resonance experiments and time

$$\underset{\mathbf{9}}{\mathrm{Ac_2S}} \xrightarrow{\mathrm{eV}} \underset{m/z\ 43}{\mathrm{CH_3CO^+}} \xrightarrow{\mathrm{Ac_2S}} \underset{m/z\ 59}{\mathrm{CH_3CS^+}} \xrightarrow{\mathrm{Ac_2S}} \underset{m/z\ 135}{\mathrm{C_4H_7OS_2^+}} + \mathrm{CH_2{=}C{=}O} \tag{6a}$$

$$\underset{\substack{\mathbf{10}\text{-}d_3\\ \mathbf{12}\text{-}d_3}}{\mathrm{CD_3C(S)XCH_3}} \xrightarrow{\mathrm{eV}} \underset{m/z\ 62}{\mathrm{CD_3CS^+}} \xrightarrow{\mathrm{Ac_2S}} \underset{m/z\ 138}{\mathrm{C_4H_4D_3OS_2^+}} + \mathrm{CH_2{=}C{=}O} \tag{6b}$$

plots confirmed the sequence of ion generation as m/z 43 → m/z 59 → m/z 135. When a *mixture* of diacetyl sulfide and the labeled ester $CD_3C(S)XCH_3$, X = O or S, was observed under similar conditions, both unlabeled and labeled ions m/z 135 and 138 were formed. The precursor to m/z 138 was CD_3CS^+ m/z 62 formed by EI cleavage of the labeled ester (equation 6b), whereas m/z 135 came from m/z 59 (equation 6a). The observation that m/z 62 from either **10**–d_3 or **12**–d_3 shows the same chemistry as m/z 59 from **9** suggests that the ions from the different sources are structurally the same. Their reactivity also appeared to be the same because the ratio m/z 59:m/z 62 was found to be equal to the ratio m/z 135:m/z 138 in reactions 6a and 6b.

In a similar set of reactions, ions having m/z 59 generated in reaction 2 were observed to react with vinyl acetate as an added neutral to produce m/z 103 (eq 7a). When m/z 62 was generated

$$\underset{\mathbf{1}}{\mathrm{CH_3C({=}O)SH}} \xrightarrow{\mathrm{eV}} \underset{m/z\ 43}{\mathrm{CH_3CO^+}} \xrightarrow{\mathbf{1}} \underset{m/z\ 59}{\mathrm{CH_3CS^+}} \xrightarrow{\mathrm{CH_3CO_2CH{=}CH_2}} \underset{m/z\ 103}{\mathrm{C_4H_7OS^+}} + \mathrm{CH_2{=}C{=}O} \tag{7a}$$

$$\underset{\substack{\mathbf{10}\text{-}d_3\\ \mathbf{12}\text{-}d_3}}{\mathrm{CD_3C({=}S)XCH_3}} \xrightarrow{\mathrm{eV}} \underset{m/z\ 62}{\mathrm{CD_3CS^+}} \xrightarrow{\mathrm{CH_3CO_2CH{=}CH_2}} \underset{m/z\ 106}{\mathrm{C_4H_4D_3OS^+}} + \mathrm{CH_2{=}C{=}O} \tag{7b}$$

from $CD_3C(S)XCH_3$ in the presence of vinyl acetate, m/z 106 was formed (eq 7b). Again, the implication is that thioacylium ions produced by EI cleavage of $CH_3C(S)XCH_3$ are structurally the same as the ions of the same composition produced in reactions 2–4.

The dominant reaction in the ion chemistry of *O*-methyl ethanethioate and methyl ethanedithioate is proton transfer to form

Table II. Heats of Formation ($\Delta H_f°$, kcal mol^{-1}) of Acylium and Thioacylium Ions[a]

HCO^+	ref	CH_3CO^+	ref	HCS^+	ref	CH_3CS^+	ref
204	15d[b]	162.6	14a	233 ± 2	17	227	14a
193	15d[c]	155.5	11b[e]	259.2	18	210	this work
198	15e	154.6	11a[e]	256.7	19		
199.4	12b	151	38	229 ± 5	16a[b]		
195	38			220 ± 5	16a[c]		
204	39			245	20[d]		

[a] $CH_2{=}C{=}OH^+$ and $CH_2{=}CSH^+$ are calculated to have heats of formation of 189.4 and 241.5 kcal mol^{-1}, respectively.[14a] [b] SCF level. [c] CI calcd. [d] MINDO/3. [e] See ref 22a.

the protonated parent MH^+ ions (see Table I). The major precursor to MH^+ is CH_3CS^+ m/z 59.

$$\underset{m/z\ 59}{\mathrm{CH_3CS^+}} + \underset{\substack{\mathbf{10},\ \mathrm{X}=\mathrm{O}\\ \mathbf{12},\ \mathrm{X}=\mathrm{S}}}{\mathrm{CH_3C({=}S)XCH_3}} \rightarrow \underset{\substack{m/z\ 91\\ m/z\ 107}}{\mathrm{(CH_3C({=}S)XCH_3)H^+}} + \mathrm{CH_2{=}C{=}S} \tag{8}$$

The product ions of reaction 8 are singularly unreactive. However, in the presence of a reactive neutral such as vinyl acetate or diacetyl sulfide, MH^+ ions from the *O*-methyl ester **10** underwent acylation according to eq 9.

$$\mathrm{(CH_3C({=}S)OCH_3)H^+} + \underset{\substack{\mathrm{X}=\mathrm{SAc}\\ \mathrm{X}=\mathrm{OCH{=}CH_2}}}{\mathrm{AcX}} \rightarrow \mathrm{(CH_3C({=}S)OCH_3)Ac^+} + \mathrm{HX} \tag{9}$$

Thermochemistry. In a related problem on the structure of ions of composition $C_2H_3O^+$, it was established that the acylium ion structure is about 45 kcal mol^{-1} more stable than the ketene structure $CH_2{=}C{=}OH^+$.[11,15a] The question at hand is whether thioketene, like ketene, prefers to protonate at carbon to produce thioacylium ions CH_3CS^+ or at sulfur to produce protonated thioketene $CH_2{=}C{=}SH^+$. The intrinsically higher gas-phase proton affinity of sulfur compounds compared to their oxygen analogues would suggest that the *difference* in energy between CH_3CS^+ and $CH_2{=}C{=}SH^+$ is *less* than the difference in energy between CH_3CO^+ and $CH_2{=}C{=}OH^+$,[12] but the magnitude of this difference is difficult to assess in the absence of reliable thermochemical data. Unfortunately, the approach that was used successfully to determine the energies of ions of structure CH_3CO^+

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(11) (a) Vogt, J.; Williamson, A. D.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 3478. (b) Davidson, W. R.; Lau, Y. K.; Kebarle, P. *Can. J. Chem.* **1978**, *56*, 1016. (c) Debrou, G. B.; Fulford, J. E.; Lewars, E. G.; March, R. E. *Int. J. Mass Spectrom. Ion Phys.* **1978**, *26*, 345. (d) Ausloos, P.; Lias, S. G. *Chem. Phys. Lett.* **1977**, *51*, 53.

(12) Consider, for example, the PA of S=C=S (166.8 kcal mol^{-1}), which is 43 kcal greater than the PA of O=C=O (128.6 kcal mol^{-1}): (a) Meot-Ner, M.; Field, F. H. *J. Chem. Phys.* **1977**, *66*, 4527. (b) Bohme, D. K.; Mackay, G. I.; Schiff, H. I. *Ibid.* **1980**, *73*, 4976.

(13) (a) Krantz, A.; Laureni, J. *J. Am. Chem. Soc.* **1981**, *103*, 486. (b) Schaumann, E.; Grabley, F. F. *Liebigs Ann. Chem.* **1979**, 1715. (c) Metzner, P. *Org. Compd. Sulphur, Selenium, Tellurium* **1979**, *5*, 118. (d) Bak, B.; Nielsen, O. J.; Svanholt, H.; Holm, A.; Toubro, N. H.; Krantz, A.; Laureni, J. *Acta Chem. Scand., Ser. A* **1979**, *A33*, 161. (e) Bock, H.; Solouki, B.; Bert, G.; Rosmus, P. *J. Am. Chem. Soc.* **1977**, *99*, 1663. (f) Georgiou, K.; Kroto, H. W.; Landsberg, B. M. *J. Chem. Soc., Chem. Commun.* **1974**, *18*, 739.

(14) (a) We are greatly indebted to Professor John Bartmess, Indiana University for the MNDO calculations reported in Table II. (b) A second estimate of $\Delta H_f°(CH_2{=}C{=}S)$ = 48.6 kcal. mol^{-1} can be made as follows: the $\Delta H_f°$ values for CO_2, COS, and CS_2 are −94.05, −33.96, and 28.05 kcal mol^{-1}, respectively, showing an increase of 60 and 62 kcal in energy for each successive replacement of carbonyl with thiocarbonyl. Accordingly, since $\Delta H_f°(CH_2{=}C{=}O)$ is −11.4 kcal mol^{-1}, then $\Delta H_f°(CH_2{=}C{=}S)$ is −11.4 + 60 = 48.6 kcal mol^{-1}.

(15) (a) Huber, H.; Vogt, J. *Chem. Phys.* **1982**, *64*, 399. (b) Berkowitz, J. *J. Chem. Phys.* **1978**, *69*, 3044. (c) Bruna, P. J.; Peyerimhoff, S. D.; Buenker, R. *Chem. Phys.* **1975**, *10*, 323. (d) Bruna, P. J. *Astrophys. Lett.* **1975**, *16*, 107. (e) Warneck, P. *Z. Naturforsch., A* **1971**, *26A*, 2047. (f) Nobes, R. H.; Radom, L. *Chem. Phys.* **1981**, *60*, 1. (g) Illies, A. J.; Jarrold, M. F.; Bowers, M. T. *J. Am. Chem. Soc.* **1983**, *105*, 2562.

is not possible for the sulfur analogue because the parent neutral thioketene is not a stable molecule; it has been prepared by several routes,[6,13] but its short lifetime has precluded full characterization of the compound, and no experimental data on its thermochemical properties have been reported. However, a MNDO calculation on the energies of **3** and **4** places the C-protonated structure **3** *lower* in energy than the S-protonated structure **4** by 14.5 kcal mol^{-1} (Table II).[14] As anticipated, this difference is less than between CH_3CO^+ and $CH_2{=}C{=}OH^+$ but remains significantly in the favor of the thioacylium ion CH_3CS^+.

A useful comparison can be made between the related formylium ion, HCO^+, and thioformylium ion, HCS^+. The formylium ion is calculated to be about 38 kcal mol^{-1} lower in energy than the isomeric ion COH^+,[12b,15f] whereas the thioformylium ion, HCS^+, is thought to be below CSH^+ by 110 kcal mol^{-1} or more.[16] It appears that C-protonation is overwhelmingly favored for the neutrals CO, CS, and $CH_2{=}C{=}O$ and somewhat less so for $CH_2{=}C{=}S$.

The heats of formation of the acylium ions HCO^+ and CH_3CO^+ are known with reasonable certainty (Table II) but comparable data for thioacylium ions is sparse and in poor agreement. Two recent values for the heat of formation of HCS^+ determined by photoionization methods are ≤233 kcal mol^{-1} [17] and ≤259.2 + 0.9 kcal mol^{-1};[18] an earlier value based on proton affinity and heat of formation data for carbon monosulfide was reported as 256.7 kcal mol^{-1},[19] whereas calculated values for $\Delta H_f^\circ(HCS^+)$ were reported as 229 ± 5,[16a] 220 ± 5,[16a] and 245 kcal mol^{-1},[20] depending on the type of calculation employed. If the assumption is made that the difference in energy between HCO^+ and HCS^+ is about equal to the difference in energy between CH_3CO^+ and CH_3CS^+, then the heat of formation of CH_3CS^+ is estimated to lie within the range 190–216 kcal mol^{-1}.[22a] The upper end of this range is also fixed by the restriction that reaction 2, R = CH_3, has to be exothermic to be observable under ICR conditions; it follows from the heats of formation of CH_3CO^+, CH_3COSH, and CH_3CO_2H taken as 155, −43, and −103.3 kcal mol^{-1}, respectively,[11ab,22] that $\Delta H_f^\circ(CH_3CS^+)$ must be less than 215 kcal mol^{-1} The MNDO calculated value of 227 kcal mol^{-1} in Table II is therefore too high.

Proton affinity data permit the range of values for ΔH_f°-(CH_3CS^+) to be narrowed somewhat. Thus, proton transfer from CH_3CS^+ to various neutrals in the ICR experiment allows the proton affinity of thioketene to be bracketed between that of ethyl acetate (PA = 202 kcal mol^{-1})[23] and *S*-methyl ethanethioate (PA = 201 kcal mol^{-1}).[23] Accordingly, the proton affinity of thioketene appears to be 201.5 ± 1.0 kcal mol^{-1} based on PA(NH_3) = 205.6 kcal mol^{-1}. Taking ΔH_f° of thioketene as 46.3 kcal mol^{-1}, as determined by the MNDO calculation;[14ab] the heat of formation of CH_3CS^+ is estimated from the PA data to be 210 kcal mol^{-1}. Taking this value for the heat of formation of **3**, a general statement can be made about the reactions in which **3** is formed (eq 2–4). The thermochemical data show that the reactions are driven in the direction of thioacylium ion formation because of the larger difference in energies between the *neutrals* than between the ions. The difference in the heats of formation of ethanethioic and acetic acids is about 60 kcal mol^{-1} but the difference in the heats of formation of thioacylium and acylium ions (CH_3CS^+ and CH_3CO^+, or HCS^+ and HCO^+) is 55 kcal mol^{-1} or less.[22,23] This means that the net reaction favors thioacylium ion formation. To the extent that the thermochemistry of reaction 2 can be extrapolated into condensed phase, it appears energetically feasible to generate thioacylium ions in condensed phase by the reaction of acylium ions with *S*-acyl compounds. Addition of the *S*-acyl neutral to a solution of an acetylium salt ($CH_3CO^+SbF_6^-$) in liquid SO_2 should result in the formation of the corresponding thioacylium salt ($CH_3CS^+SbF_6^-$) in order to produce the fully oxygenated neutral. To our knowledge, formation of thioacylium ions from acyl compounds has not yet been attempted.

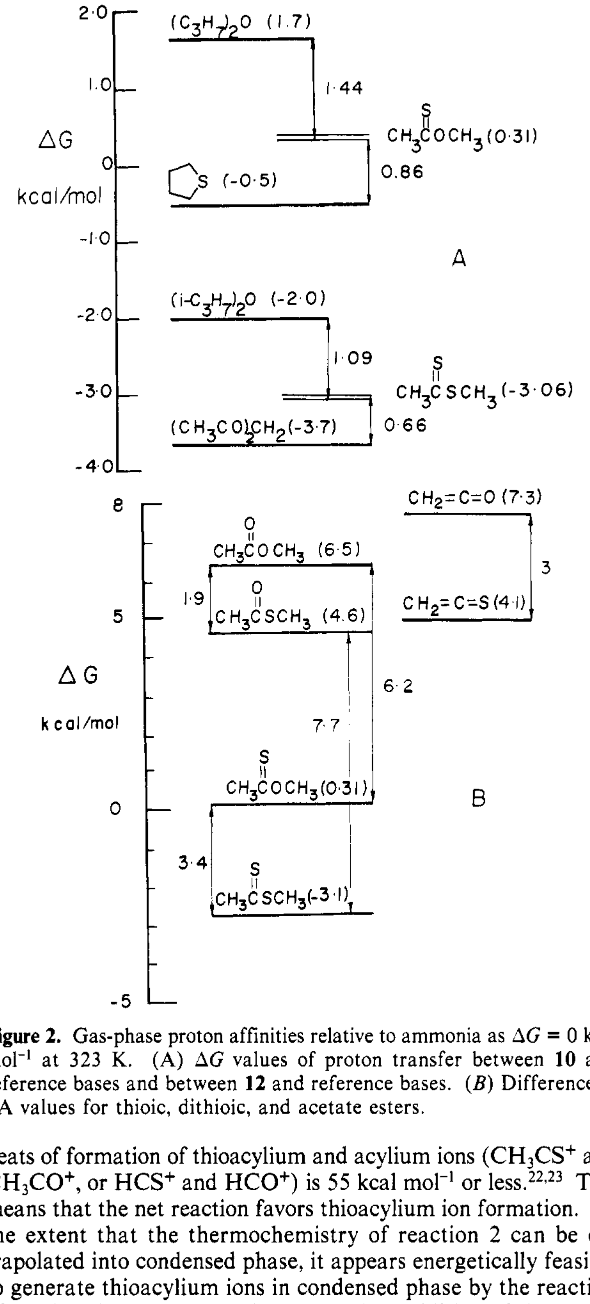

Figure 2. Gas-phase proton affinities relative to ammonia as ΔG = 0 kcal mol^{-1} at 323 K. (A) ΔG values of proton transfer between **10** and reference bases and between **12** and reference bases. (*B*) Difference in PA values for thioic, dithioic, and acetate esters.

Proton Affinities and Protonation Sites. The proton affinities of the thioic and dithioic esters used in this investigation are of interest relative to their oxo analogues. The PA's were determined by examination of proton-transfer equilibria generalized in eq 10.

$$CH_3C({=}X)YCH_3 + BH^+ \rightarrow (CH_3C({=}X)YCH_3)H^+ + B \qquad X, Y = O, S \tag{10}$$

The free energy of protonation of $CH_3C(S)OCH_3$ was found to lie between that of propyl ether and thiolane, whereas that of $CH_3C(S)SCH_3$ fell between diisopropyl ether and 2,4-pentanedione, as shown Figure 2A. From the known proton affinities of the reference bases,[23b] the PA of $CH_3C(S)OCH_3$ is estimated to be 0.31 ± 0.05 kcal mol^{-1} *less* than ammonia, and the PA of $CH_3C(S)SCH_3$ to be 3.06 ± 0.05 *greater* than ammonia. On the basis of PA(NH_3) = 205.6 kcal mol^{-1}, PA($CH_3C(S)OCH_3$) = 205.3 and PA($CH_3C(S)SCH_3$) = 208.7 kcal mol^{-1}.

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(21) Chekir, S.; Pauzat, F.; Berthier, G. *Astron. Astrophys.* **1981**, *100*, L14.

(22) (a) Based on a range of $\Delta H_f^\circ(HCS^+)$ of 233–259, $\Delta H_f^\circ(HCO^+)$ = 198, and $\Delta H_f^\circ(CH_3CO^+)$ = 155 kcal mol^{-1}. The heat of formation of the acetyl cation is from ref 11, a b, corrected for a proton affinity of NH_3 of 205.6 kcal mol^{-1}. (b) Benson, S. W. *Chem. Rev.* **1978**, *78*, 23.

(23) (a) Taft, Robert W. *NATO Adv. Study Inst. Ser. B*, **1979**, *B40*, 271–293. (b) Wolf, J. F.; Staley, R. H.; Koppel, I.; Taagepera, M.; McIver, R. T., Jr., Beauchamp, J. L.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 5417.

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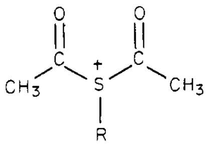
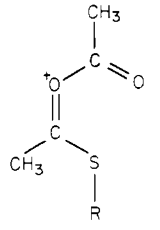
The point of interest is that the proton affinities of the *O*-methyl and *S*-methyl thioic esters differ by only 1.9 kcal, and the *O*- and *S*-methyl dithioic esters differ by 3.4 kcal. The small difference is typical of a substituent effect (OMe vs. SMe) on the gas-phase basicity of the carbonyl heteroatom.[23,25] A larger difference in proton affinities is anticipated in situations where proton transfer is to *different* atoms. The present data also bear this out because the proton affinities of $CH_3C(O)OCH_3$ and $CH_3C(S)OCH_3$ differ by as much as 6.2 kcal and of $CH_3C(O)SCH_3$ and $CH_3C(S)SCH_3$ by 7.7 kcal, as expected for proton transfer to *different* atom sites (see Figure 2B). The overall conclusion based on the proton affinity data is that, in all cases, proton transfer occurs to the hetero atom of the carbonyl or thiocarbonyl group. This result is consistent with the greater stability (lower energy) calculated for ions of structure $CH_3C(OH)_2^+$ compared with ions of oxonium structure $CH_3C(O)OH_2^+$,[26] and of ions $CH_3C(OH)SCH_3^+$ compared with $CH_3C(O)SHCH_3^+$.[27] Also, the relatively small difference in proton affinity between ketene and thioketene observed in this study (2.3 kcal mol^{-1}) is in keeping with the conclusion that both compounds protonate preferentially at carbon rather than at the heteroatoms.

Mechanism of Thioacylium Ion Formation. Quite how acylium ions displace thioacylium ions from *S*-acyl compounds in reactions 2 and 3 is not entirely obvious. Two of the conceivable collision complexes between the ion CH_3CO^+ and the neutral CH_3COSR are considered likely. In one, the ion attacks sulfur (complex I); in the other, the ion attacks the carbonyl oxygen (complex II).

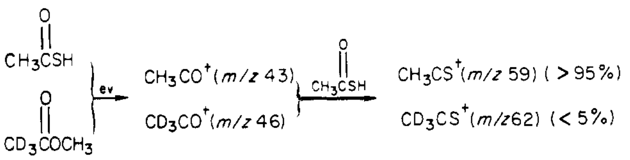


I, R = H, Ac



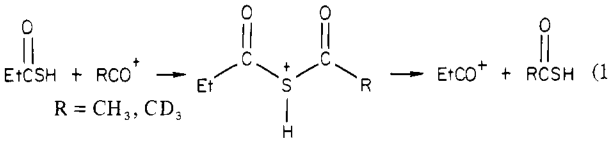
II

If the symmetrical complex I is formed, the acetyl group of the neutral reactant becomes indistinguishable from that of the ion, which means that the carbons in the product ion, CH_3CS^+, have an equal chance of originating from the reactant ion as from the neutral. In contrast, complex II is unsymmetrical and, if formed, should lead to CH_3CS^+ in which the carbons are expected to originate from the neutral reactant only. To test for the intervention of I or II, mixtures of ethanethioic acid and $CD_3CO_2CH_3$ were studied in order to provide a source of CD_3CO^+ *m/z* 46 for reaction 2. The *major* product ion observed from this mixture of neutrals was the *unlabeled* ion CH_3CS^+ *m/z* 59, although a minor amount (<5%) of the labeled ion CD_3CS^+ *m/z* 62 was also evident. Both the labeled and unlabeled acetylium ions were



precursors to *m/z* 59. This result means that the thioacylium ion produced in reaction 2 (R = Me) is *not* formed by way of I as the primary intermediate but is most likely formed by way of II. A reasonable process is outlined in Scheme I, which shows initial ion attack at oxygen to give II followed by an electrocyclic reaction with transfer of the labile R group (R = H, Ac) from sulfur to oxygen and elimination of the *O*-acyl neutral. If the R group is not labile, as in R = Me, no reaction occurs (eq 5).

However, a similar experiment performed with a mixture of propanethioic acid (**2**) and $CD_3CO_2CH_3$ gave results that were only partly consistent with Scheme I. Whereas the only thioacylium ion observed had *m/z* 73 corresponding to $EtCS^+$ (CD_3CS^+ *m/z* 62 was not formed), it was formed by the reaction sequence $CD_3CO^+ \rightarrow EtCO^+ \rightarrow EtCS^+$. That is to say, the acetylium ion CD_3CO^+ reacted with propanethioic acid to displace the 1-oxopropylium ion, $EtCO^+$, which in turn reacted with the neutral to form the 1-thioxopropylium ion, $EtCS^+$. In order for one acylium ion to displace another from the thioic acid, the ion must attack *sulfur* of the neutral to give Ib, as in eq 11.

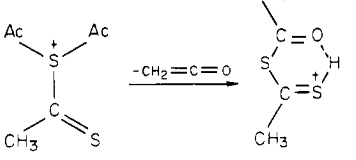


(11)

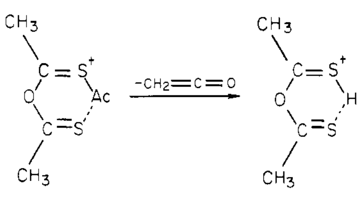
Ib

Similar results were observed with mixtures of ethanethioic and propanethioic acids. The fragment ions from the two neutrals, $MeCO^+$ *m/z* 43 and $EtCO^+$ *m/z* 57, may in principle each react with its own parent neutral and with the other neutral to produce $MeCS^+$ *m/z* 59 and $EtCS^+$ *m/z* 73. In actuality, $EtCS^+$ *m/z* 73 was the major product ion and, as can be deduced from Figure 1, appears to be formed by the sequence $MeCO^+ \rightarrow EtCO^+ \rightarrow EtCS^+$. In the first step of this sequence, the reactant ion evidently attacks sulfur of the neutral thioic acid to form $EtCO^+$ by way of Ib (eq 11), but in the second step the reactant ion attacks oxygen of the thioic acid to form $EtCS^+$ by way of II. It may at first appear surprising that an acylium ion would attack sulfur in one situation and oxygen in another, but the selective behavior can be understood from the energetics of the particular reactions involved. When the intermediate complex is symmetrical, as in complex I formed from CH_3CO^+ and $CH_3C(O)SH$, dissociation to acetylium ions is a thermoneutral process and is expected to be slower than the exothermic process of dissociation of the unsymmetrical complex II in Scheme I. However, in the reaction of CH_3CO^+ with $EtC(O)SH$, both complexes I and II are unsymmetrical, and both can dissociate along exothermic channels. The foregoing results show that acylium ions may react with *S*-acyl compounds by way of complexes I and II, but the relative importance of I and II in a given case will depend on the exothermicities of the reaction channels derived from each complex and the extent of bond reorganization necessary for the complex to dissociate to products.

Thioacylation Reactions. Besides proton transfer, the only other important reaction observed for thioacylium ions was thioacylation, as shown in reactions 6 and 7. An explanation is required for the formation of *m/z* 135 in the reaction of acetyl sulfide with CH_3CS^+ (reaction 6). There are two possible intermediates, complexes III and IV, which differ only in the position of attack of the ion on the neutral. Both complexes have an incipient acetylium ion, which on cleavage and proton transfer, could lead to *m/z* 135 and neutral ketene.



III *m/z* 135



IV *m/z* 135

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(25) Isolani, P. C.; Riveros, J. M.; Tiedman, P. W. *J. Chem. Soc., Faraday Trans. 2* **1973**, 1023.

(26) (a) Hopkinson, A. C.; Yates, K.; Csimadia, I. G. *J. Chem. Phys.* **1970**, *52*, 1784. (b) Mackay, G. I.; Hopkinson, A. C.; Bohme, D. K. *J. Am. Chem. Soc.* **1978**, *100*, 7460. (c) Benoit, F. M.; Harrison, A. G. *Ibid.* **1977**, *99*, 3980.

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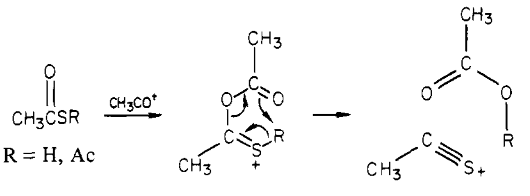
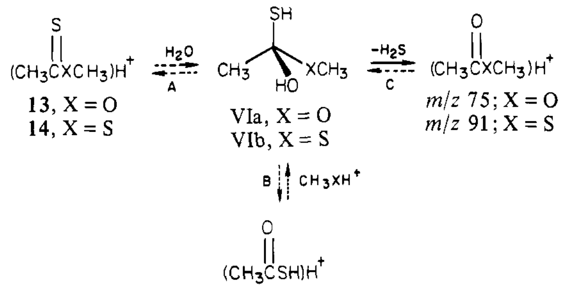
Scheme I

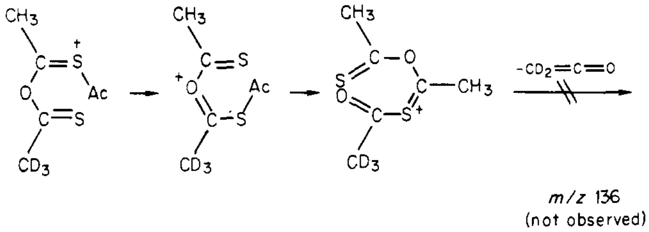


II

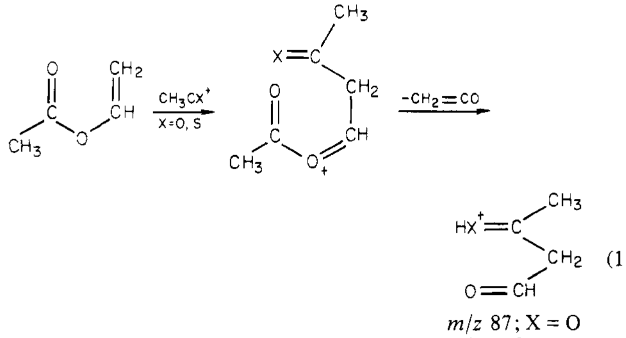
Scheme II



There is no obvious way to distinguish between these two possible complexes. Moreover, they could readily interconvert by thioacyl transfers between sulfur and oxygen. Acyl migration is also likely, but it is worth noting that when the ion CD_3CS^+ *m/z* 62 was generated from $CD_3C(S)SCH_3$ in the presence of diacetyl sulfide, only *m/z* 138 was formed (reaction 6b). The absence of *m/z* 136 includes extensive acetyl transfers within the complex prior to its dissociation to products.



A similar ambiguity as to the site of ion attack exists in the thioacylation of vinyl acetate (reaction 7). This reaction, which leads to *m/z* 103, is of minor importance, but it is analogous to the acylation of vinyl acetate, which was reported previously to proceed by the steps shown in eq 12 (X = O).[28] Thioacylation possibly proceeds in a like manner.



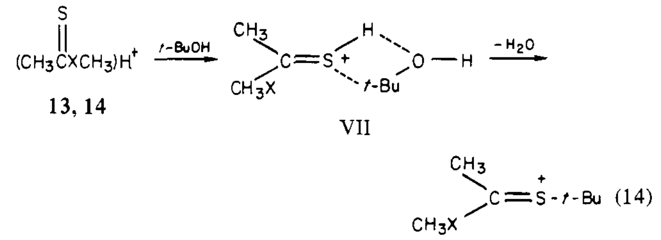
(12)

m/z 87; X = O
m/z 103; X = S

Hydrolysis and Alcoholysis of Thioic and Dithioic Esters. Hydrolysis of thioic and dithioic esters in condensed phase are acid- and base-catalyzed reactions that generally convert the parent thioacyl derivative to an acyl compound—ultimately the carboxylic acid (eq 13).[29] These reactions are believed to proceed by addition–elimination mechanisms involving tetracovalent addition intermediates. Comparable stepwise addition–elimination mechanisms have been reported in several gas-phase reactions of acyl compounds with *anions*,[30] but their prevalence in the gas-phase reactions of acyl compounds with *cations* under ICR conditions is doubtful. Previous work from this laboratory has documented that acyl transfer reactions to oxygen and sulfur nucleophiles proceed by way of ion–molecule complexes such as V rather than by tetracovalent addition intermediates such as VI.[31]

$$\mathrm{RC({=}S)SR} \xrightarrow{\mathrm{H_2O}} \mathrm{RC({=}O)SR} \xrightarrow{\mathrm{H_2O}} \mathrm{RC({=}O)OH} \qquad (13)$$

Scheme III

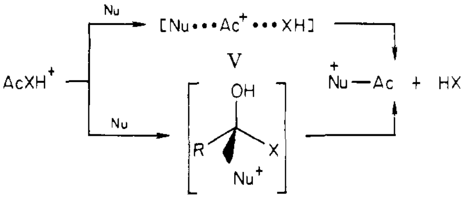


13, 14

VII

(14)

m/z 147; X = O
m/z 163; X = S



V

VI

The behavior of thioic and dithioic esters with water and alcohols in the gas phase provides a unique test for the intervention of tetracovalent intermediates. Take for instance the addition intermediates VIa and VIb visualized in Scheme II. If formed, each is expected to dissociate by the most energetically favorable pathway, A, B, or C. In earlier work we reported that protonated ethanethioic acid reacted with methanol (or methanethiol) under ICR conditions to produce *m/z* 75 (or *m/z* 91).[31] This means that if VIa (or VIb) is formed in this reaction by route B, then it dissociates exclusively along route C. We may then expect that if VIa (or VIb) can be formed by the addition of water to the protonated ester (route A), it will likewise dissociate along the path of lowest energy (route C) to give *m/z* 75 (or *m/z* 91).

However, the gas-phase hydrolysis of protonated methyl ethanethioate (**13**) gave *no* product ions attributable to reaction A. Labeled water (99% ^{18}O) and **13** produced no ions *m/z* 77 anticipated from the sequence A → C and no ions *m/z* 79 from the energetically less favorable sequence A → B, indicating that VIa is not formed.

Similarly, protonated methyl ethanedithioate **14** did not react with water in the gas phase. Labeled reactants (^{18}O-labeled water and deuterium-labeled ester $CD_3CS_2CH_3$) were used to exclude any possible ambiguity as to the source of product ions. However, the anticipated ions *m/z* 96, 97 or *m/z* 82, 83 by either the sequence A → C or A → B in Scheme II were not observed. Intermediate VIb is not then formed.

No reaction was observed between methanol and either of the protonated esters, **13** or **14**. In this respect, the behavior of **13** and **14** is entirely analogous to that of protonated methyl acetate and thioacetate, neither of which react with methanol.[31] With *tert*-butyl alcohol, the situation was different, and condensation took place in each case with elimination of water (eq 14). These results show that thioacyl transfer to simple alcohols does not occur, but alkyl transfer from the alcohol to the ester occurs when the alkyl group can form a relatively stable cation (e.g., *tert*-butyl). The alkyl transfer process is best explained by Scheme III.[32]

In summary, the evidence is negative for the intervention of

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[28] Caserio, M. C.; Kim, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 4624.

[29] See: Markley, K. S. In "Fatty Acids"; Markley, K. S., Ed.; Interscience: New York, 1964; Vol 3, Chapter XVII, pp 1717–1768.

[30] (a) McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1981**, *103*, 674. (b) Pellerite, M. J.; Braumann, J. I. *Ibid* **1981**, *103*, 676.

[31] Kim, J. K.; Caserio, M. C. *J. Am. Chem. Soc.* **1981**, *103*, 2124. Pau, J. P.; Kim, J. K.; Caserio, M. C. *Ibid.* **1978**, *100*, 3831.

[32] Beauchamp, J. L. In "Interactions Between Ions and Molecules"; Ausloos, P., Ed.; Plenum Press: New York, 1975.

addition intermediates of type VI in the reactions of thioic esters with hydroxylic nucleophiles. The few thioacylation reactions observed (reactions 6 and 7) and the acylation and alkylation reactions of thioic esters (reactions 9 and 14) can be explained rationally as displacement reactions involving complexes such as II, V, or VII.

Experimental Section

The pulsed ICR instrumentation utilized a trapped-ion analyzer cell[33] and multiple inlet valves to admit the several gaseous neutral compounds at pressures maintained at about 10^{-6} torr. Ions were generated from the neutral molecules by electron impact at 19 eV. All reaction sequences were confirmed through double-resonance experiments and scans of ion abundance with time.

All commercially available compounds employed in this study were purified before use until chromatographically pure. *O*-methyl ethanethioate (**10**) and methyl ethanedithioate (**12**) were prepared according to published procedures from the respective imidate ester hydrochlorides, $CH_3C(OCH_3)NH_2^+Cl^-$ [34] and $CH_3C(SCH_3)NH_2^+Cl^-$,[35] by treatment with H_2S in pyridine.[36,37] Deuterium-labeled esters *O*-methyl ethanethioate-d_3 and methyl ethanedithioate-d_3 were similarly prepared from the deuterium-labeled imidates $CD_3C(XCH_3)NH_2^+Cl^-$. However, extensive (40%) H-D exchange occurred on conversion of the methyl imidic ester X = S to methyl ethanedithioate with H_2S in pyridine, although no exchange occurred on conversion of the methyl ester X = O to *O*-methyl ethanethioate under the same conditions. It was necessary to keep the reaction time to within 5 h and the reaction temperature below −10 °C in order to reduce the extent of H-D exchange in the preparation of **12**-d_3. Even so, the maximum isotopic purity achieved in the thioacetyl methyl group was 90%, as determined by NMR and ICR analysis. Apparently, the exchange reaction occurs in the product ester rather than in the starting ester.

Acknowledgment. We gratefully acknowledge the support of this work in part by Grant GM-27319 awarded by the National Institute of General Medical Sciences, DHEW, and in part by Grant CHE-7807993 awarded by the National Science Foundation.

Registry No. CH_3CS^+, 59348-26-4; $EtCS^+$, 87371-73-1; $CH_3C(O)SH$, 507-09-5; $C_2H_5C(O)SH$, 1892-31-5; $(CH_3CO)_2S$, 3232-39-1; $CH_3C(O)SCH_3$, 1534-08-3; $CH_3C(S)OCH_3$, 21119-13-1; $CD_3C(S)OCH_3$, 87371-74-2; $CH_3C(S)SCH_3$, 2168-84-5; $CD_3C(S)SCH_3$, 81309-36-6.

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(33) McIver, R. T., Jr. *Rev. Sci. Instrum.* **1977**, *49*, 111; **1970**, *41*, 555.

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Studies on the Photochemical Reactions of α,β-Acetylenic Ketones with Tetramethylethylene

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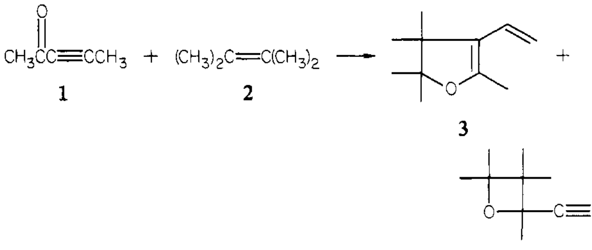
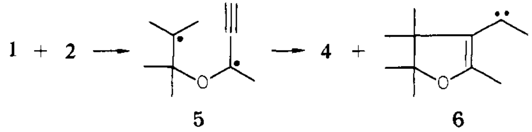
Abstract: With exclusion of acid, photolysis of mixtures of **1** and **2** in benzene yields **7a** and **8a**, which rearrange readily to **3**, the previously isolated product. Labeling experiments show that these dienes arise by intramolecular 1,4 transfer of hydrogen. Irradiation of **15a,b** and **17** with **2** yields **21a,b** and **22**, respectively. These products support the intermediacy of a carbene (as **6** and **16**), and irradiation in alcohols permitted capture of this intermediate as solvent adducts **25** and **26**. Quenching and concentration effects on the products from **1** and **2** suggest that oxetane **4** is formed by a singlet pathway and that the [3 + 2] products come from a quenchable alkynone triplet.

In an earlier publication Hussain and Agosta briefly described the photochemical reactions of 3-pentyn-2-one (**1**) with tetramethylethylene (**2**) to yield the vinyldihydrofuran **3** and the oxetane **4**.[3] They recorded several related examples and noted that the simplest mechanism accounting for their results (eq 1) was formation of a biradical intermediate **5** that could collapse to the [2 + 2] product **4** or alternatively close in the [3 + 2] fashion to carbene **6**, which on hydrogen migration would then yield **3**. These [3 + 2] cycloadditions are novel photochemical reactions; a carbene intermediate (as **6**) not only provides a credible explanation for them but also has precedent in mechanisms postulated for various other transformations of acetylenes.[3] We have now investigated the reactions of **1** and several related ketones with **2** in some detail and describe below our results concerning products, the existence of the suggested carbene intermediate, and the excited states involved in these processes.

Initial Products from 1 and 2. If particular care is exercised to exclude acid from the photochemical reaction of **1** with **2** and from the subsequent isolation of products, two new [3 + 2] adducts are obtained. To avoid traces of acid, solvent benzene was heated at reflux over calcium hydride and then distilled from molecular sieves before use, and a small amount of solid sodium carbonate



1 **2** **3** **4**



(1)

5 **6**

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(3) Hussain, S.; Agosta, W. C. *Tetrahedron* **1981**, *37*, 3301.