

# Laboratory Experiments on the Interstellar Species [HCO]<sup>+</sup> and [COH]<sup>+</sup>

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**Abstract:** The collisionally induced dissociations of [HCO]<sup>+</sup> and [COH]<sup>+</sup> ions have been studied at translational energies of 750–8000 V. [HCO]<sup>+</sup> ions were generated by a variety of methods, dissociative ionization, collisionally induced ionization of [HCO]· radicals, and collisionally induced charge reversal of [HCO]<sup>-</sup>, all of which are shown to lead to pure [HCO]<sup>+</sup> ions, i.e., free of their isomer [COH]<sup>+</sup>. It is found that after collisional activation, some [HCO]<sup>+</sup> ions isomerize into [COH]<sup>+</sup> (and vice versa) in times less than 10<sup>-7</sup> s. The degree of isomerization is virtually independent of the amount of internal energy imparted to the ions by collision in the above translational energy range.

The ions [HCO]<sup>+</sup> and [COH]<sup>+</sup> are confirmed<sup>1</sup> interstellar species and play an important role in interstellar space chemistry. Theoretical<sup>2-4</sup> and experimental<sup>5-10</sup> results have indicated that [COH]<sup>+</sup> indeed is a stable species and can be distinguished from its better known isomer by its characteristic collisional activation (CA) mass spectrum in which the abundance ratio  $m/z$  13: $m/z$  12 serves as a structure identifying feature, 0.20 for [COH]<sup>+</sup><sup>9</sup> and 0.9 for [HCO]<sup>+</sup><sup>9</sup>. The relative chemical reactivities of the two isomers have recently been examined,<sup>11</sup> and it was found that [COH]<sup>+</sup> has a much larger cross section for proton transfer to acetylene than [HCO]<sup>+</sup>. The mechanisms of the collision induced fragmentation of the two isomers have not yet been studied; it should be noted that in the CA mass spectrum of [HCO]<sup>+</sup>, covering the region  $m/z$  12–17, the peak at  $m/z$  12, which is not expected to be structure characteristic of [HCO]<sup>+</sup>, is nevertheless the base peak under conditions where single collision events predominate. A significant peak at  $m/z$  17, [OH]<sup>+</sup>, is also observed. Formation of [C<sup>+</sup>] and [OH]<sup>+</sup> from ions formally represented as [HCO]<sup>+</sup> may, in principle, be the result of generation of [COH]<sup>+</sup> in the ion source and/or isomerization of the originally formed [HCO]<sup>+</sup> ions. [HCO]<sup>+</sup> ions generated in the ion source will have internal energies of up to the critical energy 605 kJ mol<sup>-1</sup> for the reaction of lowest energy requirement, i.e., [HCO]<sup>+</sup> → H<sup>+</sup> + CO ( $\Delta H_f$ [HCO]<sup>+</sup> = 816 kJ mol<sup>-1</sup>,<sup>12</sup>  $\Delta H_f$ [H<sup>+</sup>] = 1531 kJ mol<sup>-1</sup>,<sup>12</sup>  $\Delta H_f$ [CO] = -110 kJ mol<sup>-1</sup><sup>13</sup>). The calculated energy requirement for the isomerization [HCO]<sup>+</sup> → [COH]<sup>+</sup> (307 kJ mol<sup>-1</sup><sup>4</sup>), is substantially lower than the dissociation energy and therefore a significant number of ions may well be able to undergo such rearrangement. With respect to this possibility it has been observed<sup>14</sup> that the [C<sub>3</sub>H<sub>5</sub><sup>+</sup>] ions generated in the ion source by dissociative ionization of CH<sub>2</sub>=CH—CH<sub>2</sub>—I consist of a mixture of [allyl]<sup>+</sup> and the higher energy species [2-propenyl]<sup>+</sup>: for the [C<sub>3</sub>H<sub>5</sub><sup>+</sup>] ions the barrier to isomerization also lies below the energy for the fragmentation of lowest energy requirement.

Alternatively, the generation of [C<sup>+</sup>] and [OH]<sup>+</sup> from ions represented as [HCO]<sup>+</sup> may result from a fast isomerization of collisionally activated [HCO]<sup>+</sup> followed by fragmentation within the collision cell, i.e., in <10<sup>-7</sup> s. For the formation of [C<sup>+</sup>] from [HCO]<sup>+</sup> ions another route is available, namely that leading to three particles ([C<sup>+</sup>] + O + H·). This process, however, requires 1452 kJ mol<sup>-1</sup> ( $\Delta H_f$ [C<sup>+</sup>] = 1799 kJ mol<sup>-1</sup>,<sup>12</sup>  $\Delta H_f$ [O] = 251 kJ mol<sup>-1</sup>,<sup>12</sup>  $\Delta H_f$ [H·] = 218 kJ mol<sup>-1</sup><sup>12</sup>).

In this paper we present a study of the mechanisms of the collisionally induced fragmentation of [HCO]<sup>+</sup> and [COH]<sup>+</sup> ions from an analysis of their CA mass spectra over a wide range of ion translational energies.

## Experimental Section

The collisional activation mass spectra were obtained with a Vacuum generators ZAB-2F mass spectrometer of reversed geometry under the

**Table I.** Partial Collisional Activation Mass Spectra<sup>a,b</sup> of [H, C, O]<sup>+</sup> Ions

precursor ion	$m/z$ of daughter ion			
	12	13	16	17
[CH <sub>3</sub> CHO] <sup>+</sup>	44	42	10	4
[CD <sub>3</sub> OH] <sup>+</sup>	64	19	6	11

<sup>a</sup> Accelerating voltage = 8 kV. <sup>b</sup> Intensities (peak heights) relative to sum = 100; all values ± 1.

following conditions: acceleration voltage, 8 kV; ionizing electron energy, 70 eV (unless otherwise stated); ion source temperature, 150 °C; main beam reduction of ca. 5% with He as collision gas. [H, C, O]<sup>+</sup> ions were generated in the following ways: (1) by dissociative ionization taking place in the ion source (all ions are accelerated to 8 kV and the [H, C, O]<sup>+</sup> ions are mass analyzed and subsequently collisionally activated); (2) by dissociation of a precursor ion in the region preceding the magnet (such metastably formed [H, C, O]<sup>+</sup> ions have, on average, lower internal energies than those formed in the ion source;<sup>15</sup> such [H, C, O]<sup>+</sup> ions are mass analyzed by selecting the appropriate  $m/z$  value with the magnet); (3) by collisionally induced charge reversal of the corresponding anions;<sup>16</sup> and (4) by collisionally induced ionization of the corresponding radicals. The methodology of the latter type of experiments has been described by us,<sup>17-19</sup> and they lead to successful results provided that the pressure of the collision gas is sufficiently low to prevent significant diffusion of the gas into a region close to the cell.<sup>19</sup> When this requirement is not met ions may be fragmented by the diffused gas before they are retarded or deflected and so add to the total flux of neutral species entering the cell. Generally such interferences only become noticeable at indicated

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pressures of  $>3 \times 10^{-7}$  torr, and so a pressure of  $2 \times 10^{-7}$  torr was chosen for all experiments in the present work. In addition we have found that at these pressures, effects arising from multiple collisions are negligible.

$[\text{HCO}]^-$  (ions generated by proton abstraction of  $\text{H}_2\text{CO}$  with  $[\text{NH}_2]^-$  as base, as described in ref 20.

All compounds were of research grade and were used without further purification.

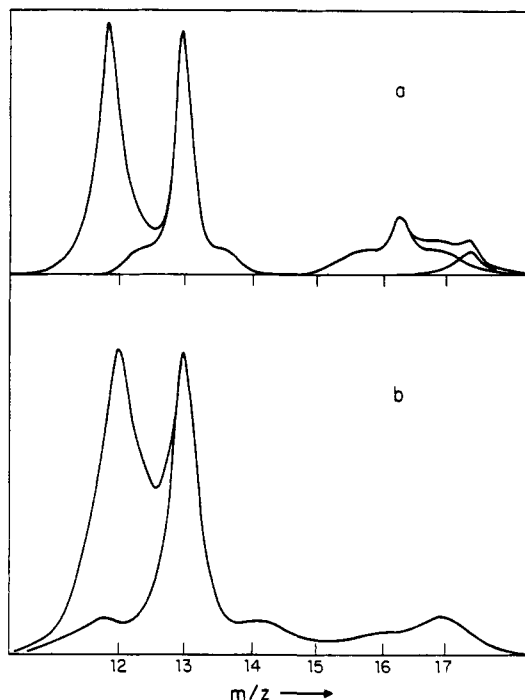
## Results and Discussion

**Formation of  $[\text{HCO}]^+$  Ions by Dissociative Ionization.** The partial CA mass spectra of the  $[\text{H}, \text{C}, \text{O}]^+$  ion formed by the dissociative ionization of  $\text{CH}_3\text{CHO}$  and  $\text{CD}_3\text{OH}$  are given in Table I. As argued in previous accounts<sup>7-10</sup> the pronounced differences between the two intensity distributions indicate that two distinct  $[\text{H}, \text{C}, \text{O}]^+$  ions, viz.,  $[\text{HCO}]^+$  and  $[\text{COH}]^+$ , exist as stable species in the gas phase. These parent ions are produced in the ion source at an ionizing energy of 70 eV and thus will have a large range of internal energies, possibly leading to isomerization prior to collisional activation. The generation of  $[\text{H}, \text{C}, \text{O}]^+$  ions of low internal energy and which therefore will have the structure  $[\text{HCO}]^+$  was achieved from the unimolecular decomposition of  $[\text{CH}_3\text{OCH}_2]^+$  in the microsecond time scale and by the dissociative ionization of  $\text{CH}_3\text{CHO}$  in the ion source, but using the lowest ionizing electron energy compatible with an acceptable signal-to-noise ratio ( $\sim 2:1$ ). Both methods will generate *pure*  $[\text{HCO}]^+$  ions, i.e., free of their isomer  $[\text{COH}]^+$ , because the AE of the above metastable peak ( $11.8 \pm 0.2$  eV) and that of  $m/z$  29 in the mass spectrum of  $\text{CH}_3\text{CHO}$  ( $11.79$  eV<sup>12</sup>) are close to those calculated for the production of  $[\text{HCO}]^+$ , 11.85 and 11.79 eV, respectively, using  $\Delta H_f[\text{CH}_3\text{OCH}_3] = -184$  kJ mol<sup>-1</sup>,<sup>13</sup>  $\Delta H_f[\text{H}\cdot] = 218$  kJ mol<sup>-1</sup>,<sup>12</sup>  $\Delta H_f[\text{CH}_4] = -75$  kJ mol<sup>-1</sup>.<sup>13</sup> It should be noted that by using an accelerating voltage of 8 kV the  $[\text{HCO}]^+$  ions generated in the above metastable dissociation have a translational energy of ca. 5.2 kV, and thus the resulting CA mass spectrum should be compared with that for the  $[\text{H}, \text{C}, \text{O}]^+$  ions generated in the ion source, but having the same translational energies.

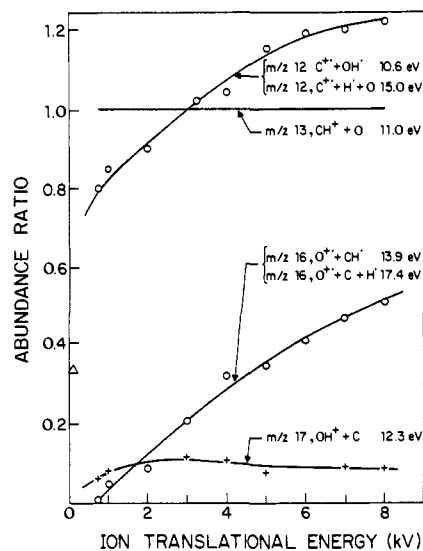
It was found that the CA mass spectra obtained by these three methods were closely similar and so we conclude that essentially only  $[\text{HCO}]^+$  ions are present *prior* to collisional activation: hence the peaks at  $m/z$  12 and 17 cannot have arisen from the pre-collisional presence of  $[\text{COH}]^+$ . Our observations are in keeping with those of Bowers and co-workers,<sup>8</sup> they detected only very small differences in the CA mass spectrum of  $[\text{HCO}]^+$  ions formed in the ion source, where the ions were produced by dissociative charge transfer and then allowed to undergo a large number of stabilizing collisions with an inert gas.

**Translational Energy Effects.** It was observed in earlier experiments<sup>10</sup> that the peaks at  $m/z$  13 and 16 in the CA mass spectrum of  $[\text{HCO}]^+$  are composite, comprising narrow and broad components, the origin of which will be discussed later. For the present experiments it is important to determine accurately the relative area of each peak in order to compare changes in ion flux. However, the aforementioned broad components extend to and overlap with the adjacent masses and so contribute significantly to their intensity. It was observed that the "horns" of the broad components shifted away from the centroid of the respective peaks when the accelerating voltage (i.e., the ion translational energy of  $[\text{HCO}]^+$ ) was lowered, consistent with a constant release of kinetic energy. This is illustrated in Figure 1, where the CA mass spectra of  $[\text{HCO}]^+$  ions are shown at accelerating voltages of 8 and 2 kV, respectively.

When a simple graphical deconvolution of the composite peaks at  $m/z$  13 and 16 was used, a reasonably accurate estimate of the relative fluxes (i.e., area) of each mass peak could be obtained for a wide range of translational energies of the  $[\text{HCO}]^+$  ion, from 0.75 to 8 kV. The results of these experiments are shown in Figure 2, where the flux of each peak, normalized to that of  $m/z$  13, is given as a function of the translational energy of the  $[\text{HCO}]^+$  ion. Included in Figure 2 are the calculated, threshold energies for the reactions leading to  $\text{C}^+ + \text{OH}\cdot$ ;  $\text{C}^+ + \text{O} + \text{H}\cdot$ ;  $[\text{CH}^+] + \text{O}$ ;



**Figure 1.** Partial collisional activation mass spectra of  $[\text{HCO}]^+$  ions: (a) ion translational energy 8 kV; (b) ion translational energy 2 kV.



**Figure 2.** Abundances (peak areas) of  $[\text{C}^+]$ ,  $[\text{O}^+]$ , and  $[\text{OH}^+]$  relative to that of  $[\text{CH}^+]$ , in the collisional activation mass spectrum of  $[\text{HCO}]^+$  ions as a function of the ion translational energy: ( $\Delta$ ) from Koski et al.,<sup>11</sup> see text. Calculated threshold energies<sup>12</sup> are relative to  $[\text{HCO}]^+$ .

$\text{O}^+ + \text{CH}\cdot$ ;  $\text{O}^+ + \text{C} + \text{H}\cdot$  and  $[\text{OH}^+] + \text{C}$ . Note that the reactions leading to three monatomic species are the most energy demanding processes. It is seen that as the translational energy is reduced  $m/z$  12 and 16 show a marked decrease in abundance, relative to  $m/z$  13, whereas the relative abundance of  $m/z$  17 remains virtually constant. Also shown in Figure 2 is the result obtained by Koski and co-workers:<sup>11</sup> they obtained a  $[\text{C}^+]/[\text{CH}^+]$  ratio of 0.34 with 100-eV  $[\text{HCO}]^+$  ions. Although their result cannot strictly be compared with ours, because different collision gases were involved (Ar vs. He), it is consistent with the trend shown in Figure 2. Low-energy collisions impart on average less the trend shown in Figure 2. Low-energy collisions impart on average less internal energy to the ions than do higher energy encounters, and so the decrease in abundance of  $m/z$  12 and 16 indicates that the high-energy reactions leading to three particles become increasingly less important as the collision energy is reduced.

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**Table II.** Collisional Activation Mass Spectra<sup>a,b</sup> of  $[\text{COH}]^+$  Ions for Various Ion Translational Energies

ion translation energy (kV)	$m/z$ of daughter ion			
	12	13	16	17
8	4.4	1.5	1.2	1.0
6	5.0	1.6	1.1	1.0
4	6.4	1.6	1.1	1.0
2	$7.6 \pm 0.5$	$1.9 \pm 0.6$	$1.1 \pm 0.4$	1.0

<sup>a</sup> Abundances (peak areas) relative to  $m/z$  17 = 1.0. <sup>b</sup> All values  $\pm 0.1$ , unless otherwise stated.

Another method for generating positive ions is by collisionally induced charge reversal of the corresponding negative ions.<sup>16</sup> Karpas and Klein<sup>20</sup> generated  $[\text{HCO}]^-$  by the gas-phase reaction of  $\text{H}_2\text{CO}$  with  $[\text{NH}_2]^-$ . The charge reversal CA mass spectrum of the  $[\text{HCO}]^-$  ions thus formed having 8 kV translational energy was as follows,  $m/z$  (relative flux) 12 (0.3), 13 (1), 16 (0.2), 17 (0.05), which, see Figure 2, is very different from that of 8 kV  $[\text{HCO}]^+$  ions, generated by dissociative ionization. Note, however, that the relative abundances of the  $[\text{HCO}]^+$  fragments,  $[\text{CH}^+]$  and  $[\text{O}^+]$ , are in the charge reversal experiment the same as for  $[\text{HCO}]^+$  ions only having 3 kV translational energy. This internal energy deficit, we propose, results from the energy required to strip two electrons from the anion (ca. 7.9–8.3 eV, from  $\Delta H_f^\circ[\text{HCO}]^- = 17\text{--}54 \text{ kJ mol}^{-1,20}$ ); similar effects have been observed with  $[\text{C}_3\text{H}_3]^\pm$ <sup>14</sup> and  $[\text{C}_3\text{H}_3]^\pm$ <sup>21</sup> ions. The lower abundance of  $m/z$  12 and 17 (0.3 and 0.05 compared to 1 and 0.13, respectively, for 3 kV  $[\text{HCO}]^+$  ions) indicates that following charge reversal the transient  $[\text{HCO}]^+$  ions preferentially undergo simple bond cleavage reactions rather than isomerization.

Positive ions can also be generated by the collisionally induced ionization of the corresponding neutral species.<sup>17,18</sup>  $[\text{HCO}]$  radicals can be cleanly generated by unimolecular decomposition of acetol molecular ions,  $[\text{HOCH}_2\text{C}(\text{O})\text{CH}_3]^+$ . The ionic species are deflected by means of an electrode,<sup>18</sup> situated in front of the collision cell, and only  $[\text{HCO}]$  radicals may enter the cell. The following CA mass spectrum was obtained:  $m/z$  (relative flux) 12 (0.3), 13 (1), 16 (0.15), 17 (0.05). Note that the  $[\text{HCO}]$  radicals have a translational energy of 3.1 kV when their precursor ion's acceleration voltage is 8 kV. Since  $[\text{HCO}]$  and  $[\text{HCO}]^-$  have similar  $\Delta H_f^\circ$ 's ( $\Delta H_f^\circ[\text{HCO}] = 37 \pm 5 \text{ kJ mol}^{-1,22}$ ), it is to be expected that their (positive ion) CA mass spectra will also be similar. The somewhat lower intensity of  $m/z$  16 for  $[\text{HCO}]$  may well be due to the lower translational energy of  $[\text{HCO}]$  compared with  $[\text{HCO}]^-$ .

Similar experiments were also performed for  $[\text{COH}]^+$  ions. We could not find a better source for these ions than dissociative ionization of  $\text{CD}_3\text{OH}$ . A small amount of  $[\text{HCO}]^+$  ions is also produced,<sup>9,10</sup> but they are not expected to contribute significantly to the CA intensity distribution.<sup>8</sup> It should be noted that  $m/z$  29 in the mass spectrum of  $\text{CD}_3\text{OH}$  is only 4% of the base peak and impurity peaks ( $\text{C}_2\text{H}_5^+$ ,  $\text{N}_2\text{H}^+$ ) were now detectable at nominal  $m/z$  29. The CA mass spectra were therefore recorded under conditions of sufficient mass resolution in the single focus mode and the  $[\text{COH}]^+$  ions were selectively transmitted. For  $[\text{COH}]^+$  ions the peaks at masses 13 and 17 are also composite and were again deconvoluted. The results are shown in Table II. The flux of  $m/z$  17 was chosen as the reference, because this is the only fragment that is structure characteristic and whose formation is unequivocal (i.e.,  $[\text{OH}]^+$  can only be generated by one bond cleavage, analogous to the formation of  $[\text{CH}^+]$  from  $[\text{HCO}]^+$ , see above).

First of all we propose that the presence of  $m/z$  17,  $[\text{OH}]^+$ , in the CA mass spectrum of initially pure  $[\text{HCO}]^+$  shows that this ion has partially isomerized to  $[\text{COH}]^+$  after collision and prior to fragmentation. The presence of  $m/z$  13 in the CA mass spectrum of  $[\text{COH}]^+$  is similarly ascribed to isomerization. For  $[\text{HCO}]^+$  the essentially constant relative abundances of  $[\text{CH}^+]$  and  $[\text{OH}]^+$  (Figure 2) shows that the post-collision  $[\text{HCO}]^+$ :  $[\text{COH}]^+$  ratio is also invariant. Similar observations were found for  $[\text{COH}]^+$  (Table II). The relative concentrations of  $[\text{HCO}]^+$  and  $[\text{COH}]^+$  cannot be determined because it may not be assumed that at the lowest translational energies only the two-particle-producing fragmentations are occurring. For example, at the lowest translational energy, 750 V, the abundance of  $m/z$  16 is ca. two orders of magnitude less than that of  $m/z$  12. Although the calculated minimum energy for  $[\text{O}^+ + \text{CH}^\cdot]$  is 1.1 eV lower than that for  $[\text{C}^+ + \text{O} + \text{H}^\cdot]$ , the threshold energies shown in Figure 2 may well not be the true energies and so it cannot be concluded that for these low-energy encounters all  $[\text{C}]^+$  must arise from  $[\text{COH}]^+$ . It can be seen (Table II) for  $[\text{COH}]^+$ , in contrast with the behavior of  $[\text{HCO}]^+$  (Figure 2), that the relative abundance of  $m/z$  12 increases as the translational energy of the ion is decreased. Now the formation of  $[\text{C}]^+$  and  $\text{OH}^\cdot$  from  $[\text{COH}]^+$  is the reaction of lowest formal energy requirement and indeed becomes more competitive with higher energy processes as less internal energy is imparted to the ion.

With respect to the behavior of  $[\text{HCO}]^+$  ions, the rise of  $m/z$  12 and 16 with increase in ion translational energy is ascribed to the concomitantly greater importance of the fragmentation into three atoms.

**Bimodal Kinetic Energy Release Associated with the Formation of  $[\text{CH}^+]$  and  $[\text{O}^+]$ .** For the  $[\text{HCO}]^+$  ions the composite nature of the peaks at  $m/z$  13 and 16 was also studied by varying the translational energy of the ion. It was observed that the broad components became, relative to their respective narrow components, more intense at lower translational energies and that the kinetic energy releases ( $T$ ), as measured from the "horns" of the deconvoluted signals, were  $3.2 \pm 0.3$  and  $2.5 \pm 0.4$  eV for formation of  $[\text{CH}^+]$  and  $[\text{O}^+]$ , respectively. These observations effectively rule out the possibility of their generation via dissociative electron detachment, because the observed  $T$  values for such a reaction leading to  $[\text{CH}^+]$  and  $[\text{O}^+]$  are too small to allow for Coulombic repulsion in such a small ion, and moreover they are not equal. The simplest explanation of the observed peak shapes is that  $[\text{CH}^+]$  and  $[\text{O}^+]$  formation occurs from two isolated electronic states of  $[\text{HCO}]^+$ . In the case of mono- and diatomic<sup>23–25</sup> ions and also for  $[\text{CH}_3\text{I}]^+$ ,<sup>26</sup> higher electronic states have been detected and assigned by using collisional activation mass spectrometry. Unfortunately we could not determine the exact positions on the energy scale of the broad components of the composite peaks because the intense adjacent peaks at  $m/z$  12 and 17 prevent any measurement of the asymmetry of the composite peaks. Thus the difference in energy loss for the two components could not be assessed.

Alternatively, either product in each fragmentation may be generated in excited states.

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