New, Stable Isomers of $[C_2H_4O]^{+\cdot}$, and $[C_2H_4O_2]^{+\cdot}$, the Radical Cations $[CH_3COH]^{+\cdot}$ and $[CH_3OCOH]^{+\cdot}$

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The ions $[CH_3COH]^{+\cdot}$ and $[CH_3OCOH]^{+\cdot}$ have been characterised by their collisional activation mass spectra and their heats of formation were measured as 865 ± 20 and 661 ± 5 kJ mol^{-1} respectively; $[CH_3COH]^{+\cdot}$ is the reacting configuration for H· loss from $[CH_2{=}CHOH]^{+}$.

A combination of mass spectrometric measurements on dissociating and non-dissociating gas-phase cations has recently led to the identification and energetics of stable ions of unconventional structure, whose existence had been predicted by *ab initio* calculations. For example the radical cation $[CH_2OH_2]^{+\cdot}$, an isomer of ionised methanol,[1] and a wide variety of analogues $[C_nH_{2n}{\cdot}XH]^{+\cdot}$ (X = OH, NH_2, SH, halogen, *etc.*) have been both predicted by calculation[2] to be stable species and observed by experiment.[1] Ionised oxycarbenes, although postulated as intermediates in fragmentation pathways,[3,4] have only lately been recognised as stable species by both theory[5] and experiment.[6] As an extension of our observations of $[COH]^+$ and $[C(OH)_2]^{+\cdot}$ we report here two oxycarbenes, $[CH_3COH]^{+\cdot}$ and $[CH_3OCOH]^{+\cdot}$, new isomers for the intensively studied systems $[C_2H_4O]^{+\cdot}$ (ref. 7) and $[C_2H_4O_2]^{+\cdot}$ (ref. 8). $[CH_3COH]^{+\cdot}$ was suggested as an intermediate species in the dissociative ionisation of pyruvic acid by Turro *et al.* in 1967[3] but an *ab initio* study by Bouma *et al.* in 1979[9] predicted it to be a stable ion in the gas phase, with a heat of formation, ΔH_f° of 830 kJ mol^{-1}.

The above dissociation of pyruvic acid, loss of CO_2 from the molecular ion, does indeed produce $[CH_3COH]^{+\cdot}$.

We had earlier concluded[10] that this ion had the vinyl alcohol structure $[CH_2{=}CHOH]^{+\cdot}$ because the shape of the metastable peak for H· loss from the ion was the same as that for ions *known* to possess the structure $[CH_2{=}CHOH]^{+\cdot}$. The recent *ab initio* calculations,[9] however, indicate that $[CH_2{=}CHOH]^{+\cdot}$ ions isomerise to $[CH_3COH]^{+\cdot}$ as the reacting configuration leading to the formation of $[CH_3CO]^+$. This $[C_2H_3O]^+$ daughter has been shown to be the acetyl cation.[11] Thus this metastable peak, instead of being solely characteristic of $[CH_2{=}CHOH]^{+\cdot}$ ions, is indicative of either these and/or $[CH_3COH]^{+\cdot}$. Distinguishing between these isomers therefore must rest upon examination of ions of *low* internal energy content, preferably those generated *via metastable* dissociation of their precursors. Figure 1 shows the structure-characteristic *m/z* 25—30 region of the collisional activation (C.A.) mass spectra of $[CH_3COH]^{+\cdot}$ and $[CH_2{=}CHOH]^{+\cdot}$ produced from appropriate metastable fragmentations. The former displays almost no signal at *m/z* 30 and 27 (loss of $:CH_2$ and OH· respectively), both of which are characteristic of $[CH_2{=}CHOH]^{+\cdot}$. The loss of C_2H_4 from ionised 1-methylcyclopropan-1-ol also generates $[CH_3COH]^{+\cdot}$ (by analogy with $[HCOH]^{+\cdot}$ formation from cyclopropanol[12]) but $[CH_2{=}CHOH]^{+\cdot}$ is cogenerated.

The heat of formation of $[CH_3COH]^{+\cdot}$ was obtained from the appearance energy (A.E.) of *m/z* 44 from $CH_3COCOOH$, pyruvic acid, ⩾10.4 eV measured using energy-selected electrons.[13] Note that only a lower limit could be assessed because of $[^{13}CCH_3O]^+$ contributions. ΔH_f° $[CH_3COCOOH] = -548$ kJ mol^{-1} [by additivity[14] and using -131 kJ mol^{-1} as the increment for CO–(CO)(O), midway between those for CO–(C)(O) and CO–(CO)(C)], ΔH_f° $[CO_2] = -394$ kJ mol^{-1} (ref. 15) whence ΔH_f° $[CH_3COH]^+ = 849$ kJ mol^{-1} in good agreement with the calculated value, 830 kJ mol^{-1} (ref. 9). The A.E. of the metastable peak accompanying reaction (1) was

$$CH_3COCOOH^{+\cdot} \rightarrow [C_2H_4O]^{+\cdot} + CO_2 \qquad (1)$$

also measured[16] and was estimated to be 10.7 ± 0.2 eV, in fair agreement with the above value. In view of these uncertainties we propose an experimentally derived ΔH_f° of 865 ± 20 kJ mol^{-1}.

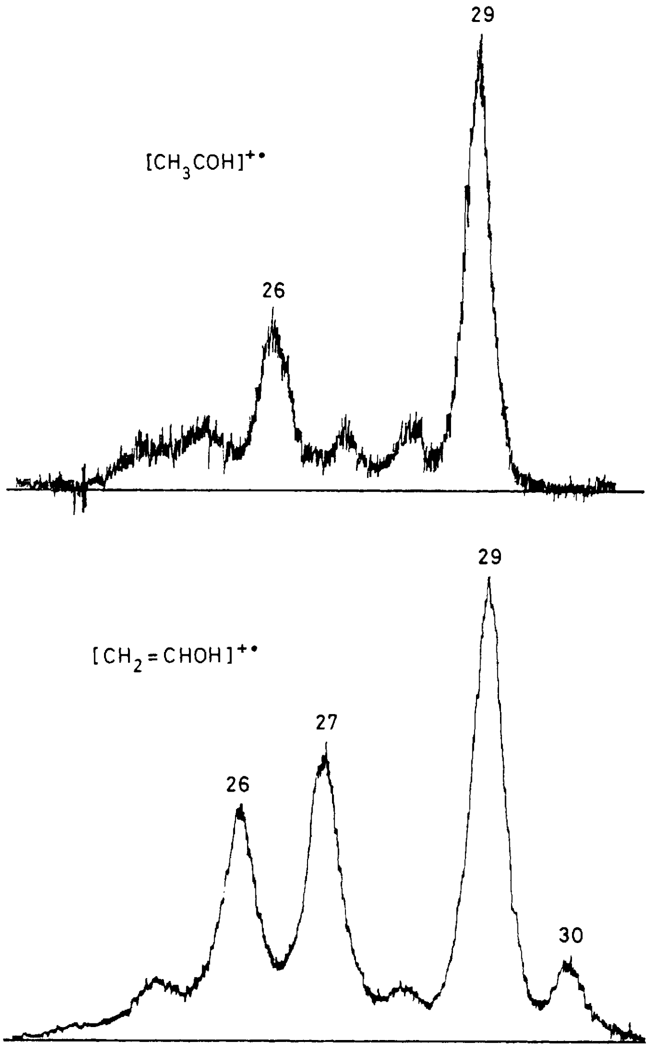

Figure 1. Partial collisional activation mass spectra of $[CH_3COH]^{+\cdot}$ (from the metastable peak for the loss of CO_2 from ionised pyruvic acid) and $[CH_2{=}CHOH]^{+\cdot}$ (from the metastable peak for the loss of C_2H_4 from ionised ethyl vinyl ether).

The ion $[CH_3OCOH]^{+\cdot}$ was readily produced *via* the dissociative ionisation of dimethyl carbonate, $(CH_3O)_2CO$, by loss of CH_2O. The ion is easily identified by means of its very structure-characteristic C.A. mass spectrum which is unlike that of any reported $[C_2H_4O_2]^{+\cdot}$ isomer.[8] The C.A. mass spectrum is dominated by *m/z* 45, $[CH_3\text{–}O\text{–}\dot{C}{=}\overset{+}{O}H] \rightarrow CH_3{\cdot} + [O{=}\underset{+}{C}\text{–}OH]$, a direct bond cleavage. A second unique characteristic is *m/z* 16, $[CH_4]^{+\cdot}$ (relative abundances: *m/z* 45, 100%; *m/z* 43, 7%; *m/z* 31, 3%; *m/z* 29, 10%; *m/z* 16, 5%, and *m/z* 15, 7%). The above $CH_3{\cdot}$ loss is also observed in the metastable ion mass spectrum (average kinetic energy release, $<T>$, = 70 meV) and the A.E. of the metastable peak (13.3 ± 0.2 eV) shows that this reaction requires an excess energy of *ca.* 1 eV above the products $[O{=}\overset{+}{C}\text{–}OH]$, ΔH_f° = 590 kJ mol^{-1} (ref. 15) and $[CH_3{\cdot}]$, ΔH_f° = 142 kJ mol^{-1} (ref 15) ΔH_f° $[(CH_3O)_2CO] = -568$ kJ mol^{-1} (ref. 14) [from ΔH_f° $(CH_3CH_2O)_2O = -639$ kJ mol^{-1} (ref. 17) and two additivity increments for replacing $(CH_3CH_2\text{–}O)$ by $(CH_3\text{–}O)$,[14] 35.5 kJ mol^{-1} each]. This critical energy is similar to that observed for the dissociation of ionised dihydroxycarbene.[6] ΔH_f° for $[CH_3OCOH]^{+\cdot}$ was measured to be 661 ± 5 kJ mol^{-1} from A.E. *m/z* 60 = 11.56 ± 0.05 eV (energy-selected electrons[13]) and A.E. of the metastable peak *m/z* 90 → *m/z* 60 = 11.5 ± 0.2 eV.

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