

MASS SPECTRAL EVIDENCE FOR THE HYDROXYMETHYLENE RADICAL CATION

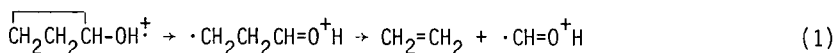
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Abstract: Collisionally-activated decompositions show that  $\cdot\text{CH}=\text{O}^+\text{H}$  ions are stable, confirming theoretical predictions.

Formaldehyde is much more stable than its isomer hydroxymethylene; their heats of formation differ by 217 kJ mol<sup>-1</sup>.<sup>1</sup> In contrast, a recent theoretical study<sup>2</sup> indicates that ionized formaldehyde (1) is only 41 kJ mol<sup>-1</sup> more stable than the hydroxymethylene radical cation (2); ionization makes possible a substantial increase in the C-O bond order,  $^+\text{CH}-\text{OH} \leftrightarrow \cdot\text{CH}=\text{O}^+\text{H}$ . The calculated barrier for the isomerization  $\underline{2} \rightarrow \underline{1}$  is 248 kJ mol<sup>-1</sup>, larger than that (60 kJ mol<sup>-1</sup>) for the dissociation of 2 into HCO<sup>+</sup> and H·, so that it was concluded that 2 might be an observable species. We report here experimental evidence confirming that prediction.

A route for the preparation of 2 ions was suggested by recent detailed studies of the mass spectra of cyclopropyl compounds;<sup>3-5</sup> the analogous dimethoxymethylene ion (CH<sub>3</sub>O)<sub>2</sub>C<sup>+</sup> has been prepared from 1,1-dimethoxycyclopropane.<sup>5</sup> Thus alpha cleavage of cyclopropanol<sup>6</sup> followed by C<sub>2</sub>H<sub>4</sub> loss, eq 1, could yield the desired isomer. Its mass spectrum does show



CH<sub>2</sub>O<sup>+</sup> ions of 6% abundance (relative to the most intense peak, C<sub>3</sub>H<sub>5</sub>O<sup>+</sup>). The collisional-activation (CA) mass spectrum<sup>7</sup> (Table) of these ions is substantially different from that

TABLE. Collisional activation mass spectra of CH<sub>2</sub>O<sup>+</sup> isomers<sup>a</sup>

<u>m/z</u>	Formaldehyde	Cyclopropanol
12	67	54
13	54	100
14	100	23
16	33	8
17	4	23

<sup>a</sup>m/z 28 and 29 ions are also formed by metastable decomposition

of 1 ions from the ionization of formaldehyde. This provides definitive evidence, as shown in extensive studies,<sup>7,8</sup> that these isomeric ions have different structures, with those from cyclopropanol containing at most ~25% of 1 (based on m/z 14). Hydroxymethylene is the only logical structure for the new CH<sub>2</sub>O<sup>+</sup> ions, based on their mode of formation<sup>5</sup> and on the probable instability of the other possible isomer  $\cdot\text{C}=\text{O}^+\text{H}_2$  (predicted heat of formation 257 kJ mol<sup>-1</sup> above that of 1).<sup>2</sup> These CA spectra also indicate the proposed structures; the relatively abundant CH<sub>2</sub><sup>+</sup> and O<sup>+</sup> ions of the first spectrum are consistent with the H<sub>2</sub>C=O<sup>+</sup> structure, while the CH<sup>+</sup> and OH<sup>+</sup> of the second are consistent with  $\cdot\text{CH}=\text{O}^+\text{H}$

(neither spectrum suggests  $\cdot\cdot\text{C-O}^+\text{H}_2$ ).

A similar effect has been observed in the case of keto/enol tautomers; the enol is the less stable form in the neutral but the more stable after ionization.<sup>9-11</sup>

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