absorption spectrum is $1.3 \times 10^{4}$ s$^{-1}$. For photochemical studies, the degassed chromatographed solution of 1 (0.03 M in CFC$\text{Cl}_3$) was irradiated at 466–610 nm at $-78 \, ^{\circ}\text{C}$. After 12 h of irradiation at $-78 \, ^{\circ}\text{C}$ the red color had completely disappeared. Vapor-phase chromatography$^{10}$ and $^1$H NMR spectroscopy reveal four hydrocarbon products 2–5 and tetrazene 6 in a 1:4 ratio. Controls show that 0.03 M solutions of the 1,1-diazene in CFC$\text{Cl}_3$ at $-78 \, ^{\circ}\text{C}$ 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 tetrazene 6, an unexpected photoproduct, probably results from the bimolecular reaction of S$_1$ and/or T$_1$ with N$_2$.

Triplet sensitization experiments were carried out at longer wavelengths at $-78 \, ^{\circ}\text{C}$. Irradiation of degassed chromatographed solutions of 1 (0.03 M in CFC$\text{Cl}_3$) at >608 nm$^{11}$ in the presence of 0.02–0.05 M azulene sensitizer ($E_T = 31$ kcal),$^{12}$ where the 1,1-diazene was shown to be unreactive on direct irradiation, affords four hydrocarbon products 2–5 and tetrazene 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$^{13,15}$ are summarized in Table I. The 2-methylpropene/tetramethylylclobutane ratios for the direct and sensitized photodecomposition of the 1,1-diazene 1 are 1.14 and 3.08, respectively. Importantly, the 2-methylpropene/tetramethylylclobutane 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.$^{16}$ 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$_1$–T$_1$ gap in the 1,1-diazene.$^{17}$ 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 tetrazene formation. Similarly, T$_1$ is deactivated in part by loss of nitrogen and tetrazene formation. The appearance of tetrazene 6 on direct irradiation is significant because, in the absence of S$_1$ → T$_1$ intersystem crossing, one can estimate an upper limit of $<7 \times 10^4$ s$^{-1}$ on the unimolecular rate for loss of N$_2$ from S$_1$. Issues that are currently under investigation include a direct measurement of the lifetime of S$_1$, a stereochemical test to quantitate the apparent spin correlation effect and a search for triplet emission which would locate the S$_1$–T$_1$ gap in the 1,1-diazene.

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

### Table I

<table>
<thead>
<tr>
<th>compd</th>
<th>conditions</th>
<th>hexenes</th>
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<tbody>
<tr>
<td></td>
<td>$0 , ^{\circ}\text{C}$, thermal$^a$</td>
<td>47 49 4.0</td>
</tr>
<tr>
<td>1</td>
<td>$-10 , ^{\circ}\text{C}$, thermal</td>
<td>53 44 3.5</td>
</tr>
<tr>
<td>6</td>
<td>$-20 , ^{\circ}\text{C}$, thermal$^a$</td>
<td>59 39 2.0</td>
</tr>
<tr>
<td>7</td>
<td>$-78 , ^{\circ}\text{C}$, hv (direct)$^a$</td>
<td>54 44 2.0</td>
</tr>
<tr>
<td>8</td>
<td>$-78 , ^{\circ}\text{C}$, hv (sens)$^a$</td>
<td>74 24 2.0</td>
</tr>
</tbody>
</table>

$^a$ CFC$_{3}$, benzene. $^c$ CH$_3$Cl$_2$. $^b$ Benzene. $^d$ CH$_3$Cl$_2$.

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

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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$^4$), 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]$^+$ from ice,$^5$ (N$_2$)$_n$$^+$ from solid nitrogen,$^6$ (CO)$_n$ from solid CO,$^6$, and (CO$_2$)$_n$ from solid CO$_2$.$^6$ The observed molecular ions and fragment ions are often accompanied by cluster ions.


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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 N₂O, NO, N₂O₃, N₂O₅, and O₂ 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 (Ar⁺, Kr⁺, 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 (NO)ₙ⁺. The dominant cluster ions have the composition [NO(N₂O₃)ₙ]⁺ up to the limit n = 11, imposed by our mass spectrometer. The series [N₂O₃(N₂O₅)ₙ]⁺, [NO(N₂O₅)ₙ]⁺, and [N(N₂O₅)ₙ]⁺ are observed much more weakly. The solvating unit, N₂O₅, is richer in oxygen than the molecules of the solid itself.

The SIMS of solid N₂O, N₂O₃, and N₂O₅ are distinctly different (Figure 2). The base peak is again NO⁺, and other fragment ions and the molecular ion are seen only very weakly. A prominent series of clusters, [NO(N₂O₃)ₙ(N₂O₅)ₙ]⁺, is observed to the instrumental limit. The relative abundance of the N₂O₅ solvating units increases in the order solid NO, N₂O₃, N₂O₅, and N₂O₆. It is noteworthy that the oxygen-rich solvating unit, N₂O₅, is so prominent in the solid with the oxygen-poor stoichiometry, N₂O₃. For solid N₂O₅, cluster ions [NO(N₂O₅)ₙ(N₂O₃)ₙ]⁺, n = 1, 2, are also observed.

The SIMS of solid O₂ is dominated by the peaks of O⁺ and O₂⁺, while O₃⁺ is hardly observable. Clusters are again observed to the instrumental limit. The strongest series is Oₙ₋₁O₂⁺, suggesting O₂ as the primary solvating unit.

The strange selectivity with which larger solvating units such as N₂O₅, N₂O₆, and O₂ are associated with a central position in spite of the excess of the molecules of the solid, such as NO, N₂O₃, or O₂, present at first, suggests the initial formation of reactive charged and neutral fragments (O, N, O₂, etc.), which then react to produce N₂O₅, N₂O₆, or O₂ 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 report⁵ that clusters of type [NO(N₂O₃)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.⁶ It is tempting to postulate that oxygen atoms play a crucial role for all five solids. In NO, one expects processes such as N + NO → N₂ + O, O + NO → NO₂, and NO₂ + NO → N₂O₅. In N₂O, the expected processes are N + N₂O → N₂ + NO, O + N₂O → N₂O₃, 2NO → N₂ + O₂, and in N₂O₅, they are N + N₂O₅ → 3NO and O + N₂O₅ → N₂O₆. In N₂O₅, reactions such as N + N₂O₅ → NO + N₂O₃, NO + N₂O₅ → NO₂ + N₂O₄, and O + N₂O₅ → N₂O₆ 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, NO₂ is likely to be converted into N₂O₃ efficiently by the excess NO present. In the SIMS of solid N₂O, this conversion should be less efficient since NO is scarce, accounting for the observed presence of N₂O₃ in the clusters. In solid N₂O₅, NO should be trapped efficiently to produce N₂O₆, while O can yield N₂O₅. The abundance of N₂O₅ present is reflected in the composition of the clusters. In the SIMS of O₂, initially formed O atoms can be expected to add to O₂ to produce O₃.

All of these postulates are compatible with the observed negative SIMS of these solids, which shows mostly O⁻ ions. The most striking among these are the negative SIMS of N₂O₅ and O₃ which show intense peaks for NO⁻, N₂O₄⁻, and N₂O₃⁻, 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 neat organic solids. In analytical applications, it would appear essential to work under conditions of higher dilution (matrix isolation), surface adsorbate analysis.⁷ Finally, we note that ion impact on low-temperature solids promises to provide a rich source of novel cluster ions.

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REFERENCES