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

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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

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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 10000 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 \times 10^{-8} torr). A gate valve is then opened and the plate pushed into position in the main vacuum chamber (base pressure, 1 \times 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 \times 10^5-3.2 \times 10^4 \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 5-8 \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\(_2\)O\(^+\), C\(_2\)O\(_2^+\) and (CO\(_2\))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 (CO\(_2\))\(_n\)O\(_2^+\) dominates, and the series (CO\(_2\))\(_n\)O\(_5^+\) [or (CO\(_2\))\(_n\)C\(_3^+\)], (CO\(_2\))\(_n\)CO\(_3^+\), (CO\(_2\))\(_n\)O\(_3^+\), (CO\(_2\))\(_n^+\), (CO\(_2\))\(_n\)CO\(^+\) and (CO\(_2\))\(_n\)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
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-
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 CO\(_2\). When primary ions of a large momentum are used, negative cluster ions appear (Fig. 4). The most prominent is (CO\(_2\))\(_n\)CO\(_3^-\); (CO\(_2\))\(_n\)O\(_2^-\) and (CO\(_2\))\(_n\)O\(_3^-\) are also clearly recognizable. Similarly as observed for negative ion clusters from solid nitrogen oxides [1], the negative cluster ions from solid CO\(_2\) have a

Fig. 4. Negative SIMS of solid CO\(_2\).

Fig. 5. Positive SIMS of CO\(_2\) 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 (CO$_2$)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
towards product ion and cluster ion formation and S\textsuperscript{2+} is observed from COS even when He\textsuperscript{+} 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 CS\textsubscript{2}, 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\textsuperscript{+} bombardment, cluster ions are not prominent and O\textsuperscript{-}, S\textsuperscript{-} and SO\textsuperscript{-} dominate the spectrum of COS, while C\textsubscript{2} and S\textsuperscript{-} are most important in CS\textsubscript{2}. With heavier primary ions, clusters appear: S\textsubscript{n} and S\textsubscript{2}O\textsuperscript{-} dominate the spectrum of COS, and S\textsubscript{n} and C\textsubscript{2}S\textsubscript{n} predominate in that of CS\textsubscript{2}.

DISCUSSION

The SIMS of solid CO\textsubscript{2} 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 CO\textsubscript{2} and of a gaseous mixture of CO\textsubscript{2}, CO
and O₂ 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

\[
\begin{align*}
\text{CO}_2 & \rightarrow \text{CO}_2^+ (X^2\Pi_{3/2g}) + e^- \quad \text{AE} = 13.7 \text{ eV} \\
\text{CO}_2 & \rightarrow \text{CO}_2^+ (X^2\Pi_{1/2g}) + e^- \quad \text{AE} = 13.79 \text{ eV} \\
\text{CO}_2 & \rightarrow \text{CO}_2^+ (A^2\Pi_u) + e^- \quad \text{AE} = 17.31 \text{ eV} \\
\text{CO}_2 & \rightarrow \text{CO}_2^+ (B^2\Sigma_u^+) + e^- \quad \text{AE} = 18.07 \text{ eV} \\
\text{CO}_2 & \rightarrow \text{CO}_2^+ (C^2\Sigma_g^+) + e^- \quad \text{AE} = 19.39 \text{ eV} \\
\text{CO}_2 & \rightarrow O^+(4S_{3/2}) + CO + e^- \quad \text{AE} = 19.07 \text{ eV} \\
\text{CO}_2 & \rightarrow \text{CO}^+(2\Sigma^+) + O(^3\Pi) + e^- \quad \text{AE} = 19.47 \text{ eV} \\
\text{CO}_2 & \rightarrow \text{CO}^+(2\Sigma^+) + O(^1\Pi) + e^- \quad \text{AE} = 21.43 \text{ eV} \\
\text{CO}_2 & \rightarrow \text{CO}^+(2\Pi) + O(^3\Pi) + e^- \quad \text{AE} = 21.98 \text{ eV} \\
\text{CO}_2 & \rightarrow C^+ + O_2 + e^- \quad \text{AE} = 22.8 \text{ eV} \\
\text{CO}_2 + e & \rightarrow \text{CO} + O
\end{align*}
\]

Neutral-forming processes such as

\[
\begin{align*}
\text{CO}_2 & \rightarrow \text{CO} + O(^1\Pi) & \Delta H = 7.5 \text{ eV}
\end{align*}
\]

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

\[
\begin{align*}
O^+ + \text{CO}_2 & \rightarrow O_2^+ + \text{CO} \quad [12] \\
O + \text{CO}_2 & \rightarrow O_2 + \text{CO} \\
O + O_2 & \rightarrow O_3
\end{align*}
\]

The species with the lowest ionization potential among those present, O₂, are likely to capture the positive charges which have not been ejected immediately. Similarly, CO₃⁻ 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

\[
\begin{align*}
2 \text{CO}_2 + O_2^+ & \rightarrow (\text{CO}_2)O_2^+ + \text{CO}_2 \\
(\text{CO}_2)O_2^+ + O_2 & \rightarrow (\text{CO}_2)O_2^+ + \text{CO}_2 \\
(\text{CO}_2)O_2^+ + O_3 & \rightarrow (\text{CO}_2)O_5^+ + \text{CO}_2
\end{align*}
\]

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]

$$CO_2 \rightarrow O_2^+ + C + e^- \quad \text{AE} = 23 \text{ eV}$$

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 CS$_2$ and the dissociation of the carbon-sulfur bond, or, less likely, of the carbon-oxygen bond, producing S$^+$, S, S$^-$ and S$_2^+$ [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 CS$_2$ present or to add to the S$_n^+$, S$_n$ and S$_n^-$ which build up, in processes such as

$$\text{COS} + S^+ \rightarrow \text{CO} + S_2^+$$
$$\text{CS}_2 + S^- \rightarrow \text{CS} + S_2^-$$
$$S_n + S^+ \rightarrow S_{n+1}^+$$
$$S_n + O^- \rightarrow S_nO^-$$

The parent ions are also very reactive and processes such as

$$\text{CS}_2^+ + \text{CS}_2 \rightarrow S_2^+ + 2 \text{CS}$$
$$\text{CS}_3^+ + \text{CS}$$
$$C_2S_3^+ + S$$
$$\text{CS}_4^+ + C$$

are well documented from gas-phase studies [14]. Qualitatively, the simpler nature of the spectra of COS relative to CS$_2$ 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.

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