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### Structures and Relative Energies of Gaseous CSH<sub>3</sub><sup>+</sup> Ions<sup>1</sup>

Sir:

Recent collisional activation (CA) mass spectral studies of gaseous C<sub>2</sub>SH<sub>5</sub><sup>2a</sup> and C<sub>3</sub>SH<sub>7</sub><sup>2b,3</sup> ions showed that ions of thioalkoxide structures, R<sub>1</sub>R<sub>2</sub>CH—S<sup>+</sup>, rearrange rapidly to the more stable protonated thioaldehyde or thioketone isomers R<sub>1</sub>R<sub>2</sub>C=SH<sup>+</sup>. In contrast, protonated thioformaldehyde, H<sub>2</sub>C=SH<sup>+</sup> (a) has been presumed<sup>4</sup> to be slightly *less* stable than thiomethoxide, H<sub>3</sub>C—S<sup>+</sup> (b), based on the lower appearance potential (AP) of CSD<sub>3</sub><sup>+</sup> vs. CSHD<sub>2</sub><sup>+</sup> from CD<sub>3</sub>SH.<sup>5,6</sup> The latter result implies a dramatic difference between CSH<sub>3</sub><sup>+</sup> ions and their oxygen-containing analogues, for which heats of formation of 169 (H<sub>2</sub>C=OH<sup>+</sup>)<sup>9,10</sup> and ~195 kcal/mol (H<sub>3</sub>C—O<sup>+</sup>)<sup>10,11</sup> have been reported. In light of the importance of these discrepancies in questions concerning sulfur vs. oxygen stabilization,<sup>2,12</sup> we have undertaken a CA study of CSH<sub>3</sub><sup>+</sup> ions generated from a variety of precursors. The results, outlined in this communication, indicate that both a and b are stable under CA conditions (lifetimes >10<sup>-5</sup> s), but that H<sub>2</sub>C=SH<sup>+</sup> (a) is significantly more stable.

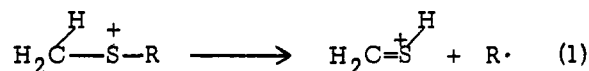
CA spectra of CSH<sub>3</sub><sup>+</sup> ions obtained as described elsewhere<sup>1,2,13</sup> are given in Table I. The spectra of CSH<sub>3</sub><sup>+</sup> produced from several alkanethiols, RCH<sub>2</sub>SH, using 70-eV ionizing electron voltage are identical within experimental error, and are assigned the H<sub>2</sub>C=SH<sup>+</sup> structure (a) based on the likelihood that such ions arise from the well-documented α-

cleavage reaction.<sup>14</sup> CA spectra of CSH<sub>3</sub><sup>+</sup> identical within experimental error are also obtained from methanethiol at low electron energy, from ethyl sulfide (by loss of methyl followed by rearrangement and loss of ethylene), and from a variety of other alkyl sulfides and thiols not listed in Table I.

The 70-eV spectrum of CSH<sub>3</sub><sup>+</sup> from dimethyl disulfide is significantly different from that of a in two regards: the disulfide spectrum has a higher relative abundance of *m/e* 15 (CH<sub>3</sub><sup>+</sup>), and gives a higher ratio of *m/e* 32 to 33 (S<sup>+</sup>/SH<sup>+</sup>). Both features are consistent with the fragmentation pattern expected for CH<sub>3</sub>—S<sup>+</sup> (b), providing firm evidence for the stability of the thioalkoxide isomer. However, the disulfide does not produce b exclusively; its CA spectrum changes to resemble more closely that of a upon going to low energies. The 70-eV ionization of CH<sub>3</sub>SSCH<sub>3</sub> gave the highest value of [b]/[a] found for any CSH<sub>3</sub><sup>+</sup> ions in this study. This CA spectrum was assumed to be that of pure b to analyze CSH<sub>3</sub><sup>+</sup> isomeric mixtures containing lower proportions of b; so these [b] values will represent maxima (Table I). The relative proportion of b was found to decrease on lowering the electron energy for both dimethyl disulfide and methyl methylsulfenylmethyl sulfide.

The apparent higher proclivity for a formation suggests that isomer a is more stable than b. Because this is in apparent contrast to the lower appearance potential observed for CSD<sub>3</sub><sup>+</sup> vs. CSHD<sub>2</sub><sup>+</sup> from CD<sub>3</sub>SH,<sup>4,6</sup> the CA spectra of these ions were examined; ions of both types formed with 70-eV electrons give CA spectra identical (Table I, after correction for shifted *m/e* values) with that of a within experimental error. Low energy spectra are similar, but of lower accuracy due to interference from overlapping CD<sub>3</sub>SH signals. The CA spectrum of CSH<sub>3</sub><sup>+</sup> formed from CH<sub>3</sub>SD at low electron energies also shows no evidence for the formation of b. Despite the larger experimental error in the low energy measurements, it would appear that it is isomer a, not b, that is formed at threshold energies from methanethiol, even for CSD<sub>3</sub><sup>+</sup> formed from CD<sub>3</sub>SH.<sup>15</sup>

The results can be interpreted using an alternative mechanism for the threshold energy loss of H from H<sub>3</sub>CSH to give H<sub>2</sub>C=SH<sup>+</sup> which involves an anchimerically assisted process previously suggested with regard to the C<sub>2</sub>SH<sub>5</sub> and C<sub>3</sub>SH<sub>7</sub> systems<sup>2</sup> (eq 1). For methanethiol (R = H) both this and α-



cleavage H loss would give a; for CD<sub>3</sub>SH the lower AP observed for loss of H could be due to a kinetic isotope effect. For dimethyl disulfide (R = SCH<sub>3</sub>) reaction 1 would compete with S—S cleavage to produce b; as a result of the tightness of the transition state for anchimeric vs. direct-cleavage reactions,

Table I. Collisional Activation Spectra of CSH<sub>3</sub><sup>+</sup> Ions

Compd	<i>m/e</i> of daughter ion <sup>a</sup>							Structure <sup>b</sup>
	12	13	14	15	32	33	34	
CH <sub>3</sub> SH <sup>c</sup>	1.4	3.1	9.0	1.1	35	50	5.3	a
12 eV <sup>d</sup>	1.8	4.7	9.2	1.2	36	48	4.8	a
CH <sub>3</sub> SD, <sup>e</sup> 14 eV (-D)	2.4	3.4	10.6	1.4	34	48	7.1	a
CH <sub>3</sub> CH <sub>2</sub> SH	1.4	2.7	9.3	0.6	35	51	7.4	a
C <sub>2</sub> H <sub>5</sub> SC <sub>2</sub> H <sub>5</sub>	2.0	3.8	10.5	0.8	34	49	6.8	a
CH <sub>3</sub> SSCH <sub>3</sub> <sup>c</sup>	1.8	3.4	8.5	6.2	39	41	8.4	b <sup>f</sup>
12 eV <sup>d</sup>	2.0	3.3	10.3	2.1	37	45	6.0	a (75%), b
CH <sub>3</sub> SOCH <sub>2</sub> SCH <sub>3</sub> <sup>c</sup>	1.6	2.4	7.9	5.1	38	45	5.2	a (20%), b
14 eV <sup>d</sup>	3.1	3.3	13.9	1.6	32	46	7.2	a (85%), b
CD <sub>3</sub> SH (-H) <sup>g</sup>	1.4	3.5	13.1	1.0	29	52	6.9	a
CD <sub>3</sub> SH (-D) <sup>h</sup>	2.0	3.1	11.4	0.6	36	47	5.4	a

<sup>a</sup> Abundances relative to total ion abundance = 100 for all ions shown except *m/e* 34, which is of lower accuracy due to the presence of <sup>34</sup>S from CH<sup>34</sup>S. <sup>b</sup> a, H<sub>2</sub>C=SH<sup>+</sup>; b, H<sub>3</sub>C—S<sup>+</sup> calculated from [15<sup>+</sup>]/[14<sup>+</sup>], ±15%. <sup>c</sup> Corrected for isotopic contributions to the *m/e* 47 precursor from large peaks at *m/e* 45 and 46. <sup>d</sup> Ionizing electron energy; in other cases 70 eV was used. <sup>e</sup> Contains ~7% CH<sub>3</sub>SH; so only ~55% of CSH<sub>3</sub><sup>+</sup> originates from CH<sub>3</sub>SD. <sup>f</sup> Arbitrarily assumed to be pure b (see text). <sup>g</sup> Spectrum of CSD<sub>3</sub><sup>+</sup>; *m/e* values adjusted for presence of D. <sup>h</sup> Spectrum of CSD<sub>2</sub>H<sup>+</sup>; *m/e* values adjusted for presence of D.

eq 1 should be more competitive at low electron energies. Under these conditions  $[a] \geq [b]$ , despite the unfavorable entropy of the transition state for a formation. This would suggest that  $\Delta H_f(a)$  is at least 5–10 kcal/mol less than  $\Delta H_f(b)$ ; however,  $\Delta H_f(b)$  derived by Lossing<sup>7</sup> from  $\text{CH}_3\text{S}^\bullet$  suggests this is an upper limit to the difference. Molecular orbital calculations (MINDO/3;<sup>12</sup> ab initio, to be reported in the full paper) are in general agreement with such relative stabilities.<sup>16</sup>

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## References and Notes

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- (15) Kinetic energy release values for  $\text{C}_3\text{H}_3^+ \rightarrow \text{C}_3\text{H}_2^+ + \text{H}_2$  have been found to be identical for ions with the nominal structures  $\text{CH}_3\text{S}^+$  and  $\text{CH}_2=\text{SH}^+$ , such as  $\text{CSD}_3^+$  and  $\text{CSD}_2^+$  from  $\text{CD}_3\text{SH}$ : A. G. Harrison unpublished work.
- (16) NOTE ADDED IN PROOF. A detailed study of the effect of ionizing electron energy shows that  $[b]/[a]$  reaches a maximum value at  $\sim 17$  eV, suggesting that higher energy b ions isomerize to a.

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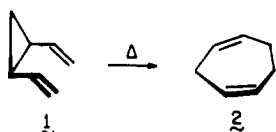
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## Impact of Methyl Imidate Functionality upon Cope Rearrangements. The Heteroatomic *cis*-1,2-Divinylcyclopropane Example<sup>1</sup>

Sir:

The irreversible thermal isomerization of *cis*-divinylcyclopropane (**1**) to 1,4-cycloheptadiene (**2**) has played a pivotal role in the development of our understanding of the Cope rearrangement. Although the pioneering efforts of Doering<sup>2</sup> and Vogel<sup>3</sup> did not result in the actual isolation of **1**, their findings set the stage for rapid development of this field in many directions. More recent work by Brown<sup>4</sup> and Schneider<sup>5</sup> has led to the successful preparation of **1** and permitted quantitative



measurement of its electrocyclic conversion to **2**. From the experimentally determined activation parameters ( $\Delta H^\ddagger = 19.4$  kcal/mol;  $\Delta S^\ddagger = -5$  eu), an appreciation is quickly gained of the driving force provided by release of strain in the three-membered ring.

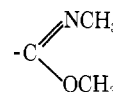
In the present study, we consider whether the ground-state

**Table I.** Kinetic Data and Activation Parameters for the Reversible Conversion of **4** to **5** ( $\text{Cl}_2\text{C}=\text{CCl}_2$  solution)

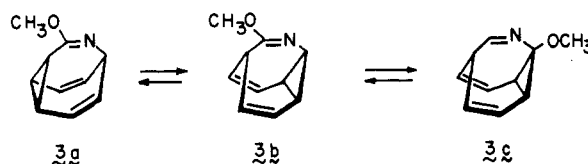
$T, ^\circ\text{C}$	$k_f (\times 10^5), \text{s}^{-1}$	$k_r (\times 10^5), \text{s}^{-1}$	Mol fraction of <b>5</b> <sup>a</sup>
110.0 <sup>b</sup>	3.03	0.978	0.76
110.0	3.1	0.98	0.76
120.0	7.7	2.7	0.74
120.0	8.3	3.0	0.74
130.0	17.7	6.88	0.72
130.0	17.3	6.08	0.74
	$\Delta H^\ddagger = 26.0 \pm 0.7$ kcal/mol	$\Delta H^\ddagger = 28 \pm 1$ kcal/mol	
	$\Delta S^\ddagger = -12 \pm 2$ eu	$\Delta S^\ddagger = -8 \pm 3$ eu	

<sup>a</sup> At equilibrium. <sup>b</sup> Experiments were conducted in sealed NMR tubes placed in a thermostated oil bath ( $\pm 0.1$  °C) and the progress of reaction was monitored by <sup>1</sup>H NMR (at ambient temperature).

destabilization intrinsic to such molecules as **1** can be used to advantage in the assessment of the magnitude of resonance stabilization available to simple diatomic structural units of the type  $\text{M}=\text{N}$ , or, in this specific instance, the *O,N*-dimethyl imidate moiety



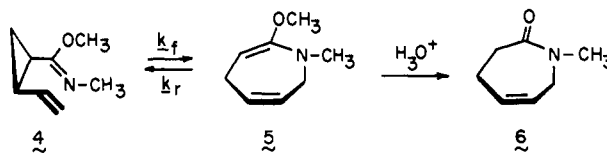
Our interest in this question arose from past studies of 2-methoxyazabullvalene (**3**)<sup>6</sup> where the activation energy for conversion of **3a** to **3b** (12 kcal/mol) was found to be significantly lower than that required for isomerization to **3c** (15–20 kcal/mol) where deconjugation of the imino ether necessarily occurs.<sup>7</sup>



The principal compound of interest, **4**, was prepared conveniently from *cis*-2-vinylcyclopropanecarboxylic acid<sup>8</sup> by adaptation of a procedure developed earlier for the desvinyl system:<sup>9</sup>  $\nu_{\text{max}}^{\text{neat}} 1670 \text{ cm}^{-1}$ ; <sup>1</sup>H NMR ( $\text{CCl}_4, \delta$ ) 5.4–4.75 (m, 3), 3.65 (s, 3), 2.98 (s, 3), 2.0–1.6 (m, 2), and 1.4–0.75 (m, 2).<sup>10</sup> At temperatures below 100 °C, **4** did not rearrange sufficiently rapidly for kinetic purposes. Under somewhat more forcing conditions, however, this cyclopropyl imidate was converted to **5** with a rate profile accommodated nicely by the differential rate expression

$$\frac{d[\mathbf{5}]}{dt} = k_f[\mathbf{4}] - k_r[\mathbf{5}]$$

indicative of a first-order reversible reaction (Table I). Although the exact ratio of **5**:**4** at equilibrium was somewhat temperature dependent, the value was seen to border on 3:1.



Dihydroazepine **5** whose ring protons generate a characteristic <sup>1</sup>H NMR pattern (( $\text{C}_6\text{D}_6, \delta$ ) 6.0–5.3 (m, 2), 4.03 (t,  $J = 7$  Hz, 1), 3.37 (m, 2), and 2.80 (m, 2)) proved expectedly to be extremely air and moisture sensitive. For characterization purposes, a tetrachloroethylene solution of the equilibrium