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Orth, Robert G.; Jonkman, Harry T.; Michl, Josef

Published in:
International Journal of Mass Spectrometry and Ion Physics

DOI:
[10.1016/0020-7381\(82\)80089-2](https://doi.org/10.1016/0020-7381(82)80089-2)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
1982

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Orth, R. G., Jonkman, H. T., & Michl, J. (1982). Secondary Ion Mass Spectrometry of Small-Molecule Solids at Cryogenic Temperatures. IV. Carbon Dioxide, Carbonyl Sulfide and Carbon Disulfide. *International Journal of Mass Spectrometry and Ion Physics*, 43(1). [https://doi.org/10.1016/0020-7381\(82\)80089-2](https://doi.org/10.1016/0020-7381(82)80089-2)

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SECONDARY ION MASS SPECTROMETRY OF SMALL-MOLECULE SOLIDS AT CRYOGENIC TEMPERATURES. IV [1]. CARBON DIOXIDE, CARBONYL SULFIDE AND CARBON DISULFIDE

ROBERT G. ORTH *, HARRY T. JONKMAN and JOSEF MICHL

Department of Chemistry, University of Utah, Salt Lake City, UT 84112 (U.S.A.)

(Received 28 December 1981; in final form 1 February 1982)

ABSTRACT

Secondary ion mass spectra of neat solid CO₂, COS and CS₂ and of CO₂ diluted in solid argon were measured as a function of the nature and energy of the primary ions (He⁺, Ne⁺, Ar⁺, Kr⁺, Xe⁺, 1.0-4.5 keV). All of the solids produced a rich variety of positive and negative secondary ions. Many of these have masses considerably in excess of the molecular weight of the parent molecules, particularly with primary ions of large momentum. Carbon dioxide produces well-defined cluster series with CO₂ as the solvating unit. Carbonyl sulfide and carbon disulfide yield a complex pattern of positive and negative cluster ions.

INTRODUCTION

The recently-reported secondary ion mass spectra of low-temperature solids composed of small molecules (water [2], nitrogen and carbon monoxide [3,4], rare gases [5], nitrogen oxides [1,6] and small hydrocarbons [2,3,7]) show that an abundance of ions of high molecular weight is formed upon bombardment of these solids with energetic primary ions. Except for the case of the hydrocarbons, the observed cluster masses indicate the presence of simple repeated solvating units. In some instances, the solvating unit is identical with the molecule of the solid (H₂O, N₂, CO, Ar, Kr, Xe), but nitrogen oxides appear to be exceptional in that the composition of their solvating units seems to be in no simple relation to the composition of the solid. The mechanism of the formation of the large clusters and the chemistry involved in the strange stoichiometry of the cluster ions produced from solid nitrogen oxides are presently not understood. A working hypothesis for the observed phenomena has been proposed [1,6] and clearly, additional

* Present address: Department of Chemistry, Montana State University, Bozeman, MT 59717, U.S.A.

investigations are called for. In the present paper, we report the behavior of solid CO_2 , COS and CS_2 .

EXPERIMENTAL

A detailed description of the low-temperature secondary ion mass spectrometry (SIMS) equipment is given in ref. 1 and 4. Briefly, at least 10 000 monolayers of the sample (reagent grade CS_2 and >99.5% pure CO_2 and COS, checked for absence of impurities by mass spectrometry) are deposited from gas phase on a copper plate held at 18 K by a closed-cycle helium cryostat in a preparation chamber (base pressure, 1×10^{-8} torr). A gate valve is then opened and the plate pushed into position in the main vacuum chamber (base pressure, 1×10^{-9} torr). A differentially pumped Riber C150RB ion gun uses electron impact (50 eV) on a research grade rare gas (Matheson) to produce the primary ion beam, which is 3 mm in diameter and is rastered over an area of 1 cm^2 . The ion energies were 1-4.5 keV, the current densities were 10-50 nA cm^{-2} . This corresponds to one impacting primary ion per 1.6×10^5 - $3.2 \times 10^4 \text{ \AA}^2$ of surface area during a 1 s spectral scan. Generally, it took a few minutes to obtain the first spectrum, but we have observed no change in the spectra as a function of the number of scans for up to an hour of measurement. After many hours of bombardment, the spectra of COS and CS_2 became weaker and a thin layer of sulfur was visible on the sample. During ion bombardment, the pressure in the main chamber rises to $5\text{-}8 \times 10^{-9}$ torr. The spectra are recorded with an Extranuclear Laboratory quadrupole mass spectrometer equipped with an energy prefilter (Bessel box), which selects a secondary ion energy from 0 to 20 eV (bandwidth 0.5 eV). An electron flood gun biased at -5 V serves to neutralize surface charge. Excessive flooding without adjustment of the transmission window on the Bessel box reduces the intensities of higher mass ions, as reported previously [1,5,8], at least in part by displacing the energy distribution curve due to surface charge buildup. However, a poor setting of the flood gun cannot be compensated fully by adjustment of the transmission energy setting on the Bessel box. The spectra reported here were obtained by maximizing the intensity of a cluster peak first by adjusting the energy transmitted by the Bessel box, then by adjusting the flood-gun controls, and finally, readjusting the Bessel box setting if necessary. This procedure yields well reproducible results.

During the measurement, the sample was generally held at 18 K. The temperature was varied between 16 and 70 K for CO_2 and over smaller ranges for COS and CS_2 but no effect on the spectra was observed.

RESULTS

Carbon dioxide

The positive SIMS of solid CO_2 is shown in Figs. 1 and 2. When 1 keV He^+ is used as the primary ion, the spectrum shows only the molecular ion CO_2^+ , its fragments C^+ , O^+ , and CO^+ , and the ion O_2^+ (Fig. 1). Other peaks, i.e. of C_2O^+ , C_2O_2^+ and $(\text{CO}_2)\text{O}_2^+$, are present but are very weak. As the energy of the primary He^+ ions is raised to 4 keV, the intensity of the fragment ions CO^+ and O^+ increases somewhat relative to the molecular ion CO_2^+ , and that of C^+ does not change greatly. The most striking changes are an increase in the abundance of O_2^+ and of a series of cluster ions. The intensity of the cluster ion peaks and of the O_2^+ peak is enhanced further when 1 keV Ar^+ ions, and even more so when 4 keV Ar^+ ions are used as the primary ion (Fig. 2). The series $(\text{CO}_2)_n\text{O}_2^+$ dominates, and the series $(\text{CO}_2)_n\text{O}_5^+$ [or $(\text{CO}_2)_n\text{C}_3^+$], $(\text{CO}_2)_n\text{CO}_3^+$, $(\text{CO}_2)_n\text{O}_3^+$, $(\text{CO}_2)_n^+$, $(\text{CO}_2)_n\text{CO}^+$ and $(\text{CO}_2)_n\text{C}^+$ are also distinct. Further increase in the momentum of the primary ion (Kr^+ , Xe^+) has little additional effect.

As observed in previous work [1,4,5,9], the energy distribution of the secondary ions is different for the parent ion and its fragments on the one

Fig. 1. Positive SIMS of solid CO_2 .

Fig. 2. Positive SIMS of solid CO_2 .

hand and for the cluster ions on the other hand. The former are broader and peak at higher energies and the latter are narrower and peak at lower energies. The O_2^+ ion behaves like a cluster ion in this respect (Fig. 3). As described in the experimental part, the instrumental settings were chosen so as to maximize the intensity of cluster ions. Because of the differences in the secondary ion energy distributions, the intensities displayed in the illustra-

Fig. 3. Secondary ion energy distributions in positive SIMS of solid CO_2 (primary ion: Ar^+ at 4 keV). An unknown constant is added to the horizontal scale.

Fig. 4. Negative SIMS of solid CO₂.

tions do not reflect faithfully the total relative ion yields but are biased in favor of the cluster ions.

The O⁻ peak is the strongest in the negative SIMS of solid CO₂. When primary ions of a large momentum are used, negative cluster ions appear (Fig. 4). The most prominent is (CO₂)_nCO₃⁻; (CO₂)_nO₂⁻ and (CO₂)_nO₃⁻ are also clearly recognizable. Similarly as observed for negative ion clusters from solid nitrogen oxides [1], the negative cluster ions from solid CO₂ have a

Fig. 5. Positive SIMS of CO₂ diluted 1/50 in solid argon.

very narrow energy distribution and are easy to miss when taking the spectra.

When CO_2 is diluted with solid argon, its SIMS undergoes a dramatic change (Fig. 5). The fragment ions C^+ and O^+ nearly disappear and the CO_2 solvating unit is replaced by argon atoms in cluster ion formation. The O_2^+ peak is suppressed and even with 4 keV Ar^+ primary ions its intensity is only comparable with that of CO_2^+ . At a dilution of 1:200, and with 4 keV Ar^+ primary ions, the only observed ion which definitely originates in more than one CO_2 molecule is $(\text{CO}_2)\text{O}_2^+$. It appears only very weakly; in addition to the Ar_n^+ series, the only strong peaks are CO^+ , O_2^+ , CO_2^+ , ArO^+ and ArCO^+ . With He^+ primary ions, almost no clusters are observed.

Carbonyl sulfide and carbon disulfide

The positive SIMS of solid COS and CS_2 obtained with Xe^+ as the primary ion is shown in Fig. 6. Both of these molecules have a pronounced tendency

Fig. 6. Positive SIMS of solid COS and solid CS_2 . The distinction between O_2 and S was based on a consideration of isotopic intensities.

Fig. 7. Negative SIMS of solid COS and solid CS₂. The distinction between O₂ and S was based on a consideration of isotopic intensities.

towards product ion and cluster ion formation and S₂⁺ is observed from COS even when He⁺ is used as the primary ion. A multitude of sulfur-based cluster ions is observed in both spectra. However, the two spectra are different from each other, indicating that the sulfur-containing clusters originate in COS and CS₂, respectively, rather than in elemental sulfur produced on the surface by the bombardment.

The negative SIMS of these two solids is shown in Fig. 7. With He⁺ bombardment, cluster ions are not prominent and O⁻, S⁻ and SO⁻ dominate the spectrum of COS, while C₂⁻ and S⁻ are most important in CS₂. With heavier primary ions, clusters appear: S_n⁻ and S_nO⁻ dominate the spectrum of COS, and S_n⁻ and C₂S_n⁻ predominate in that of CS₂.

DISCUSSION

The SIMS of solid CO₂ can be accounted for in a relatively straightforward manner. The ions observed in our spectra are the same as those observed in the photoionization of gaseous CO₂ and of a gaseous mixture of CO₂, CO

and O_2 at pressures of the order of 1 torr [10] but our intensity distribution is different and favors higher mass ions, presumably because of the much higher particle densities in the formation region. The initial ionization and fragmentation processes involved are likely to be

Neutral-forming processes such as

are likely to occur at the same time [11].

The initial damage formation will then be followed by a rich variety of further reactions of those reactive species which have not been knocked out of the solid upon the initial impact. For instance, the likely secondary processes involving monoatomic oxygen are

The species with the lowest ionization potential among those present, O_2 , are likely to capture the positive charges which have not been ejected immediately. Similarly, CO_3^- is likely to carry the negative charge. It is possible to account for the observed clusters in terms of association and replacement reactions such as

However, the molecules of the solid are associated to start with and previous

results for solid nitrogen oxides [1] suggest that the cluster composition may well be dominated by a process of selective evaporation, in which a warmed-up piece of the original solid is ejected and loses preferentially those components which are attracted the least to the central positive (O_2^+) or negative (CO_3^-) charge. This, too, will rationalize the observed composition of cluster ions from solid CO_2 .

The effects of dilution with solid argon can also be understood in simple terms. The O^+ and C^+ fragment ions have much lower intensities since the impacting particles now do most of the initial damage on solid argon itself, producing reactive centers such as Ar^+ , Ar_2^+ , Ar^* and Ar^{+*} , which are capable of moving rapidly in the matrix until they are scavenged by the CO_2 molecules present, producing CO_2^+ and/or its fragments. It is possible that much of the observed fragmentation of CO_2 is due to secondary electrons produced by the impacting ion, since thermalized Ar^+ or Ar_2^+ are not energetic enough to produce fragment ions from CO_2 .

The ionic and neutral fragments produced from CO_2 within the argon matrix are less likely to encounter another CO_2 molecule as the degree of dilution increases, and it is not surprising that products from such encounters become rarer with increasing dilution. Instead, ions such as O^+ , CO^+ , and CO_2^+ are likely to end up solvated with one or more argon atoms.

An interesting problem is posed by the observed intensities of the O_2^+ ion relative to the CO_2^+ ion. At first, dilution suppresses it considerably suggesting that it is of bimolecular origin [12], and this is supported by the energy distribution curve of this secondary ion obtained on neat CO_2 , which resembles that of cluster ions rather than that of fragment ions. However, with further dilution the intensity of the O_2^+ peak relative to the CO_2^+ peak does not change much. Perhaps some of the O_2^+ is formed in a unimolecular fragmentation process [13]

or perhaps the small size of particles such as O allows them to diffuse very rapidly through the warmed-up portion of the matrix.

Less can be said at the moment about the mechanism producing the SIMS of solid COS and CS_2 . Similar to the nitrogen oxides [1], and unlike CO, N_2 [4] and CO_2 , they produce clusters with solvating units which bear no simple resemblance to the original molecules of the solid. Similarly as for the nitrogen oxides, we hypothesize that extensive radiation damage occurs along the track of the primary particle and that a large piece of the solid, containing some of the damage track, is then ejected and cools off by losing those constituent molecules which cling the least firmly to the central positive or negative charge. Many transformed species can thus collect around a single charged entity to produce a secondary cluster ion whose structure differs totally from that of the initial solid.

The composition of the observed positive and negative ions can be accounted for by a set of plausible reaction steps. The most likely initial

damage is the ionization of COS and CS₂ and the dissociation of the carbon-sulfur bond, or, less likely, of the carbon-oxygen bond, producing S⁺, S, S⁻ and S₂⁺ [14,15], and O⁺, O, O⁻ as the primary reactive centers. Those which are not ejected immediately are likely to abstract a sulfur atom from the excess solid COS or CS₂ present or to add to the S_n⁺, S_n and S_n⁻ which build up, in processes such as

The parent ions are also very reactive and processes such as

are well documented from gas-phase studies [14]. Qualitatively, the simpler nature of the spectra of COS relative to CS₂ is in keeping with the low reactivity of CO relative to CS, which is prone to dimerization and further reactions.

CONCLUSIONS

The ejection of very large positive and negative secondary cluster ions upon bombardment of low-temperature solids with energetic primary ions now begins to emerge as a general phenomenon. It may be of use as a source of cluster ions for further study. The chemical composition of the clusters formed from some of the solids is strikingly different from the composition of the solids themselves. This observation is likely to be of importance for efforts to understand the detailed mechanism underlying secondary ion mass spectrometry (SIMS, FAB). We have proposed a qualitative model which accounts for the cluster compositions observed so far, but clearly, additional more quantitative work will have to follow our initial observations before the mechanism of the formation of the cluster ions can be elucidated.

ACKNOWLEDGEMENT

We are grateful to Mr. Boris Sinković and Mr. James Thompson-Colón for technical assistance and to NSF for financial support (CHE 78-27094).

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