J. Phys. Chem. 1993, 97, 13673-13676

Ion-Molecule Chemistry of $H_nC_3O^+$, $C_3O_2^+$, and C_3O^+

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Received: August 11, 1993; In Final Form: September 30, 1993[®]

Rate coefficients and product distributions have been measured using a selected ion flow tube for reactions of the ions $H_nC_3O^+$ (n = 0–3) and $C_3O_2^+$ with the neutral species H_2, CO, N_2, O_2, CH_4, NH_3, H_2O, C_2H_2, HCN, and CH_3CCH at 300 K. The structures of the ions are discussed, and a survey of relevant enthalpies of formation is presented.

Introduction

Tricarbon monoxide, CCCO, and propynal, HCCCHO, are among the growing list of molecules that have been observed in interstellar clouds.[1,2] Although the $H_nC_3O^+$ ions have not been observed in the interstellar medium, they are believed to have a part in the production of C_3O and propynal. One of the mechanisms suggested for the production of these species in the interstellar medium is dissociative recombination of the $H_3C_3O^+$ ion, which can be produced as a result of the radiatively-stabilized association reaction between $C_2H_3^+$ and CO.[3,4] Other unsaturated organo-oxygen molecular ions can be formed by the association of unsaturated hydrocarbon ions $C_xH_y^+$ (x = 2 or 3) with CO and perhaps also by reaction of these ions with atomic oxygen,[4,5] molecular oxygen, H_2O, and CO_2.[6]

$$C_2H_3^+ + CO \rightarrow H_3C_3O^+ + h\nu \qquad (1)$$

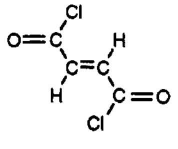
$$H_3C_3O^+ + e^- \rightarrow C_3O + H_2 + H \qquad (2a)$$

$$\rightarrow HC_3HO + H \qquad (2b)$$

In the interstellar context it is important to establish the behavior of the $H_nC_mO^+$ ions, for if they are to play a role in the synthesis of propynal and tricarbon monoxide, then their lifetimes must be sufficiently long for dissociative recombination processes to present a significant loss mechanism. Their chemical reactivity therefore needs to be established. Few studies have been published on the reactivity of $H_nC_mO^+$ ions, and the present work was undertaken to examine the reactivity of a range of these ions, with m = 3, with selected neutral reactants.

Experimental Section

The selected ion flow tube (SIFT) apparatus and the procedures used to measure the rate coefficients and branching ratios reported here have been described previously.[7] In brief, ions produced by electron impact on a suitable reagent are mass-selected and injected into a flow tube. Neutral reactants are introduced into the flow tube at fixed reaction ports, and the ensuing reactions are monitored by a second quadrupole mass spectrometer located behind a small sampling orifice at the downstream end of the flow tube. Electron impact (typically 30 eV) on appropriate source gases produced the required $H_nC_3O^+$ ions: HC_3O^+ and $H_2C_3O^+$ from fumaroyl dichloride (**1**) and $H_3C_3O^+$ from acrylic anhydride (**2**). $C_3O_2^+$ and C_3O^+ were both formed in the ion source by electron impact on carbon suboxide, C_3O_2. All reagents, except for acrylic anhydride and carbon suboxide, were obtained commercially and were generally purified by additional vacuum distillation. Acrylic anhydride was prepared from acrylic acid which was treated with triethylamine followed by phosgene, before purification by filtration and distillation.[8] Carbon suboxide was generated by the action of P_2O_5 on malonic acid.[9,10] All measurements were taken at room temperature (295 ± 5 K) and at a helium bath gas pressure of 0.30 Torr.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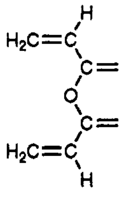
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Identity of Ions Formed by Electron Impact. The $H_nC_3O^+$ ions produced in the manner described above are all assumed to exist as the lowest-energy isomers, and the relevant thermodynamic data for these species, along with some of their isomeric counterparts, are summarized in Table I. No isomer of HC_3O^+, other than $HC{\equiv}C{-}C{\equiv}O^+$, has been identified, and we assign the HC_3O^+ ion produced from fumaroyl dichloride to this structure. The $H_2C_3O^+$ structure is assigned as $H_2C{=}C{=}CO^+$ on the grounds that this is the most stable $H_2C_3O^+$ isomer, and it can be formed readily from fumaroyl dichloride during electron impact with only a 1,2-hydrogen shift, which is known to be facile in ions produced by electron bombardment.[19] The alternative $HC{=}CH{-}CO^+$ isomer proposed in a theoretical study[16] cannot be excluded as a possibility although we had no evidence in our experiments with the $H_2C_3O^+$ ion that more than one isomer was present. Of the $H_3C_3O^+$ isomers investigated (see Table I), the most stable acyclic species by about 171 kJ mol^{-1} has the protonated propadienone structure, $H_2C{=}CH{-}CO^+$. This structure can be produced from acrylic anhydride by cleavage of the $H_2CCHC(O)$–$OC(O)CHCH_2$ bond without further rearrangement, and we thus expect the $H_3C_3O^+$ ion in our study to be almost exclusively $H_2C{=}CH{-}CO^+$. The observation of linear semilogarithmic decays of these ions with added neutral reactants indicates that only one isomeric form of each ion is present in the flow tube.[7,20]

Results and Discussion

$H_nC_3O^+$ Chemistry. A summary of the reaction chemistry of the $H_nC_3O^+$ ions is given in Table II. It is evident, from the results presented in the table, that both of the ions HC_3O^+ and H_2CCCO^+ are relatively unreactive. Only the reactions with NH_3 and CH_3CCH exhibit rate coefficients that are a substantial fraction of the collision rate. Also, HC_3O^+ exhibits an association

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[®] Abstract published in *Advance ACS Abstracts*, November 15, 1993.

0022-3654/93/2097-13673$04.00/0

TABLE I: Thermochemistry of $H_nC_3O^+$ (n = 0–3), $C_3O_2^+$, and Related Neutrals (Values in Bold Type Denote Those Chosen for the Indicated Structures in This Work)

molecule/ion	$\Delta H_f°$ (kJ mol^{-1})	method^a	ref
C_3O			
$C{=}C{=}C{=}O^+$	**>1252**	R	this work
	1393	MNDO	11
$C{=}C{=}C{=}O$	**326**	PA	12
	282	MO	13
	390	MO	14
HC_3O			
$HC{\equiv}C{-}C{=}O^+$	**971**	AP	15
$HC{=}C{=}C{=}O$	**<299**	R	this work
H_2C_3O			
$H_2C{=}C{=}C{=}O^+$	**975**	IP	15
$HC{=}CH{-}CO^+$	996	MO^b	16
$\mathrm{H\overline{C{=}CH{-}C}{=}O^+}$	1052	IP	15
	1089	MO^b	16
$HC{\equiv}C{-}C{-}OH^+$	1120	MO^b	16
$HC{\equiv}C{-}CHO^+$	1157	IP	17
	1216	MO^b	16
$\mathrm{H\overline{C{=}CH{-}C}{=}O}$	138	est	15
$HC{\equiv}C{-}CHO$	115	est	15
$H_2C{=}C{=}C{=}O$	**95**	est	15
H_3C_3O			
$H_2C{=}CH{-}CO^+$	**751**	AP	15
	749	MNDO	18
$\mathrm{H\overline{C{=}CH{-}C}{=}OH^+}$	868	MO^c	18
$HC{\equiv}C{-}CH{-}OH^+$	922	MO	18
$H_2C{=}C{=}COH^+$	969	MO^c	18
$HC{\equiv}C{-}CH_2O^+$	950	AP	15
$H_2C{=}CHCO$	72		15
C_3O_2			
$O{=}C{=}C{=}C{=}O^+$	**929**	IP	15
	832	MNDO	11
$O{=}C{=}C{=}C{=}O$	−94		15

[a] AP = appearance potential determination, est = estimated value, IP = ionization potential determination, MNDO = MNDO calculation, MO = ab initio MO calculation; PA = ab initio calculation of proton affinity, and R = reaction study. [b] Referenced to $\Delta H_f°(H_2CCCO^+)$. [c] Referenced to $\Delta H_f°(H_2CCHCO^+)$.

product channel with NH_3 while $H_2C_3O^+$ similarly associates with CH_3CCH. In each case the association channel is competing with other bimolecular channels.

$$HC_3O^+ + NH_3 \rightarrow CH_3CO^+ + HCN \quad (0.55) \qquad (3a)$$

$$\rightarrow HC_3O{\cdot}NH_3^+ \quad (0.45) \qquad (3b)$$

$$k_3 = 2.1 \times 10^{-10}\ \mathrm{cm^3\ s^{-1}}$$

$$H_2C_3O^+ + CH_3CCH$$

$$\rightarrow C_5H_6^+ + CO\ (\text{or } C_4H_2O^+ + C_2H_4) \quad (0.30) \qquad (4a)$$

$$\rightarrow C_5H_2O^+ + CH_4 \quad (0.20) \qquad (4b)$$

$$\rightarrow H_2C_3O{\cdot}CH_3C_2H^+ \quad (0.50) \qquad (4c)$$

$$k_4 = 1.2 \times 10^{-9}\ \mathrm{cm^3\ s^{-1}}$$

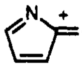
Although the association process (3b, 4c) is usually represented as the result of a bimolecular reaction, it is in fact a termolecular process, where the initial complex is stabilized by multiple collisions with the helium bath gas at 0.30 Torr. We have previously found association to be competitive with exothermic bimolecular channels in a number of systems,[22,23] and reactions 3b and 4c are two further examples. The association products are strongly bound adducts in which covalent bonding occurs, but in the present cases the isomeric forms of the adducts are not known. In reaction 3b the most stable acyclic ion known is protonated pyruvonitrile, CH_3COCNH^+, but this product cannot be formed from $HC_3O^+ + NH_3$ without substantial rearrangement. Also, examination of the variation of the adduct $H_4C_3NO^+$ signal with NH_3 flow showed that no rapid reaction with NH_3 occurred. A rapid reaction would be expected if the $H_4C_3NO^+$ product was CH_3COCNH^+ in view of the fact that its proton affinity (PA) is known to be much less than that of NH_3. One possible product that has a PA greater than that of NH_3 is the cyclic molecule protonated oxazole. Similarly, in reaction 4c the most stable $H_6C_6O^+$ ion identified is the phenol cation $C_6H_5OH^+$.

A slightly slower association reaction was also observed to occur between $H_2C_3O^+$ and HCN

$$H_2C_3O^+ + HCN \rightarrow H_2C_3O{\cdot}NCH^+ \quad (1.0) \qquad (5)$$

$$k_5 = 1.9 \times 10^{-10}\ \mathrm{cm^3\ s^{-1}}$$

Again the isomeric form of the $H_3C_4NO^+$ adduct is not known although one cyclic possibility could be the cation of pyrrol-2-one,



Alternatively, a six-membered aromatic molecular ion has also been suggested.[5] In reactions 3b, 4c, and 5 where the stabilized adduct is observed, some stability of the collision complex is inferred as it must survive sufficiently long for stabilization to occur via collisions with the helium bath gas.

The reaction chemistry of H_2CCHCO^+ is also summarized in Table II. From this it is evident that this ion is even less reactive than either HC_3O^+ or $H_2C_3O^+$. Again, association reactions, although occurring at low efficiency, are the major reaction channels, and the adduct ion $H_7C_6O^+$ is the major product of the reaction between H_2CCHCO^+ and CH_3CCH

$$H_2CCHCO^+ + CH_3CCH \rightarrow H_3C_5O^+ + CH_4 \quad (0.15) \qquad (6a)$$

$$\rightarrow H_7C_6O^+ \quad (0.85) \qquad (6b)$$

$$k_6 = 6.8 \times 10^{-11}\ \mathrm{cm^3\ s^{-1}}$$

The most stable $H_7C_6O^+$ species is protonated phenol, $C_6H_5OH_2^+$, which would correspond to a well depth of about 325 kJ mol^{-1} below ground-state reactants on the $H_7C_6O^+$ potential energy surface. Generally, when the complex ion formed as a result of association has a particularly stable configuration, then its lifetime with respect to unimolecular dissociation is long enough to allow stabilization via collisions with the bath gas to occur before the complex has time to dissociate back to reactants.[24] Consequently, at higher pressures the association process can move into the pressure-saturated regime and appear to be independent of pressure. It is the large density of states above a deep well that contributes to the longer lifetime. When the well depth between initial reactants and association product is shallower, corresponding to metastable isomeric forms, the average complex lifetime decreases with a consequent reduction in the association rate. Herbst et al.[25] predicted the presence of metastable isomers in several associating systems when statistical calculations overestimated the observed association rate coefficients. In view of the small association rate coefficient observed for the reaction between H_2CCHCO^+ and CH_3CCH (reaction 6b) and the deep well to the potential product, $C_6H_5OH_2^+$, we

TABLE II: Reactions of $H_nC_3O^+$ + X[p]

	HC_3O^+			H_2CCCO^+			H_2CCHCO^+			
X	products	branching ratio	k_{obs}[a]	products	branching ratio	k_{obs}[a]	products	branching ratio	k_{obs}[a]	k_c[a,b]
O_2	no reaction		<0.001	$CHO^+ + HCO + CO$[c]	0.60	0.036	no reaction		<0.001	0.65
				$C_2H_2O^+ + CO_2$[d]	0.40					
NH_3	$CH_3CO^+ + HCN$[e]	0.55	0.21	$NH_4^+ + HC_3O$[f]	1.0	1.3	$H_3C_3O{\cdot}NH_3^+$	1.0	0.021	2.2
	$HC_3O{\cdot}NH_3^+$	0.45								
C_2H_2	no reaction		<0.001	$C_5O^+ + 2H_2$[g]	0.30	0.43	no reaction		<0.001	1.0
				$C_5HO^+ + H_2 + H$[h]	0.55					
				$C_5H_2O^+ + H_2$[i]	0.15					
HCN	$HC_3O{\cdot}HCN^+$	1.0	0.004	$H_2C_3O{\cdot}NCH^+$	1.0	0.19	$C_3H_3O{\cdot}HCN^+$	1.0	0.002	3.3
CH_3CCH	$C_5H_5^+ + CO$[j]	1.0	0.92	$C_5H_6^+ + CO$[l]	0.30	1.2	$H_3C_5O^+ + CH_4$[o]	0.15	0.068	1.4
	(or $C_4HO^+ + C_2H_4$)[k]			(or $C_4H_2O^+ + C_2H_4$)[m]			$H_3C_3O{\cdot}CH_3C_2H^+$	0.85		
				$C_5H_2O^+ + CH_4$[n]	0.20					
				$H_2C_3O{\cdot}CH_3C_2H^+$	0.50					

[a] Rate coefficients in units of 10^{-9} cm^3 s^{-1}. [b] Calculated collision rate coefficients at 300 K using either Langevin theory when X has no dipole moment or the theory of Su and Chesnavich.[21] [c] $\Delta H° = -215$ kJ mol^{-1} for this channel. [d] $\Delta H° = -489$ kJ mol^{-1} for the H_2CCO^+ isomer and -336 kJ mol^{-1} for alternative possibility, $HCCOH^+$. [e] Production of CH_3CO^+ is exothermic by 137 kJ mol^{-1} while production of CH_2COH^+ is endothermic by 13 kJ mol^{-1}. [f] Proton transfer is exothermic if $\Delta H_f°$ (HC_3O) < 299 kJ mol^{-1}. [g] Requires $\Delta H_f°$ (C_5O^+) < 1203 kJ mol^{-1}. [h] Requires $\Delta H_f°$ (C_5HO^+) < 985 kJ mol^{-1}. [i] Requires $\Delta H_f°$ ($C_5H_2O^+$) < 1203 kJ mol^{-1}. [j] Formation of several possible $C_5H_5^+$ isomers is energetically possible. [k] If $C_4HO^+ + C_2H_4$ are the products, then $\Delta H_f°$ (C_4HO^+) < 1105 kJ mol^{-1}. [l] Calculated for ionized cyclopentadiene, c-$C_5H_6^+$, but other $C_5H_6^+$ isomers may also be formed. [m] Requires $\Delta H_f°$ ($C_4H_2O^+$) < 1109 kJ mol^{-1}. [n] Exothermic by more than 33 kJ mol^{-1} using a value of $\Delta H_f°$ ($C_5H_2O^+$) < 1203 kJ mol^{-1}. [o] Requires $\Delta H_f°$ ($H_3C_5O^+$) < 1012 kJ mol^{-1}. [p] Note: reactions with several other neutrals were investigated but were observed as "no reactions". These experiments gave the following upper limits for k_{obs} values, with all three $H_nC_3O^+$ ions, as follows: H_2, 0.0005; CO, N_2, and CH_4, 0.001; H_2O, 0.01.

TABLE III: Reactions of C_3O^+ + X

X	products	branching ratio	k_{obs}[a]	k_c[a,b]	$-\Delta H°$ (kJ mol^{-1})[c]
H_2	$HC_3O^+ + H$	1.0	0.8	1.5	>63
CH_4	$HC_3O^+ + CH_3$	1.0	0.83	1.1	>60
NH_3	$HC_3O^+ + NH_2$[d]		1.9	2.2	>46
	$C_3O{\cdot}NH_3^+$				
H_2O	$HC_3O^+ + OH$	1.0	0.5	2.4	>0
C_2H_2	$C_4H_2^+ + CO$	0.45	1.08	1.0	>69
	$C_3O{\cdot}C_2H_2^+$	0.55			
HCN	$HC_3N^+ + CO$[d]		2.9	3.3	>24
	$C_3O{\cdot}CN^+ + H$				
CO	$C_4O_2^+$	1.0	0.07	0.79	
N_2	no reaction		<0.001	0.73	
O_2	$CO^+ + 2CO$	0.20	0.22	0.67	>232
	$C_3O_2^+ + O$	0.80			>74
CO_2	no reaction		<0.001	0.78	

[a] Rate coefficients in units of 10^{-9} cm^3 s^{-1}. [b] Calculated collision rate coefficients at 300 K using either Langevin theory when X has no dipole moment or the theory of Su and Chesnavich.[21] [c] Enthalpies are derived from the values tabulated in Table I and from the compilation of Lias et al.[15] [d] Product ratio not determined. See text for discussion.

feel that protonated phenol is unlikely as the association product in this case and that a less stable isomer of $H_7C_6O^+$ is produced.

C_3O^+ and $C_3O_2^+$ Chemistry. A summary of the reaction chemistry of C_3O^+ is given in Table III. The reaction enthalpies shown assume a value for $\Delta H_f°(C_3O^+) > 1252$ kJ mol^{-1} which is based on the observation of the rapid reaction

$$C_3O^+ + H_2O \rightarrow HC_3O^+ + OH \qquad (7)$$

$$k_7 = 5 \times 10^{-10}\ cm^3\ s^{-1}$$

Terlouw et al. have determined $\Delta H_f°(HC_3O^+) = 971 \pm 5$ kJ mol^{-1} from the measured appearance potential of HC_3O^+.[26] This value, when linked with Botschwina's ab initio calculation for the proton affinity of C_3O of 885 kJ mol^{-1},[12] yields $\Delta H_f°(C_3O) = 326$ kJ mol^{-1}. Accurate branching ratios for the product channels of the reactions with NH_3 and HCN could not be found under the conditions of the experiment because of low signal intensities and the fact that, in each case, one of the product ions was adjacent in mass to the reactant C_3O^+ ion.

There is a marked increase in the reactivity of C_3O^+ ions over the reactions presented in Table II for $H_nC_3O^+$, and this can be attributed to the carbene character of $O{=}C{=}C{=}C{:}^+$. McElvany et al. have attributed the reactivity of C_3O^+ toward O_2 as being due to the carbene character of C_3O^+ such that complexation of O_2 occurs at the carbene end being followed by O atom loss.[11]

$$OCCC{:}^+ + O_2 \rightarrow OC_3O_2^+ \rightarrow OC_3O^+ + O \qquad (8)$$

In their low-pressure study (≤1 × 10^{-6} Torr) they reported just one channel (reaction 8) with a rate coefficient of 1.3×10^{-10} cm^3 s^{-1}. In the present work, at the higher pressures of the flow tube, we have observed two channels

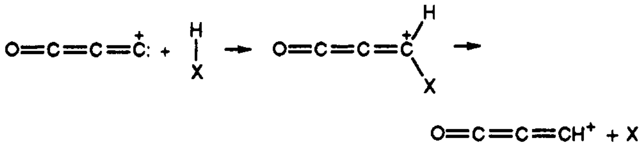
$$C_3O^+ + O_2 \rightarrow CO^+ + 2CO \quad (0.20) \qquad (9a)$$

$$\rightarrow C_3O_2^+ + O \quad (0.80) \qquad (9b)$$

$$k_9 = 2.2 \times 10^{-10}\ cm^3\ s^{-1}$$

The additional channel 9a possibly arises from partial collisional deactivation of the $C_3O{\cdot}O_2^+$ complex, increasing its lifetime and thus allowing a further exit channel from the complex to occur.

Much of the reaction chemistry of C_3O^+ in this study can also be interpreted in terms of carbene insertion into the H–X σ bond as



in the reactions with H_2, CH_4, NH_3, and H_2O. This type of process did not occur in the reactions with C_2H_2 and HCN where H atom transfer is not as energetically favorable and may be endothermic.

The reaction which controls the chemistry of C_3O^+ in interstellar clouds is the rapid reaction with H_2

$$OCCC{:}^+ + H_2 \rightarrow OCCCH^+ + H \qquad (10)$$

$$k_{10} = 8.0 \times 10^{-10}\ cm^3\ s^{-1}$$

and this reaction ensures that C_3O^+ will have a relatively short lifetime in dense clouds.

A summary of the reaction chemistry of $C_3O_2^+$ is presented in Table IV. It is evident that $C_3O_2^+$ exhibits less reactivity

TABLE IV: Reactions of $C_3O_2^+$ + X

X	products	branching ratio	k_{obs}[a]	k_c[a,b]	$-\Delta H°$ (kJ mol^{-1})
H_2	no reaction		<0.0001	1.5	
NH_3	$NH_3^+ + C_3O_2$	0.75	2.0	2.1	43
	$H_2C_2O^+$ + HNCO	0.25			109[c]
CH_4	$C_3O_2H^+ + CH_3$	1.0	0.3	1.05	*d*
H_2O	$C_3O_2{\cdot}H_2O^+$	1.0	0.001	2.0	
C_2H_2	$C_4H_2O^+$ + CO	1.0	1.2	1.0	*e*
HCN	$C_3O_2{\cdot}HCN^+$	1.0	0.015	3.2	
N_2	no reaction		<0.001	0.70	
CO	no reaction		<0.001	0.76	
O_2	$CO^+ + CO + CO_2$	0.10	0.12	0.63	194
	CO_2^+ + 2CO	0.75			215
	$C_2O_2^+ + CO_2$	0.15			288[f]
CO_2	no reaction		<0.001	0.74	

[a] Rate coefficients in units of 10^{-9} cm^3 s^{-1}. [b] Calculated collision rate coefficients at 300 K using either Langevin theory when X has no dipole moment or the theory of Su and Chesnavich.[21] [c] Calculated for the products $H_2C{=}CO^+$ + HNCO. [d] The observation of this channel yields $\Delta H_f°(C_3O_2H^+)$ <709 kJ mol^{-1}; i.e., PA(C_3O_2) >727 kJ mol^{-1}. [e] The observation of this channel yields $\Delta H_f°(C_4H_2O^+)$ < 1268 kJ mol^{-1}. [f] Calculated using $D(OC{-}CO^+)$ = 93.7 kJ mol^{-1} (ref 27).

than does C_3O^+ as only the reactions with NH_3 and C_2H_2 proceed at the collision rate.

$$C_3O_2^+ + NH_3 \rightarrow NH_3^+ + C_3O_2 \quad (0.75) \tag{11a}$$

$$\rightarrow C_2H_2O^+ + HNCO \quad (0.25) \tag{11b}$$

$$k_{11} = 2.0 \times 10^{-9}\ \mathrm{cm^3\ s^{-1}}$$

$$C_3O_2^+ + C_2H_2 \rightarrow C_4H_2O^+ + CO \tag{12}$$

$$k_{12} = 1.2 \times 10^{-9}\ \mathrm{cm^3\ s^{-1}}$$

The extent of rearrangement required in both reactions 11b and 12 supports mechanisms whereby the reactions proceed through tight collision complexes.

Conclusion

The ion chemistry of $H_nC_3O^+$ ions is characterized by a noticeable lack of reactivity with the major known neutral constituents of interstellar clouds. As a consequence, all the $H_nC_3O^+$ ions, viz HC_3O^+, $H_2C_3O^+$, and H_2CCHCO^+, are likely to have relatively long cloud lifetimes with their major loss processes being dissociative recombinations. Association reactions of $H_nC_3O^+$ were found to present an important outcome for several reactions, and these can lead to the efficient formation of new and more complex molecular ions. The much greater reactivity of the C_3O^+ ion over the other ions investigated in this study can be attributed to the carbene character of C_3O^+.

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