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MASS SPECTRAL EVIDENCE FOR THE HYDROXYMETHYLENE RADICAL CATION

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

Formaldehyde is much more stable than its isomer hydroxymethylene; their heats of formation differ by 217 kJ mol^{-1}.[1] In contrast, a recent theoretical study[2] indicates that ionized formaldehyde (1) is only 41 kJ mol^{-1} more stable than the hydroxymethylene radical cation (2); ionization makes possible a substantial increase in the C-O bond order, $\overset{+}{\cdot}CH{-}OH \leftrightarrow \cdot CH{=}O^+H$. The calculated barrier for the isomerization $2 \rightarrow 1$ is 248 kJ mol^{-1}, larger than that (60 kJ mol^{-1}) for the dissociation of 2 into HCO^+ 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;[3-5] the analogous dimethoxymethylene ion $(CH_3O)_2C^{+\cdot}$ has been prepared from 1,1-dimethoxycyclopropane.[5] Thus alpha cleavage of cyclopropanol[6] followed by C_2H_4 loss, eq 1, could yield the desired isomer. Its mass spectrum does show

$$\overline{CH_2CH_2CH}{-}OH^{+\cdot} \rightarrow \cdot CH_2CH_2CH{=}O^+H \rightarrow CH_2{=}CH_2 + \cdot CH{=}O^+H \qquad (1)$$

$CH_2O^{+\cdot}$ ions of 6% abundance (relative to the most intense peak, $C_3H_5O^+$). The collisional-activation (CA) mass spectrum[7] (Table) of these ions is substantially different from that of 1 ions from the ionization of formaldehyde. This provides definitive evidence, as shown in extensive studies,[7,8] 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 $CH_2O^{+\cdot}$ ions, based on their mode of formation[5] and on the probable instability of the other possible isomer $\cdot\!:C{-}O^+H_2$ (predicted heat of formation 257 kJ mol^{-1} above that of 1).[2] These CA spectra also indicate the proposed structures; the relatively abundant $CH_2^{+\cdot}$ and $O^{+\cdot}$ ions of the first spectrum are consistent with the $H_2C{=}O^{+\cdot}$ structure, while the CH^+ and OH^+ of the second are consistent with $\cdot CH{=}O^+H$

TABLE. Collisional activation mass spectra of $CH_2O^{+\cdot}$ isomers[a]

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

[a] m/z 28 and 29 ions are also formed by metastable decomposition

(neither spectrum suggests $\cdot\!:\!C\text{-}O^{+}H_2$).

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.[9-11]

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