

CH₃OC⁺: A Long-sought Molecule, predicted to Exist by Theory, Identified

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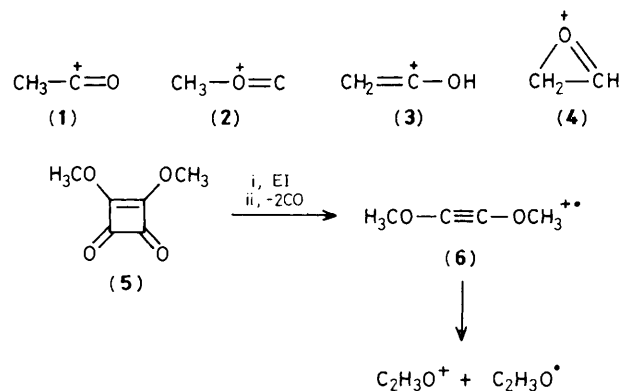
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The oxygen-methylated carbon monoxide cation, CH₃OC⁺ (2), has been generated and identified in the gas phase as a stable species (lifetime $t > 10^{-5}$ s) using mass spectrometry based experiments.

The ions HCO⁺ and HOC⁺ have been studied in great detail both experimentally¹ and theoretically² not the least because of their central importance in the genesis of organic molecules in interstellar clouds.³ The homologous ions, *i.e.* the acetyl cation (1) and oxygen methylated carbon monoxide (2) [together with the 1-hydroxyvinyl cation (3) and the oxiranyl cation (4)] have been the subject of recent high level *ab initio* MO studies.⁴ All four isomers (1)–(4) were predicted to lie in potential wells of sufficient depth to make experimental observations feasible. Indeed, (1), (3), and (4) have been generated as stable species in the gas phase and their chemistry has been studied in detail.⁵ The as yet unobserved ion CH₃OC⁺ (2) is predicted⁴ to lie 216 kJ mol⁻¹ above its well-known isomer (1). The magnitude of the calculated barriers for the isomerization reaction (2) → (1) and for the dissociation of lowest energy requirement (2) → CH₃⁺ + CO (68 and 79 kJ mol⁻¹) indicates that the oxygen-methylated carbon monoxide (2) should also be experimentally accessible in the gas phase.⁴ In this communication we report the generation and identification of (2).

It appeared to us that a promising route to make (2) might be C–C cleavage in ionized dimethoxyacetylene, CH₃OC≡COCH₃⁺ (6). Neutral dimethoxyacetylene can only be handled at low temperatures; it is very sensitive towards polymerization and reacts rapidly upon acid catalysis to form methyl methoxyacetate.⁶ However, we observed that (6) can conveniently be generated in high yield by the electron impact (EI) induced successive losses of two CO molecules from dimethyl squarate (5) which was synthesized according to ref. 7 (70 eV electron impact ionization using a Vacuum Generator ZAB-2F mass spectrometer).

Once (5) is generated it further dissociates to produce m/z 43 (C₂H₃O⁺), as shown by the presence of an accompanying intense metastable ion peak. The collisional activation (CA)⁸ mass spectra of these C₂H₃O⁺ ions generated in both the ion source and the first field-free region are distinct from those of the known C₂H₃O⁺ isomers and their patterns are compatible with the structure CH₃OC⁺ (2). This is corroborated by a comparison of the CA mass spectra (Figure 1) of the [²H₃]-labelled analogues CD₃CO⁺ [²H₃]-(1), generated from



[²H₆]acetone, and CD₃OC⁺ [²H₃]-(2), generated from [²H₆]dimethyl squarate. Because of the better peak separation, achieved by isotopic substitution, the spectra of these isotopomers will be used throughout for discussion and structure assignment. [The peak at m/z 28, CO⁺, is very broad (and composite) and therefore overlaps the peak at m/z 29, HCO⁺, from the unlabelled C₂H₃O⁺ ion.] (a) The signals at m/z 24 (C₂⁺) and m/z 26 (C₂D⁺) are very weak in the spectrum of [²H₃]-(2) and this indicates that the new ion does not contain a C–C bond and cannot easily isomerize into a species which does contain this structural element [as into for example [²H₃]-(1)]; all the previously identified C₂H₃O⁺ species have this structural element. (b) The CA spectrum of [²H₃]-(2) features a signal at m/z 32 (CD₂O⁺), a peak which is absent in the spectra of all the other C₂H₃O⁺ isomers. We take this as evidence that, upon collisional activation, [²H₃]-(2) splits off a carbon atom to generate a (presumably triplet) methoxy cation, D₃CO⁺; the latter ion is known⁹ subsequently to lose a deuterium atom or molecule thus forming D₂CO⁺ and DCO⁺. (c) The peak at m/z 30, DCO⁺, present in the CA mass spectrum of [²H₃]-(2) is much broader than that in the spectrum of [²H₃]-(1). This too is in keeping with the production of D₃CO⁺, for these methoxy ions are known to eliminate D₂ with a large kinetic energy release. (d) The ion ¹³CH₃OC⁺ [¹³C]-(2), generated from [¹³C₂]dimethyl squarate upon collision, produces signals at m/z 30 (H¹³CO), and m/z 31 (H²¹³CO), but not at m/z 29 (H²CO). This result lends further strong support to the above finding that the new ion has the structure ¹³CH₃OC⁺, which upon collision produces unstable ¹³CH₃O⁺. In a control experiment, CH₃¹³CO⁺

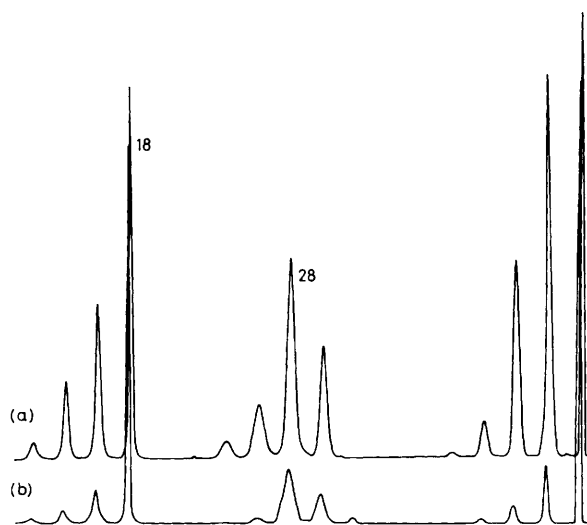


Figure 1. Collisional activation mass spectra of (a) CD₃CO⁺ [²H₃]-(1) and (b) CD₃OC⁺ [²H₃]-(2). Acceleration voltage 8 kV. Collision gas (He) pressure 5×10^{-7} Torr. The peaks at m/z 28 (CO⁺) and m/z 16 (CD₂⁺) in spectrum (b) are composite, indicating the occurrence of two reaction channels for the production of either ion.

(generated from $\text{CH}_3^{13}\text{CO}_2\text{H}$) upon collision yields signals at m/z 29 ($^{13}\text{CO}^+$) and m/z 30 (H^{13}CO^+), and the intensity ratio m/z 29: m/z 30 is equal to the ratio m/z 28: m/z 29 in the unlabelled ion CH_3CO^+ . Thus, we conclude that the $\text{C}_2\text{H}_3\text{O}^+$ ion generated from (6) is the long-sought CH_3OC^+ ion (2). In line with the theoretical predictions,⁴ (2) does not isomerize via 1,2-methyl migration to CH_3CO^+ (1) the global minimum on the $\text{C}_2\text{H}_3\text{O}^+$ potential energy surface. The distinct behaviour of (1) and (2) is also reflected in the remarkably different kinetic energy releases associated with the unimolecular dissociation $\text{C}_2\text{H}_3\text{O}^+ \rightarrow \text{CH}_3^+ + \text{CO}$. The $T_{0.5}$ values are 3 meV for (1) and 7 meV for (2), both signals having a Gaussian shape.¹⁰ The magnitudes of these kinetic energy release values indicate that the reverse exothermic ion/molecule reactions ($\text{CH}_3^+ + \text{CO} \rightarrow \text{CH}_3\text{CO}^+$ and $\text{CH}_3^+ + \text{OC} \rightarrow \text{CH}_3\text{OC}^+$) proceed via small or zero energy barriers; hence the ion CH_3OC^+ should also be produced by gas phase methylation of CO. Finally, we note that the above mentioned ^{13}C -labelling experiments show that the degenerate isomerization $^{13}\text{CH}_3-\overset{+}{\text{O}}=\text{C} \rightarrow ^{13}\text{C}=\overset{+}{\text{O}}-\text{CH}_3$ (via consecutive hydrogen migrations) does not take effect.

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