Gas-Phase Ion-Molecule Reactions of the CH_3O^+ Cation

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The methoxy cation, CH_3O^+ , formed by collision-induced charge reversal of methoxy anions with a kinetic energy of 8 keV, has been differentiated from the isomeric CH_2OH^+ ion by performing low kinetic energy ion-molecule reactions in the radiofrequency-only quadrupole of a reverse-geometry double-focusing quadrupole hybrid mass spectrometer. The methoxy cation reacts with CH_3SH , $\text{CH}_3 - \text{CH} = \text{CH}_2$, $(\text{CH}_3)_2\text{O}$, and $\text{CH}_3\text{CH}_2\text{Cl}$ by electron transfer, whereas the CH_2OH^+ ion reacts by proton transfer with these substrates (*J Am Soc Mass Spectrom* 1992, 3, 515–517)

The determination of the physical and chemical properties of small gaseous cations remains a challenging task despite the versatility of existing experimental methods [1] and the current insight in the chemistry of such ions in the gas phase [2]. Considerable effort has been devoted to elucidate the structure of the $(\text{H}_3, \text{C}, \text{O})^+$ ions formed in the gas-phase unimolecular reactions of simple ether and alcohol radical cations or as products of ion-molecule reactions. The established structures include oxygen-protonated formaldehyde, CH_2OH^+ ; the methoxy cation, CH_3O^+ ; and a weakly bound $(\text{H}_2 \cdot \text{HCO}^+)$ cluster [3], which can be formed by an association reaction in a high pressure mass spectrometer (HPMS) ion source [1]. The reported evidence indicates that the stable $(\text{H}_3, \text{C}, \text{O})^+$ ions arising by fragmentation of ether and alcohol radical cations have only the CH_2OH^+ structure [4]. Transient CH_3O^+ ions—with respect to fragmentation into $\text{H}_2 + \text{HCO}^+$ —have been suggested to be formed in a spin-forbidden predissociation of the molecular ion of methanol leading to the loss of the hydroxylic hydrogen atom [5, 6] and in the elimination of a methyl radical from the molecular ion of dimethyl ether [7]. By contrast, collision-induced charge reversal [8] of methoxy anions [9] accelerated to a kinetic energy of 8 keV is reported to yield stable methoxy cations, which fragment according to their structure upon 8 keV ion kinetic energy collision-induced dissociation (CID) [10]. The lifetime of the methoxy cations formed by the charge reversal process was judged to be $\geq 10^{-5}$ s [10], which thus allows further study of the chemistry of these species, including their bimolecular chemistry in low kinetic

energy ion-molecule reactions. Such bimolecular chemistry of the methoxy cation may be of particular interest since ab initio calculations predict that the singlet CH_3O^+ ion undergoes a 1,2-hydride shift without an energy barrier to form the CH_2OH^+ ion, whereas the triple CH_3O^+ ion is calculated to be stable with a heat of formation 387 kJ/mol above that of CH_2OH^+ [11, 12].

The combination of ion generation by high kinetic energy collision processes with bimolecular reactions at low kinetic energies is not readily achieved with methods such as ion cyclotron resonance (ICR) mass spectrometry, HPMS, and flowing afterglow, which have traditionally been used in studies of ion-molecule reactions [1]. However, the development of hybrid mass spectrometers [13] consisting of a double-focusing mass spectrometer linked to a quadrupole section [14, 15] or an ion trap [16] makes it possible to form ions by high kinetic energy processes such as charge reversal [8] or charge stripping [17] and subsequently to study their chemistry at low kinetic energies in the second stage of the instruments. The objectives of the present study were (1) examination of the ion-molecule chemistry of the methoxy cation, (2) structural differentiation between the CH_3O^+ and CH_2OH^+ isomers on the basis of their bimolecular chemistry, and (3) investigation of the capability of a hybrid mass spectrometer for studies of gas-phase ion-molecule reactions.

Experimental

The experiments were performed with a VG Analytical ZAB-2HFqQ (Fisons Instruments, Manchester, England) reverse-geometry double-focusing quadrupole mass spectrometer [15]. Briefly, the BE (B, magnetic sector; E, electric sector) stage is followed by a deceleration lens system, a radiofrequency (RF)-only

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quadrupole (q) collision cell, and a second quadrupole (Q) for mass analysis. The ions were formed by electron impact in the ion source and accelerated to 8 keV prior to momentum and kinetic energy analysis in the BE stage of the instrument. The ion beam leaving the BE stage is reshaped, refocused, and retarded by a series of electrostatic lenses before reaching the quadrupole section of the instrument. The entire quadrupole assembly is operated at a potential that is continuously variable from 0 V up to the full acceleration potential. This allows the kinetic energy of the ions entering the RF-only quadrupole to be adjusted from thermal or near-thermal up to about 500 eV. The mass-analyzing quadrupole is operated at a small dc bias voltage (10–50 V) relative to the RF-only quadrupole in order to optimize the collection of the ions generated by ion-molecule reactions. The kinetic energy distribution of the ions in the quadrupole section was crudely determined to be about 1 eV (full width half maximum) in the laboratory frame by monitoring the ion peak intensity while the potential of the RF-only quadrupole was scanned through a value that corresponded to a nominal ion kinetic energy of 0 eV [18, 19]. An ion beam with thermal to near-thermal kinetic energy was obtained by adjusting the potential applied to the quadrupole section to the highest possible value, which allowed for transmission of ions. To test the experimental performance qualitatively, CD_4^+ ions formed by electron impact in the ion source were allowed to react with CH_4 admitted to the RF-only quadrupole. This reaction is known to proceed in part by deuteron transfer giving CH_4D^+ ions and in part by hydrogen atom transfer leading to CD_4H^+ ions [20]. The ratio between the abundances of the CH_4D^+ and CD_4H^+ product ions was about 1.0 at the lowest possible ion kinetic energy that could be achieved while maintaining an acceptable transmission through the quadrupoles. This result is in qualitative agreement with crossed-beam experiments, which show that the relative contributions of proton transfer and hydrogen atom transfer in the formation of CH_5^+ by reaction between CH_4^+ and CH_4 are 1.35:1, 1.23:1, and 1.62:1 at center-of-mass energies, E_{CM} , of 0.69, 1.23, and 2.29 eV, respectively [21].

The reagent gases were admitted to the gas-tight RF-only quadrupole until a pressure of about 10^{-5} Pa was indicated by an ionization gauge placed in the sidearm of the entrance to the diffusion pump placed directly under the reaction region.

The experiments were performed with the fully deuterium-labeled ions because the charge reversal process has been reported to be approximately six times more efficient for CD_3O^+ than for the unlabeled ion [10]. The CD_2OD^+ ion was generated by electron impact on CD_3OD . The methoxy anions were formed in a chemical ionization source by electron impact on a mixture of CD_3OD , N_2O , and CH_4 [22]. The total pressure in the ion source housing was about 10^{-4} Pa, the source temperature 200 °C, and the electron

energy about 100 eV. Charge reversal of the mass-selected CD_3O^+ ions was achieved by introducing O_2 to the collision cell located in the field free region between the B and E sectors. The charge reversal process was associated with a loss in kinetic energy [23] of the methoxy ions of about 20 eV. This loss in kinetic energy was taken into account when selecting the stable methoxy cations by the E sector and adjusting the quadrupole section for the purpose of studying the bimolecular chemistry of the ions.

Results and Discussion

The CD_3O^+ ions entering the RF-only quadrupole are estimated to have a lifetime of $\geq 5 \times 10^{-5}$ s. In agreement with a previous report [10], loss of D_2 to form DCO^+ ions occurs to a significant extent ($\approx 20\%$) even at this ion lifetime. In keeping with the theoretical results [11], we interpret the relatively intense loss of D_2 as related to a finite lifetime of the triplet state of the methoxy cation with respect to decay into the lower lying singlet state, which collapses to a CD_2OD^+ ion with an internal energy content above the threshold for decomposition.

Upon admission of a gas into the RF-only quadrupole, ions are formed as a result of reactions between the CD_3O^+ or CD_2OD^+ ions and the selected substrate. The CD_3O^+ ions react by electron transfer (eq 1) with CH_3SH , $CH_2 = CH - CH_3$, NO_2 , $(CH_3)_2O$, and CH_3CH_2Cl (see Table 1). No evidence is obtained for reactions other than electron transfer with the various substrates, including NO_2 and NO , which were chosen in order to examine whether the methoxy cation would react differently with an odd-electron species than with an even-electron molecule. By contrast, the CD_2OD^+ ion reacts solely by exothermic or near-thermoneutral deuteron transfer, as indicated in Table 1 and eq 2.

Recently the adiabatic ionization energy (IE) of the methoxy radical has been determined by photoionization mass spectrometry to be 10.726 ± 0.008 eV [25], in agreement with calculations [26] and in line with an earlier report, which placed the IE at 10.6 ± 0.25 eV on the basis of the experimentally determined heat of formation of the triplet CH_3O^+ ion ($\Delta H_f^\circ = 1034 \pm 20$ kJ/mol) [10] and the tabulated heat of formation of the $CH_3O \cdot$ radical ($\Delta H_f^\circ = 15.5 \pm 3$ kJ/mol) [24]. Based on the IE of the methoxy radical and the data in Table 1, the electron transfer reactions occurring between the methoxy cation and the substrates CH_3SH , $CH_2 = CH - CH_3$, NO_2 , and $(CH_3)_2O$ are estimated to be exothermic, whereas electron transfer to N_2O is endothermic with 210–220 kJ/mol and accordingly was not observed. With CH_3CH_2Cl as the substrate, electron transfer is estimated to be endothermic with

Table 1. Primary product ions formed in the reaction of the CD_3O^+ and CD_2OD^+ ions with selected substrates

Substrate (M)	Product ion		Ionization energy (M) ^a (eV)	Proton affinity (M) ^a (kJ/mol)
	CD_3O^+ ^b	CD_2OD^+ ^c		
$\text{NO}^\cdot$	— ^d	No reaction	9.26	531
CH_3SH	CH_3SH^+	CH_3SHD^+	9.44	784
$\text{CH}_3 - \text{CH} = \text{CH}_2$	C_3H_6^+	$\text{C}_3\text{H}_6\text{D}^+$	9.73	751
$\text{NO}_2^\cdot$	NO_2^+	No reaction	9.75	585
$(\text{CH}_3)_2\text{O}$	$(\text{CH}_3)_2\text{O}^+$	$(\text{CH}_3)_2\text{OD}^+$	10.03	804
$\text{C}_2\text{H}_5\text{Cl}$	$\text{C}_2\text{H}_5\text{Cl}^+$	$\text{C}_2\text{H}_5\text{ClD}^+$	10.97	707
N_2O	No reaction	No reaction	12.89	581

^a Values from ref. 24.^b The ionization energy of the methoxy radical to form the triplet methoxy cation is given as 10.726 ± 0.008 eV in ref 25 and as 10.6 ± 0.25 eV in ref 10.^c The proton affinity, defined as the negative of the enthalpy change of the reaction $\text{M} + \text{H}^+ \rightarrow \text{MH}^+$, of formaldehyde is 718 kJ/mol (ref 24).^d The resolution of the mass-analyzing quadrupole is insufficient to separate the NO^+ ions from the isobaric DCO^+ ions arising by fragmentation of the methoxy cations (see text).

25–35 kJ/mol. The intensity of the signal of the product ions relative to the main ion beam signal was particularly low in the experiments with $\text{CH}_3\text{CH}_2\text{Cl}$, implying that the slight endothermicity of the reaction causes it to be less efficient than the exothermic electron transfer reactions of the CD_3O^+ ion. This suggests that the methoxy cations that reacted with the substrates did not possess a large amount of internal energy or a kinetic energy significantly above thermal. In combination with the absence of endothermic deuteron transfer from the CD_2OD^+ ion (Table 1), the results reveal that it is possible to adjust the parameters such that the ions undergoing ion-molecule reactions in the RF-only quadrupole of the BEqQ instrument have thermal to near-thermal kinetic energies.

The reactions of the CD_3O^+ and CD_2OD^+ ions are followed by some dissociation of the initially formed product ions or secondary ion-molecule reactions involving the added substrate (or both). For example, the C_3H_6^+ radical cation reacts with the propene molecules to form C_3H_3^+ (10%), C_3H_5^+ (15%), C_3H_7^+ (30%), C_4H_7^+ (20%), C_4H_9^+ (15%), and C_5H_9^+ (10%) ions, in agreement with results obtained by the ICR method [27] and under chemical ionization conditions [28]. The secondary reactions are in accordance with the known chemistry of the primary product ions and substantiate the assignment of a different initial reaction pathway of the CD_3O^+ and CD_2OD^+ ions.

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