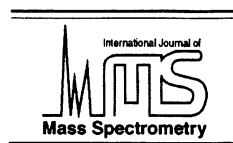




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International Journal of Mass Spectrometry 190/191 (1999) 171–179

# Ion-molecule chemistry of carbon suboxide in an ion-trap mass spectrometer

O. Bortolini<sup>a</sup>, L. Pandolfo<sup>b</sup>, C. Tomaselli<sup>b</sup>, P. Traldi<sup>c,\*</sup><sup>a</sup>Dipartimento di Chimica, Università di Ferrara, Via Borsari 46, 44100 Ferrara, Italy<sup>b</sup>Dipartimento di Chimica Inorganica, Metallorganica e Analitica, Università di Padova, Via Marzolo 1, 35131 Padova, Italy<sup>c</sup>CNR, Centro di Studi sulla Stabilità e Reattività dei Composti di Coordinazione, Via Marzolo 1, 35131 Padova, Italy

Received 5 August 1998; accepted 15 December 1998

## Abstract

The gas phase ion molecule reactions between carbon suboxide, neutral or radical cation, and different ionic or neutral substrates have been investigated or reviewed. The experiments show that neutral C<sub>3</sub>O<sub>2</sub> is reactive with ionized target, reflecting the high nucleophilicity of carbon suboxide. (Int J Mass Spectrom 190/191 (1999) 171–179) © 1999 Elsevier Science B.V.

**Keywords:** Carbon suboxide; Ion trap mass spectrometry; Ion-molecule reaction

## 1. Introduction

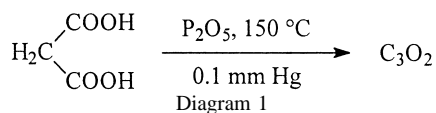
In the last decade, ion trap [1] has definitively moved from the research and development phase to its extensive application in the analytical field. The availability of this new and powerful mass spectrometric approach is because of the efforts of different research groups, among which the Ray March and John Todd ones were a reference point. It was, for one of us (P.T.), an honor and a pleasure to collaborate with them.

In our opinion the great power of ion trap lies in its capabilities for study of ion-molecule reactions and here we report the results obtained on the reactivity of an unusual reactant, carbon suboxide.

At the beginning of the century, while studying the high temperature behavior of diethyl malonate in the

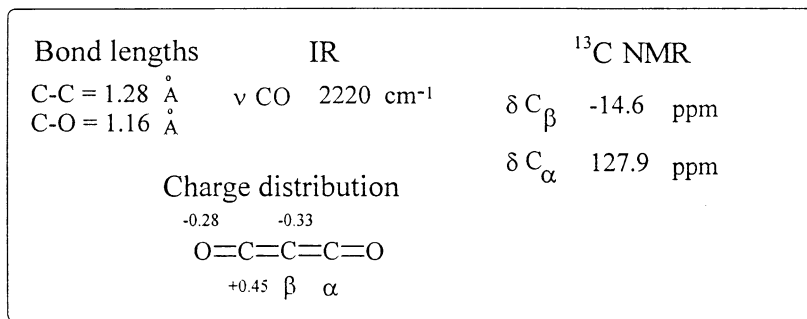
presence of P<sub>4</sub>O<sub>10</sub>, Diels [2] observed the formation of small quantities of a previously unreported substance, which attracted his attention mainly for its unpleasant characteristics. In fact, it was a very bad smelling, highly irritating, lachrymatory, suffocating gas (B.p.: 7 °C). On the basis of the elemental analysis and typical reactivity, Diels proposed for this substance an heterocumulenic structure and, because of the low O/C ratio, named it *carbon suboxide*. In time, C<sub>3</sub>O<sub>2</sub> was variously named, (allenedione, 1,3-propadiendione and even evil gas) but, even if it is not a classical oxide, the name proposed by Diels is still commonly used.

Carbon suboxide can also be considered as the anhydride of malonic acid, from which it can be conveniently prepared by dehydration reaction, Eq. (1), but it is more correctly viewed



\* Corresponding author.

Dedicated to J.F.J. Todd and R.E. March in recognition of their original contributions to quadrupole ion trap mass spectrometry.



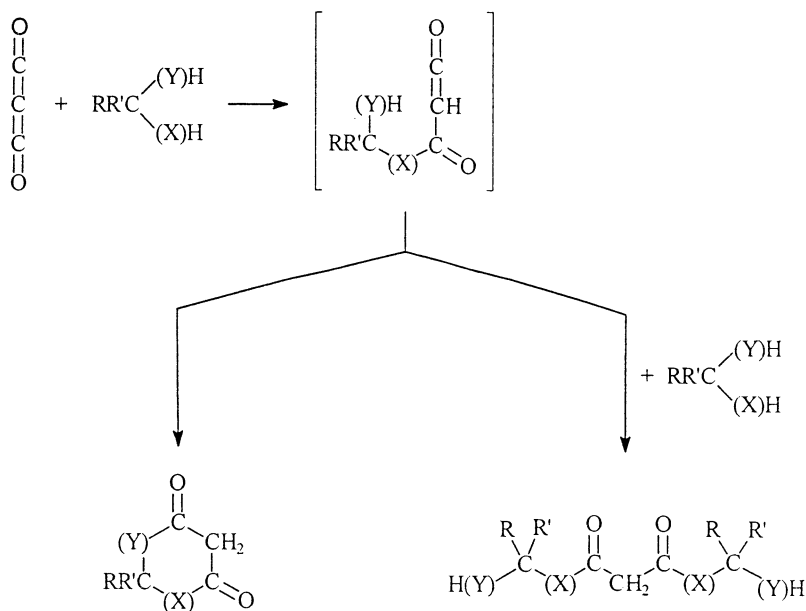
Scheme 1.

as the prototype of bis ketenes. Bond lengths, the most important spectroscopic features and the charge distribution of  $\text{C}_3\text{O}_2$  are reported in Scheme 1.

A massive number of papers, mainly dealing with the organic chemistry of  $\text{C}_3\text{O}_2$ , has been produced and comprehensive reviews have been published on this subject [3]. The most evident feature observed is that the organic reactivity of carbon suboxide is mostly driven by its peculiar charge distribution, indicating the central carbon atom as the most nucleophilic center [4]. Actually,  $\text{C}_3\text{O}_2$  is reported to react, in the

condensed phase, yielding malonil derivatives or heterocyclic compounds, produced by attacks to the olefinic double bond(s). Both options are synthetically depicted in Scheme 2, in which X and Y indicate nucleophilic moieties.

It is rather surprising that, despite its reactivity, until few years ago the organometallic chemistry of carbon suboxide has been practically ignored and only recently the first results in this field have been reviewed [5]. Another field almost ignored until recently, was the gas-phase reactivity of carbon sub-



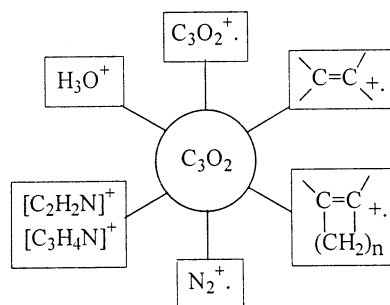
Scheme 2.

oxide, even if some photochemical reactions [6] indicated the relative facile decarbonylation of  $C_3O_2$  and its possible use as a monocarbon source, mainly toward unsaturated systems. With regard to this particular kind of reactivity it is to be further emphasized that carbon suboxide has been suggested to be the source of some extra carbon found in Halley's comet [7] and it has been reported to decompose thermally [8] or by application of a microwave plasma [9] yielding atomic carbon, with a behavior reasonably connected with the high thermodynamic stability of the outgoing CO molecule(s). Furthermore,  $C_3O_2^+$  has been claimed to be present in dense interstellar clouds [10] and neutral carbon suboxide or its polymers have been proposed as possible starting materials for the synthesis of biomolecules on the primitive Earth [11].  $(C_3O_2)_n$  has been taken in to account as a constituent of the surface of Mars [12] and of the Venus haze [11 (a)(b)].

Leaving aside these general considerations, in this article we wish to report the results obtained in the study of the reactivity of carbon suboxide using an ion trap mass spectrometer.

## 2. Experiment

Carbon suboxide was prepared by reported methods [13] and stored at  $-20^\circ\text{C}$ , a temperature at which it can be maintained without polymerization, for some days. It was transferred into the mass spectrometer by a septum/cannula device. Propene, cyclopentene, cyclohexene, cycloheptene were commercially available products, used without further purification, and introduced by means of a micrometering valve to achieve a nominal pressure of  $2 \times 10^{-6}$  Torr. Ion-molecule reactions were performed using an ion trap mass spectrometer (ITMS, Finnigan MAT, San Jose CA) operating in electron impact conditions, ionization time in the range 6000–9000  $\mu\text{s}$ , trap temperature  $80^\circ\text{C}$ . The selected ions were isolated by the apex method [1] and left to react with the neutral targets at  $q_z$  values in the range 0.25–0.35, for reaction times of 10–500 ms. Tickle voltages and tickle times were in the range of 100–400 mV and 1–8 ms.



## 3. Results and discussion

The gas-phase chemistry of carbon suboxide has been the subject of investigations that include electron impact of  $C_3O_2$  at low and high pressure conditions [14], the reactivity of  $C_3O_2^+$  with neutrals [15] such as  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{C}_2\text{H}_2$ ,  $\text{HCN}$ ,  $\text{O}_2$ , and the reaction of neutral carbon suboxide against different nucleophiles [16] like  $\text{OH}^-$ ,  $\text{NH}_2^-$ ,  $\text{HS}^-$ . Properties such as the 50 eV mass spectrum, photoelectron spectrum, infrared and raman spectra, ultraviolet spectrum, electron diffraction pattern, electron affinity and proton affinity have been described [17].

During the last five years, the reactivity of carbon suboxide either as ionized or as neutral precursor has been studied by means of an ion trap mass spectrometer. By this approach the unequivocal selection of the reactive ion is easily achieved and the charged species may be left to react with neutral molecules for variable reaction times up to seconds. Furthermore, on one hand side reactions involving ionic species other than those of interest are almost completely suppressed, allowing an easy description of the reaction patterns, on the other hand the structure of the product ions can be investigated by MS/MS experiments.

In this article we report an overview of the gas-phase chemistry of  $C_3O_2$  with different ionized targets, in the order carbon suboxide itself, acyclic and cyclic alkenes, ionic species from acetonitrile,  $\text{N}_2^+$  and  $\text{H}_3\text{O}^+$ , as summarized in Scheme 3.

As it will be seen below, the chemistry here presented is guided by a unique leitmotif, that is the

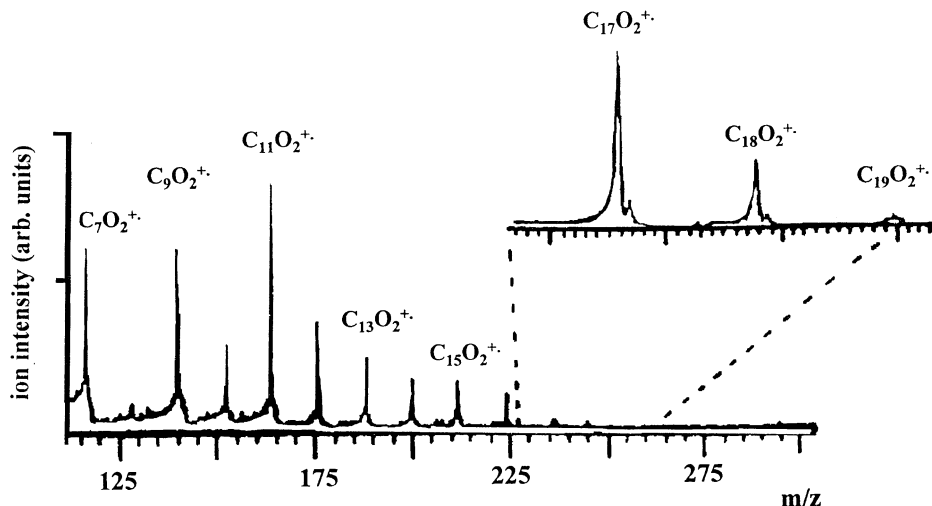


Fig. 1. Mass spectrum of the products arising from the reaction of  $C_3O_2^+$  with  $C_3O_2$ .

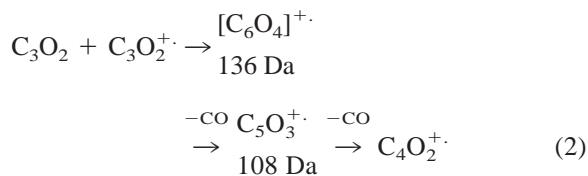
electrophilic addition of the different ions on the electron rich central carbon of the suboxide, followed by CO loss (or losses).

### 3.1. Reactions of $C_3O_2$ with $C_3O_2^+$

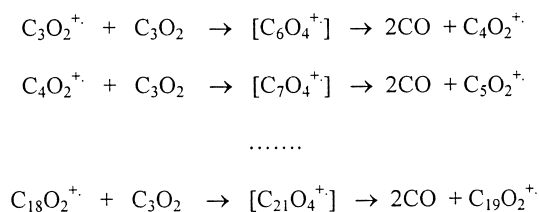
When  $C_3O_2$  is ionized by electron impact and the selected molecular ion ( $m/z$  68) is allowed to react with neutral  $C_3O_2$  present in the ion trap, the predominant formation of  $C_4O_2^+$  ( $m/z$  80, 100% r.a.) is observed, accompanied by the presence of  $C_nO_2^+$  ions ( $n \leq 19$ ), Fig. 1 [18–20]. The general mechanism related to this unusual and progressive “monocarbon” insertion was proposed as the result of the reaction of  $C_nO_2^+$  radical cations with a neutral  $C_3O_2$  molecule, leading to an activated addition complex  $[C_{n+3}O_4]^+$ . This highly reactive intermediate rapidly decomposes through the loss of two CO molecules, thus, leading the observed product radical cations  $C_{n+1}O_2^+$ . An overall view of the reactions is given in Scheme 4.

In order to provide evidence for the above proposed intermediates, the reaction between  $C_3O_2^+$  and  $C_3O_2$  was investigated in a lower time window  $10^{-7}$  s. This was obtained by performing the reaction in the chemical ionization ion source of a double focusing,

reverse geometry VG ZAB 2F instrument. In these conditions, together with the  $C_3O_2^+$  ( $m/z$  68) and  $C_4O_2^+$  ( $m/z$  80) ionic species, a new ion was detected at  $m/z$  108 corresponding to  $C_5O_3^+$  and representing a further intermediate originating by single CO loss from the activated complex  $[C_6O_4]^+$ , Eq. (2).



These findings are confirmed by the product ion spectrum of  $C_5O_3^+$ , in which the most favored decomposition pathway is CO loss, yielding  $C_4O_2^+$ . The MS/MS mass spectrum of  $C_4O_2^+$  species, obtained in



Scheme 4.

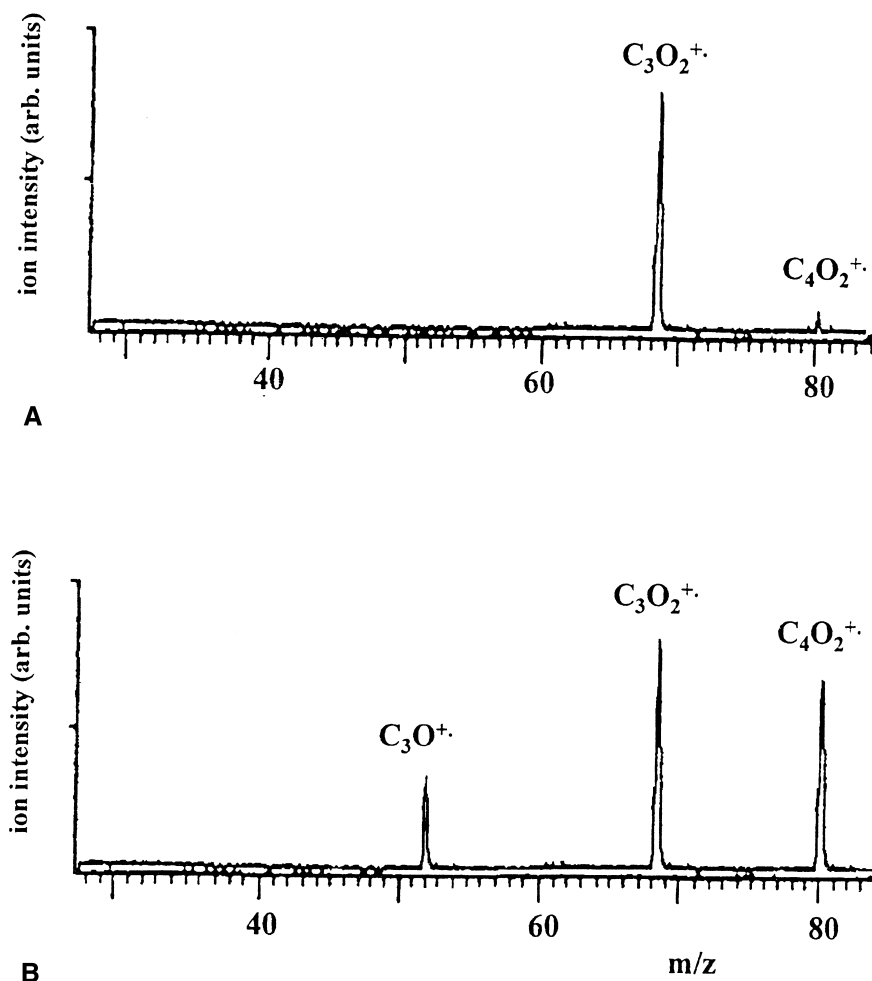


Fig. 2. Daughter-ion mass spectrum of the ionic species at  $m/z$  80 formed during the ion-molecule reaction of  $C_3O_2^+$  with  $C_3O_2$  at (a)  $2 \times 10^{-4}$  Torr  $C_3O_2$  pressure conditions and (b)  $5 \times 10^{-6}$  Torr pressure conditions.

low-energy (ITMS) and high-energy (CID-MIKE) collision conditions, gave conflicting results. In the low-energy regime, Fig. 2(a), an apparently retro-synthetic process is observed, corresponding to the loss of monocarbon atom, whereas the CID-MIKE spectrum of the same ion shows CO elimination. Ab initio calculations performed on  $C_4O_2^+$  revealed the presence of a linear cumulenic structure with oxygens placed at both extremities,  $O=C=C=C=O$ , as the preferred energy-minimized geometry. This structure was perfectly conceivable with CID-MIKE experiments, but it was at odd with the low-energy

collision spectrum. More recently, ab initio calculations and further experiments performed in low  $C_3O_2$  pressure conditions proved that the formal loss of carbon atom from  $C_4O_2^+$  affording  $C_3O_2^+$ , observed in ITMS, originated by a charge-exchange reaction between  $C_4O_2^+$  and neutral  $C_3O_2$  present inside the trap. As it can be seen in Fig. 2(b), the MS/MS mass spectrum of selected  $C_4O_2^+$  ions, as obtained by ITMS at  $5 \times 10^{-6}$  Torr carbon suboxide pressure conditions, show the presence of an ion at  $m/z$  52, loss of CO, and of a second species at  $m/z$  68, ascribed to the above discussed charge-exchange reaction.

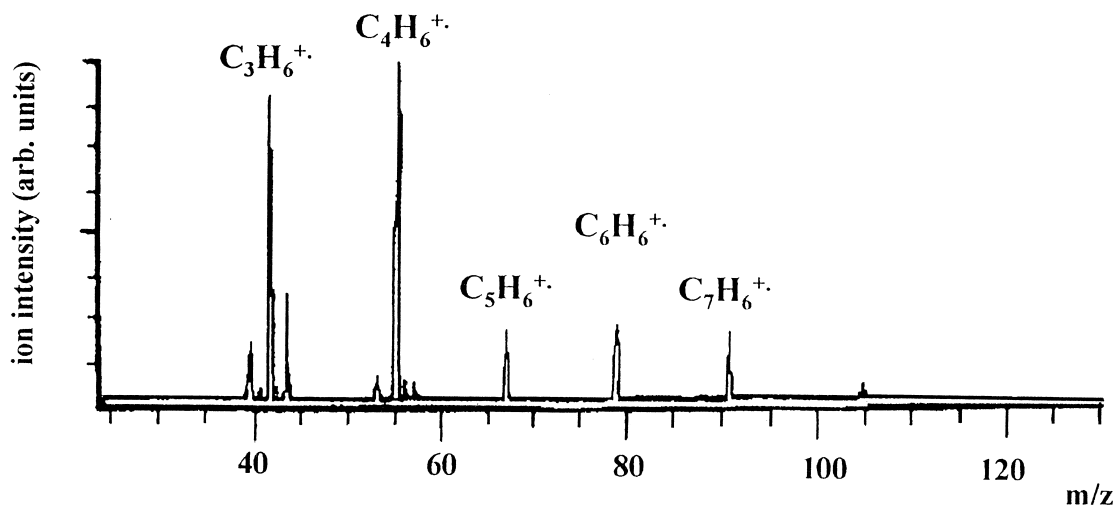
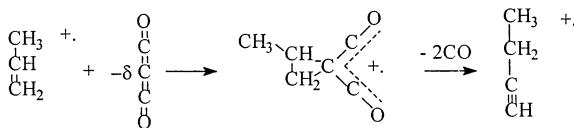


Fig. 3. Mass spectrum of the products arising from the reaction of  $C_3H_6^+$  with  $C_3O_2$ .

### 3.2. Reactions of $C_3O_2$ with acyclic and cyclic alkene radical cations

Progressive insertion of monocarbon is observed during the reaction of  $C_3O_2$  with propene molecular ions ( $m/z$  42) and the pertinent spectrum is shown in Fig. 3. The reaction product ions at  $m/z$  54, 66, 78, and 90 correspond to the addition of one, two, three, and four carbon atoms to the alkene, respectively [21]. The MS/MS mass spectrum of the most abundant addition product ( $m/z$  54) shows fragment ions at  $m/z$  39 and 29, corresponding to losses of  $CH_3^+$  and  $C_2H^+$ . On the basis of such results and of preliminary ab initio calculations, the reaction was postulated to take place in analogy to what observed between  $C_3O_2$  and  $C_3O_2^+$ , i.e. nucleophilic addition of the central carbon of  $C_3O_2$  on the propene radical cation double bond, followed by expulsion of carbon monoxide in two steps, as shown in Scheme 5.

The inverse reaction, performed by reacting ion-



Scheme 5.

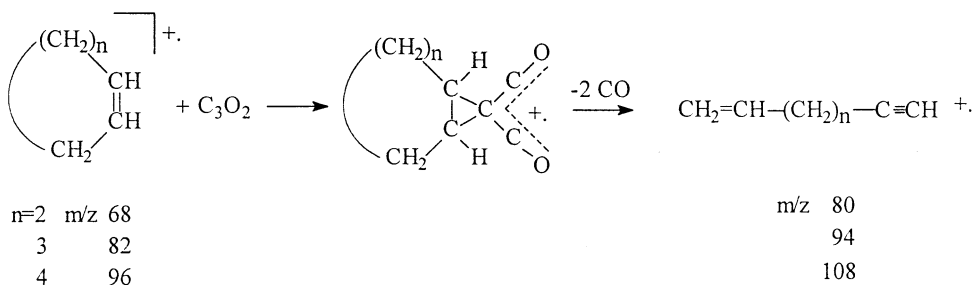
ized  $C_3O_2$  and neutral propene, did not lead to any addition or insertion product.

The reaction between carbon suboxide and cyclic alkenes is under investigation using cyclopentene ( $C_5H_8$ ,  $m/z$  68), cyclohexene ( $C_6H_{10}$ ,  $m/z$  82) and cycloheptene ( $C_7H_{12}$ ,  $m/z$  96) radical cations. In all cases, insertion of monocarbon is observed affording the addition products at  $m/z$  80, 94, and 108, respectively. Despite the low yield of these additions even for relatively long reaction times (0.1 s) which compromised the study, a general trend may be noted. The MS/MS spectra of the selected addition product ions  $C_6H_8^+$ ,  $C_7H_{10}^+$ , and  $C_8H_{12}^+$  show loss of  $C_2H_4$  in all cases, that could reasonably derive from a common structure, according to Scheme 6.

The complete characterization of the monocarbon atom insertion products is currently in progress. Attempts to perform the inverse reaction between  $C_3O_2^+$  and neutral cyclic alkenes were unsuccessful.

### 3.3. Reactions of $C_3O_2$ with $[C_2H_2N]^+$ and $[C_3H_4N]^+$ ions from acetonitrile

The reaction of the selected  $C_2H_2N^+$  ions of acetonitrile with  $C_3O_2$  affords a single reaction product ion at  $m/z$  80, conceived as the result of a nucleophilic attack of carbon suboxide on the positive



Scheme 6.

charge localized on the carbon atom of  $^+\text{CH}_2\text{CN}$ , followed by a single CO loss. The second molecule of CO is retained in the product ion structure, as confirmed by the MS/MS mass spectrum of  $m/z$  80 ions [22].

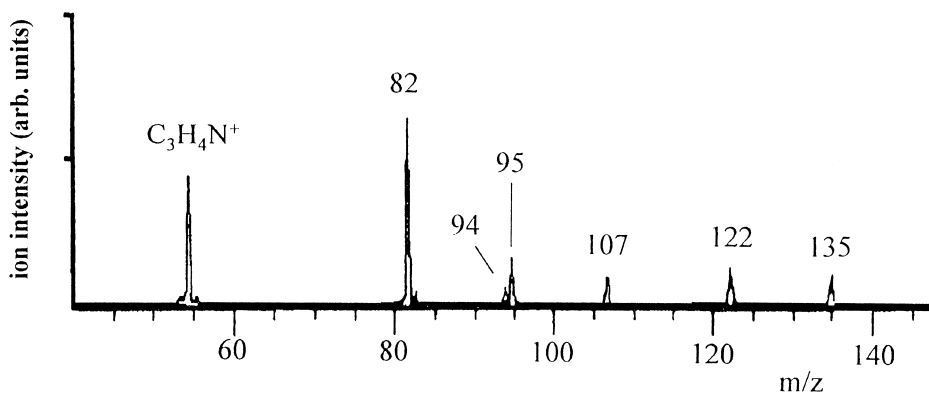
Compared with  $\text{C}_2\text{H}_2\text{N}^+$ , the reaction of  $[\text{C}_3\text{H}_4\text{N}]^+$  ( $m/z$  54) toward the same neutral target is more complex, affording several peaks at  $m/z$  82, 94, 95, 107, 122, and 135, Fig. 4. These experimental findings were explained on the basis of at least three different reactivities pertaining to  $[\text{C}_3\text{H}_4\text{N}]^+$ : (1) the reaction with carbon monoxide, responsible for ions at  $m/z$  82; (2) the genuine ion-molecule reaction with  $\text{C}_3\text{O}_2$ , and (3) the reaction with  $\text{CH}_3\text{CN}$ , affording the ionic species at  $m/z$  95. The ion-molecule reaction between  $[\text{C}_3\text{H}_4\text{N}]^+$  ( $m/z$  54) and neutral carbon suboxide affords the addition product at  $m/z$  122. The proposed assignment of its structure and mechanism of formation is based on three major pieces of evidence: (1) the collision induced decomposition

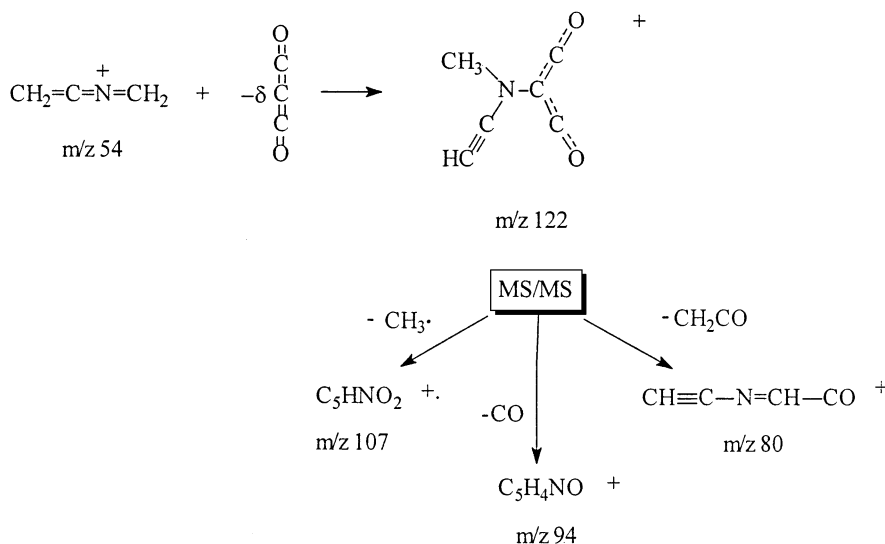
spectrum of the addition ion, (2) the proposed mechanism of reaction of  $[\text{C}_3\text{H}_4\text{N}]^+$  with alkenes obtained with the aid of labeled analytes [23], and (3) the MS/MS spectrum of  $m/z$  54 ions [22].

All these findings are consistent with the  $m/z$  54 ion arranged in a heterocumulene-type structure  $\text{CH}_2=\text{C}=\text{N}^+=\text{CH}_2$  acting as electrophile on the electron rich central carbon of  $\text{C}_3\text{O}_2$ , leading to the formation of the ionic species at  $m/z$  122, as shown in Scheme 7. The ions at  $m/z$  94 and 107, present in low abundance in the spectrum of Fig. 4, could be explained as the result of a fast expulsion of CO and methyl radical from the addition product at  $m/z$  122, according to Scheme 7.

### 3.4. Reactions of $\text{C}_3\text{O}_2$ with $\text{N}_2^+$

Attempts to react neutral  $\text{C}_3\text{O}_2$  with dinitrogen radical cation were unsuccessful for a large range of

Fig. 4. Mass spectrum of the products arising from the reaction of  $\text{C}_3\text{H}_4\text{N}^+$  with  $\text{C}_3\text{O}_2$ .



Scheme 7.

reaction times and reactant partial pressures. The only peaks observed ( $m/z$  68, 80, and 92) are primarily because of charge exchange reaction between  $\text{N}_2^+$  and  $\text{C}_3\text{O}_2$ , generating  $\text{C}_3\text{O}_2^+$  ( $m/z$  68) which in turn reacts with neutral carbon suboxide yielding cascade mono-carbon insertion reactions as previously observed [18–20]. As expected the yield in  $\text{C}_n\text{O}_2^+$  increases by increasing both reaction times and carbon suboxide partial pressure.

Analogous results, i.e. the formation of  $\text{C}_n\text{O}_2^+$ , has been observed in the attempts to perform the inverse reaction, by isolating  $\text{C}_3\text{O}_2^+$  and letting it react with  $\text{N}_2$ . Molecular nitrogen is completely inert and behaves as “buffer” gas, thus, favoring the reactivity of  $\text{C}_3\text{O}_2^+$  with  $\text{C}_3\text{O}_2$  yielding ions at  $m/z$  80, 92, and 104. Even in this case this behavior has been observed for a large range of reaction times (0.2–800 ms) and pressures.

### 3.5. Reactions of $\text{C}_3\text{O}_2$ with $\text{H}_3\text{O}^+$

In the reaction of  $\text{H}_3\text{O}^+$  ( $m/z$  19) and  $\text{C}_3\text{O}_2$  it has been possible to observe the protonation of carbon suboxide with formation of a peak at  $m/z$  69. This reactivity is fully consistent with the proton affinity values of the two analytes  $\text{H}_2\text{O}$  ( $697 \text{ kJ mol}^{-1}$ ) [24]

and  $\text{C}_3\text{O}_2$  ( $791 \text{ kJ mol}^{-1}$ ) [17]. The MS/MS mass spectrum of protonated carbon suboxide afforded a single peak at  $m/z$  68, thus, indicating a relatively easy loss of  $\text{H}^+$ .

## 4. Conclusions

Ion trap mass spectrometry proved to be a valuable tool in studies on the reactivity of  $\text{C}_3\text{O}_2$  (neutral or radical cation) with different ionic or neutral substrates. The obtained results show that reactivity is present among neutral  $\text{C}_3\text{O}_2$  and ionized targets, reflecting the nucleophilicity of the former. Such behavior can be explained in terms of an enhanced negative charge density on the central carbon of carbon suboxide that leads to addition with the different ionic species under study, followed by CO loss or losses.

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