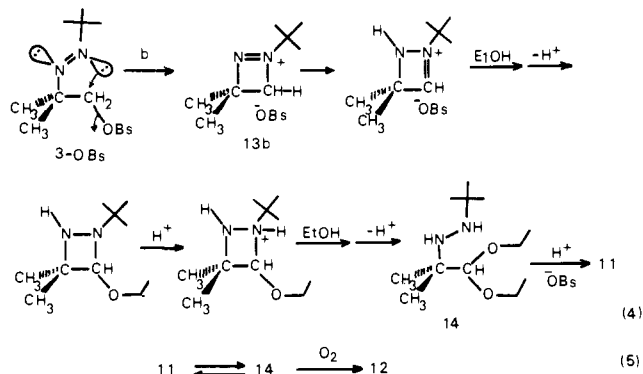
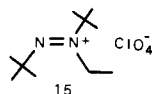


possibilities are illustrated by eq 3 and 4. An equilibrium between **11** and **14**<sup>19</sup> with accompanying oxidation of **14** (eq 5) readily accounts for formation of azo acetal **12**. A comparison



of the mechanistic features of processes 3 and 4 show that the only intrinsic difference between them occurs in the initial achimerically assisted ionization step a or b.

Evidence for **13a** or **13b** as an intermediate in the ethanolysis of **3-OBs** was sought from information about the chemical properties of trialkyldiazanium ions. The literature failed to show any reaction results for the conditions of eq 2.<sup>20</sup> Consequently, we examined the ethanolysis (lutidine) of **15**<sup>21</sup> as a model system. Pertinent products were acetaldehyde diethyl



acetal (**16**, 35%), isobutylene (**17**, 50%), and ethyl *tert*-butyl ether (**18**, 40%).<sup>22</sup> A substantial yield of **16** demonstrates that diazenium ions containing a -CH<sub>2</sub>-N<sup>+</sup> moiety react with ethanol to give acetal. The combined formation of **17** and **18** is diagnostic of the high propensity of diazenium ions with *t*-C<sub>4</sub>H<sub>9</sub>-N<sup>+</sup> to react with the loss of *tert*-butyl cation. This finding suggests that ethanolysis of **3-OBs** occurs by eq 3 via **13a**.<sup>23</sup>

**Acknowledgment.** We express appreciation to the National Science Foundation for support of this work with Grant No. CHE76-01129.

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- Hydrazinium salt **11** was identified by its <sup>1</sup>H NMR spectrum which was in complete accord with the assigned structure. A recovered, purified sample of **11** had satisfactory elementary analyses. Azo acetal **12** had the expected <sup>1</sup>H NMR and UV spectra. The yield of product was estimated by NMR integration of <sup>1</sup>H signals against 1,1,2,2-tetrachloroethane internal standard. Within the limits of this method **11**, **12**, or **11 + 12** were formed quantitatively. GC analysis did not show formation of other primary products (isobutylene and/or ethyl *tert*-butyl ether might have been expected from the solvolysis results with **15a**).<sup>18</sup> No nitrogen elimination was detected by the previously described method.<sup>6a</sup>
- Control experiments indicated that prolonged heating of **11** in EtOH caused decomposition. In this case isobutylene was observed as a secondary product. For this reason the product measurement cited in note 17 for **11** is for <30% ethanolysis.
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- Alkylation of 1,2-di-*tert*-butylhydrazine with triethyloxonium fluoroborate followed by treatment with KOH gave 1-ethyl-1,2-di-*tert*-butylhydrazine. Oxidation with AgClO<sub>4</sub> yielded **15** (mp 117-118 °C) with the proper NMR spectrum and elemental analysis.
- Determined by a combination of GC and NMR analyses.
- Further study with **3-OBs** and related systems is in progress.

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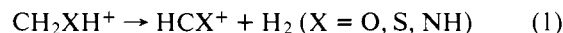
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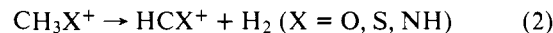
## Kinetic Energy Release in the Fragmentation of CSH<sub>3</sub><sup>+</sup> Ions

Sir:

It is well established<sup>1,2</sup> that the reaction



occurs with significant release of kinetic energy. This has been interpreted<sup>2</sup> in terms of a symmetry-forbidden 1,2-H<sub>2</sub> elimination reaction which imposes an activation energy barrier greater than the endothermicity of the reaction. Recent theoretical calculations<sup>3,4</sup> have confirmed the presence of such a barrier. By contrast 1,1-H<sub>2</sub> elimination is not symmetry forbidden and it has been observed that such fragmentation reactions show little kinetic energy release.<sup>5</sup> This suggests that the reaction



for CH<sub>3</sub>X<sup>+</sup> ions, isomeric with CH<sub>2</sub>XH<sup>+</sup>, should occur with little kinetic energy release. For X = O it has been noted<sup>6</sup> that reaction 2 (CH<sub>3</sub>O<sup>+</sup> → HCO<sup>+</sup> + H<sub>2</sub>) is thermoneutral or exothermic<sup>7</sup> and no metastable ion is observed. Indeed, because of the facile loss of H<sub>2</sub> the *m/e* 31 ion (COH<sub>3</sub><sup>+</sup>) is of very low abundance, compared with HCO<sup>+</sup>, in compounds where simple bond rupture to give the methoxy cation might be expected.<sup>6</sup>

By contrast, the CSH<sub>3</sub><sup>+</sup> ion (nominally CH<sub>3</sub>S<sup>+</sup>) is abundant in the mass spectra of compounds of the general formula CH<sub>3</sub>SR.<sup>7</sup> In addition, the available thermochemical data<sup>8,9</sup> suggest similar heats of formation for CH<sub>3</sub>S<sup>+</sup> and CH<sub>2</sub>SH<sup>+</sup>. These observations lead to the possibility that for the sulfur

**Table I.** Kinetic Energy Release in Loss of H<sub>2</sub> from CSH<sub>3</sub><sup>+</sup>

precursor	nominal reaction	T <sub>0.5</sub> , eV
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> SH	CH <sub>2</sub> SH <sup>+</sup> → CHS <sup>+</sup> + H <sub>2</sub>	0.93
CH <sub>3</sub> SSCH <sub>3</sub>	CH <sub>3</sub> S <sup>+</sup> → CHS <sup>+</sup> + H <sub>2</sub>	0.94
CD <sub>3</sub> SH	CD <sub>2</sub> SH <sup>+</sup> → CDS <sup>+</sup> + HD	0.91
CD <sub>3</sub> SH	CD <sub>3</sub> S <sup>+</sup> → CDS <sup>+</sup> + D <sub>2</sub>	0.93

system one might be able to compare kinetic energy releases for the 1,2-H<sub>2</sub> elimination reaction 1 and the 1,1-H<sub>2</sub> elimination reaction 2 for isomeric ions. Table I records the kinetic energy releases calculated from the half-height widths of the metastable peaks observed<sup>10</sup> for fragmentation of ions nominally of structures CH<sub>2</sub>SH<sup>+</sup> and CH<sub>3</sub>S<sup>+</sup>. Both metastable peaks were observed to be "flat-topped" and showed kinetic energy releases identical within experimental error. The mass spectrum of CD<sub>3</sub>SH shows<sup>8</sup> ion currents corresponding, nominally, to CD<sub>3</sub>S<sup>+</sup> and CD<sub>2</sub>SH<sup>+</sup> in the ratio 1:2.2. The former ion showed a metastable peak for loss of D<sub>2</sub>, while the latter showed a metastable peak for loss of HD only, the ratio of intensities for the two metastable peaks being the same as the ratio of precursor ion abundances. As shown in Table I, the kinetic energy releases for the two fragmentation reactions are the same and are in agreement with the kinetic energy releases measured for the unlabeled analogues.

Clearly the ions nominally with the thio methoxide structure are not losing H<sub>2</sub> by a simple 1,1-H<sub>2</sub> elimination reaction involving the small kinetic energy release characteristic of 1,1-H<sub>2</sub> elimination reactions.<sup>5</sup> The identity of the kinetic energy releases suggest an identical reaction pathway for ions with the CH<sub>3</sub>S<sup>+</sup> and CH<sub>2</sub>SH<sup>+</sup> nominal structure. This conclusion can be rationalized in three possible ways. (1) The dissociative ionization of CH<sub>3</sub>SR leads not to CH<sub>3</sub>S<sup>+</sup> but rather to CH<sub>2</sub>SH<sup>+</sup> as a result of H migration from carbon to sulfur concurrent with fragmentation.<sup>11</sup> (2) The dissociative ionization of CH<sub>3</sub>SR and RCH<sub>2</sub>SH leads to structurally distinct ions which isomerize to a common structure (or mixture of structures) prior to fragmentation. (3) The CH<sub>3</sub>S<sup>+</sup> and CH<sub>2</sub>SH<sup>+</sup> ions remain structurally distinct but fragment through a common transition state (of energy higher than HCS<sup>+</sup> + H<sub>2</sub>) with the observed kinetic energy release originating from conversion of part of the reverse activation energy into kinetic energy.

The data do not allow a distinction between these possibilities. The available thermochemical data<sup>8,9</sup> suggest  $\Delta H_f(\text{CH}_3\text{S}^+) = 210\text{--}214 \text{ kcal mol}^{-1}$  with  $\Delta H_f(\text{CH}_2\text{SH}^+)$  being slightly higher (215–219 kcal mol<sup>-1</sup>).<sup>12</sup> No reliable experimental value for  $\Delta H_f(\text{HCS}^+)$  exists; however, a recent theoretical calculation<sup>4</sup> gives a value of 245 kcal mol<sup>-1</sup> compared with a calculated value of 212 kcal mol<sup>-1</sup> for  $\Delta H_f(\text{CH}_2\text{SH}^+)$ . Thus the fragmentation reactions of both CH<sub>3</sub>S<sup>+</sup> and CH<sub>2</sub>SH<sup>+</sup> are significantly endothermic and metastable ions for fragmentation of both would be expected. The small difference in the heats of formation of the isomeric CSH<sub>3</sub><sup>+</sup> ions does not permit a clear distinction as to the structure formed by dissociative ionization; at the same time there does not appear to be any energetic driving force for rearrangement during fragmentation of CH<sub>3</sub>SR to form CSH<sub>3</sub><sup>+</sup>. With regard to isomerization after fragment ion formation, the MINDO/3 calculations of Dewar and Rzepa<sup>4</sup> reveal stable bridged structures for CSH<sub>3</sub><sup>+</sup> which are lower in energy than HCS<sup>+</sup> + H<sub>2</sub> and could serve as transition states for such an isomerization. However, the observation that the CD<sub>2</sub>SH<sup>+</sup> ion loses only HD (i.e., H/D randomization does not occur) argues against such an isomerization prior to fragmentation. In their MINDO/3 calculations Dewar and Rzepa<sup>4</sup> have identified a transition state for loss of H<sub>2</sub> from CH<sub>2</sub>SH<sup>+</sup>, although they did not report any calculations relating to the CH<sub>3</sub>S<sup>+</sup> structure or the transition state for H<sub>2</sub> loss from this structure. Thus, the

possibility remains that both CH<sub>3</sub>S<sup>+</sup> and CH<sub>2</sub>SH<sup>+</sup> are structurally distinct but fragment through a common transition state, possibly preceded by a bridged intermediate. In any event, the present results are in agreement with the recent conclusions from collisional activation studies<sup>13</sup> that the fragmentation reactions of nominally isomeric CSH<sub>3</sub><sup>+</sup> ions are identical for ions of low internal energy.

Work on this and related systems is continuing.

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## CIDNP Evidence for Electron Transfer between Two Neutral Radicals in Solution<sup>1</sup>

Sir:

It has long been known that mixed diacyl peroxides (**1a**) decompose thermally<sup>2</sup> by the pathways shown in Scheme I. The polar pathway,<sup>2,3</sup> which yields a "carboxyl inversion" product<sup>4</sup> (**4a**), has many of the characteristics of an alkyl-group migration to electron-deficient oxygen.<sup>3</sup> The remaining reactions represent collectively the well-known radical pathway for decomposition<sup>5</sup> in which a pair of radicals (**2**) either recombine or escape from the solvent cage and are scavenged by reaction with the solvent, added scavenger, another molecule of peroxide, or other radicals.

We report here evidence for a previously undocumented electron-transfer pathway for recombination (Scheme II) which competes with radical coupling and disproportionation.<sup>6</sup> The peroxide employed was *tert*-butylacetyl-*m*-chlorobenzoyl peroxide (**1b**).<sup>7</sup> In this reaction an electron is transferred between the neopentyl (**9**) and *m*-chlorobenzoyloxy radicals to form *m*-chlorobenzoate (**11**) and the neopentyl cation (**8**). Subsequent Wagner-Meerwein rearrangement of **8** yields cation **10** which loses a proton to produce 2-methyl-1-butene (**5**), 2-methyl-2-butene (**6**), and 1,1-dimethylcyclopropane (**7**) (yields are reported in Table I).

Evidence that products **5–7** arise from the geminate radical pair (**2**) is obtained from the observation of CIDNP during the reaction. In Figure 1 is shown the <sup>1</sup>H NMR spectrum obtained