absorption spectrum is $1.3 \times 10^4$ s$^{-1}$. For photochemical studies, the degassed chromatographed solution of 1 (~0.03 M in CFCl$_3$) was irradiated at 466–610 nm at $-78^\circ$C. After 12 h of irradiation at $-78^\circ$C the red color had completely disappeared. Vapor-phase chromatography and $^1$H NMR spectroscopy reveal four hydrocarbon products 2-5 and tetrazen 6 in a 1:4 ratio. Controls show that 0.03 M solutions of the 1,1-diazene in CFCl$_3$ at $-78^\circ$C are stable. The four hydrocarbon products 2-5 appear to be products from the photochemical extrusion of molecular nitrogen from 1. The details of the mechanism for the loss of nitrogen are as yet unknown, but the products are the same as found in the thermal decomposition of 1. The tetrazen 6, an unexpected photoproduct, probably results from the bimolecular reaction of $S_1$ and/or $T_1$ with $S_0$.

Triplet sensitization experiments were carried out at longer wavelengths at $-78^\circ$C. Irradiation of degassed chromatographed solutions of 1 (0.03 M in CFCl$_3$) at >608 nm in the presence of 0.02–0.05 M azulene sensitizer ($E_T = 31$ kcal) where the 1,1-diazene was shown to be unreactive on direct irradiation, affords four hydrocarbon products 2-5 and tetrazen 6 in a 1:9 ratio. The product compositions from the thermal, direct irradiation and sensitized decompositions of 1 and the 1,2-diazene isomer $7^1,15$ are summarized in Table I.

The 2-methylpropane/tetramethylyclobutane ratios for the direct and sensitized photodecomposition of the 1,1-diazene 1 are 1.14 and 3.08, respectively. Importantly, the 2-methylpropene/tetramethylyclobutane ratios are the same from the 1,1- and 1,2-diazene isomers in the direct and sensitized photolyses. Common singlet and triplet 1,4-biradicals formed from loss of nitrogen from $S_1$ and $T_1$, respectively, from 1 and 7 would be sufficient to explain these results. Bartlett and Porter have shown a spin correlation effect on the product ratios in the direct and triplet sensitized photodecomposition of cyclic 1,2-diazenes similar to 7,11,14. Because the hydrocarbon product ratios from 1 are different for direct vs. sensitized photolyses, but in agreement with the product ratios from the 1,2-diazene isomer 7, this may indicate a spin correlation effect in the 1,1-diazene case. This apparent lack of significant intersystem crossing would be consistent with the large calculated $S_0$-$T_1$ gap in the 1,1-diazene.$^{11}$ Control experiments show that the 1,1-diazene 1 does not rearrange ($<1\%$) to the more stable 1,2-isomer 7 under direct or sensitized photolysis.$^{19}$

In summary, evidence has been provided that $S_1$ of the 1,1-diazene 1 is deactivated at least in part by fluorescence, loss of nitrogen, and tetrazen formation. Similarly, $T_1$ is deactivated in part by loss of nitrogen and tetrazen formation. The appearance of tetrazen 6 on direct irradiation is significant because, in the absence of $S_1$ and $T_1$, intersystem crossing, one can estimate an upper limit of $\geq 10^4$ s$^{-1}$ on the unimolecular rate for loss of $S_1$ from $S_1$. Issues that are currently under investigation include a direct measurement of the lifetime of $S_1$, a spectrochemical test to quantitate the apparent spin correlation effect and a search for triplet emission which would locate the $S_0$-$T_1$ gap in the 1,1-diazene.

Acknowledgment. We are grateful to the National Science Foundation (CHE80-06495) for support of this research.

Secondary Ion Mass Spectrometry of Molecular Solids: A Source of Cluster Ions

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Received January 26, 1981

Secondary ion mass spectrometry (SIMS) shows considerable promise as a method for characterization of nonvolatile molecular solids.$^{1}$ The observed molecular ions and fragment ions are often accompanied by cluster ions. In the case of solid hydrocarbons (methane,$^2$ cyclohexane,$^3$ benzene)$^3$, a rich variety of cluster ions is formed, but no repeating solvating unit is readily detected. On the other hand, several solids composed of small molecules yield cluster ions of regular composition [$H^+$(H$_2$O)$_n$] from ice,$^3$ (N$_2$)$_m$ and (N$_2$)$_m$ from solid nitrogen,$^3$ CO(CO)$_n$ and CO(CO)$_n$ from solid CO$_2$,$^5$ CO$_2$.$^3$

(19) However, we cannot rule out that photoexcited 1 rearranges to phototetrazene 7 which then undergoes reaction.
(20) Assuming $k(S_1 + S_0) \leq 3.9 \times 10^4$ s$^{-1}$, concentration of $S_1$ at 0.03 M, and ratio of hydrocarbons/tetrazen products = 0.25.

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leading one to believe that the solvating units will generally reflect the molecular component of solids composed of small molecules.

We now wish to report that SIMS of solid \( \text{N}_2\text{O}, \text{NO}, \text{N}_2\text{O}_3 \), \( \text{N}_2\text{O}_4 \), and \( \text{O}_2 \) produces strange clusters of readily characterized compositions in which the solvating unit is not simply related to the molecular composition of the solid. The measurements were performed as in ref 4, and the purity of the gases used was monitored carefully by mass spectrometry. The nature of the secondary ions was independent of the conditions of the experiment, but the relative abundance of heavy cluster ions was maximized by the use of heavy primary ions (\( \text{Ar}^+, \text{Kr}^+, \text{Xe}^+ \)) and higher primary ion energies (4 keV).

The SIMS of solid NO, shown in Figure 1, is dominated by the molecular ion. Fragment ions are nearly absent, as are the expected simple cluster ions (\( \text{NO}^+ \)). The dominant cluster ions have the composition \([\text{NO}(\text{N}_2\text{O}_3)]^+\) up to the limit \( n = 11 \), imposed by our mass spectrometer. The series \([\text{NO}(\text{N}_2\text{O}_3)]^+, [\text{NO}(\text{N}_2\text{O}_3)]^+, \text{and } [\text{N}(\text{N}_2\text{O}_3)]^+\) are observed much more weakly. The solvating unit, \( \text{N}_2\text{O}_3 \), is richer in oxygen than the molecules of the solid itself.

The SIMS of solid \( \text{N}_2\text{O}, \text{N}_2\text{O}_3 \), and \( \text{N}_2\text{O}_4 \) are distinctly different (Figure 2). The base peak is again \( \text{NO}^+ \), and other fragment ions and the molecular ion are seen only very weakly. A prominent series of clusters, \([\text{NO}(\text{N}_2\text{O}_3)n(\text{N}_2\text{O}_4)n]^+\), is observed to the instrumental limit. The relative abundance of the \( \text{N}_2\text{O}_4 \) solvating units increases in the order solid \( \text{N}_2\text{O}, \text{N}_2\text{O}_3, \text{N}_2\text{O}_4 \), and \( \text{N}_2\text{O}_5 \). It is noteworthy that the oxygen-rich solvating unit, \( \text{N}_2\text{O}_4 \), is so prominent in the solid with the oxygen-poor stoichiometry, \( \text{N}_2\text{O}_2 \). For solid \( \text{N}_2\text{O}_4 \) cluster ions \([\text{NO}(\text{N}_2\text{O}_3)n(\text{N}_2\text{O}_4)n]^+, n = 1, 2, \) are also observed.

The SIMS of solid \( \text{O}_2 \) is dominated by the peaks of \( \text{O}^+ \) and \( \text{O}_2^+ \), while \( \text{N}_2\text{O}^+ \) is hardly observable. Clusters are again observed to the instrumental limit. The strongest series is \( \text{O}_2(\text{N}_2\text{O})^+ \), suggesting \( \text{O}_2 \) as the primary solvating unit.

The strange selectivity with which larger solvating units such as \( \text{N}_2\text{O}_3, \text{N}_2\text{O}_4 \), and \( \text{O}_2 \) are associated with a central positive ion is one of the excess of the molecules of the solid, such as \( \text{NO}, \text{N}_2\text{O}, \text{or } \text{O}_2 \) present at first, and suggests the initial formation of reactive charged and neutral fragments (\( \text{O}, \text{N}, \text{O}^+, \text{etc.} \)), which then react to produce \( \text{N}_2\text{O}_3, \text{N}_2\text{O}_4 \), or \( \text{O}_2 \) units, either before or after the separation of a piece of the molecular solid carrying a positive charge from the bulk solid. The warmed-up cluster will then shake off its least firmly held components, leaving the more polarizable larger solvating units observed. The feasibility of this is indicated by the report that clusters of type \([\text{NO}(\text{N}_2\text{O}_3)n]^+\) are formed upon electron impact on gaseous NO expanding from a nozzle, with an intensity distribution similar to that shown in Figure 1.

The chemical reactions involved can be compared to those occurring in high-pressure mass spectrometry and radiation chemistry.\(^7\) It is tempting to postulate that oxygen atoms play a crucial role for all five solids. In \( \text{NO} \), one expects processes such as electron impact on gaseous \( \text{NO} \) expanding from a nozzle, with an intensity distribution similar to that shown in Figure 1.

\( \text{N}_2\text{O}_2, \text{N}_2\text{O}_3 \text{, and } \text{N}_2\text{O}_4 \text{. ions. The most striking among these are the negative SIMS of } \text{N}_2\text{O}_3 \text{ and } \text{N}_2\text{O}_4 \text{ which show intense peaks for } \text{NO}^+, \text{N}_2\text{O}_3^-, \text{and } \text{N}_2\text{O}_4^-, \text{and a series of higher clusters extending to the instrumental limit.} \)

We conclude that even for solids composed of small molecules, cluster composition need not be indicative of the composition of the solid. The complexity of the processes suggested by the present results already for solids composed of very simple molecules has ominous connotations for attempts to analyze in detail the SIMS of near organic solids. In analytical applications, it would appear essential to work under conditions of higher dilution (matrix isolation).\(^8\) Surface adsorbate analysis.\(^9\)

Finally, we note that ion impact on low-temperature solids promises to provide a rich source of novel cluster ions.

**Acknowledgment.** This work was supported by the National Science Foundation (CHE 78-270944). We are grateful to Dr. Z. Herman for useful discussions.

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**Figure 1.** Positive SIMS of solid NO with \( \text{Ar}^+ \) at 4 keV.

**Figure 2.** Positive SIMS of solid \( \text{N}_2\text{O}, \text{N}_2\text{O}_3 \), and \( \text{N}_2\text{O}_4 \) with \( \text{Ar}^+ \) at 3 keV (~18 K). The dots indicate the positions of intense peaks in the SIMS of solid NO.

As \( \text{N} + \text{NO} \to \text{N}_2 + \text{O}, \text{O} + \text{NO} \to \text{NO}_2 \), and \( \text{NO}_2 + \text{NO} \to \text{N}_2\text{O}_3 \). In \( \text{N}_2\text{O}_3 \), the expected processes are \( \text{N} + \text{N}_2\text{O} \to \text{N}_2 + \text{O} + \text{N}_2\text{O}_4 \to \text{NO}_2 + \text{O}_2 \). In \( \text{N}_2\text{O}_3 \), reactions such as \( \text{N} + \text{N}_2\text{O} \to \text{NO} + \text{N}_2\text{O}_4 \to \text{NO}_2 + \text{N}_2 \text{O}_4 \), and \( \text{O} + \text{N}_2\text{O}_4 \to \text{N}_2\text{O}_6 \) appear probable. In many of these processes, the reactive species may actually be an ion rather than a neutral.

In the SIMS of solid NO, \( \text{NO}_2 \) is likely to be converted into \( \text{N}_2\text{O}_4 \) efficiently by the excess NO present. In the SIMS of solid \( \text{N}_2\text{O}_3 \), this conversion should be less efficient since NO is scarce, accounting for the observed presence of \( \text{N}_2\text{O}_2 \) in the clusters. In solid \( \text{N}_2\text{O}_4 \), \( \text{NO} \) should be trapped efficiently to produce \( \text{N}_2\text{O}_3 \), while \( \text{O} \) can yield \( \text{N}_2\text{O}_2 \). The abundance of \( \text{N}_2\text{O}_2 \) present is reflected in the composition of the clusters. In the SIMS of \( \text{O}_2 \), initially formed \( \text{O} \) atoms can be expected to add to \( \text{O}_2 \) to produce \( \text{O}_3 \).

All of these postulates are compatible with the observed negative SIMS of these solids, which shows mostly \( \text{O}^- \) ions. The most striking among these is the negative SIMS of \( \text{N}_2\text{O}_3 \) and \( \text{N}_2\text{O}_4 \) which show intense peaks for \( \text{NO}^-, \text{N}_2\text{O}_3^-, \text{and } \text{N}_2\text{O}_4^- \), and a series of higher clusters extending to the instrumental limit.

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