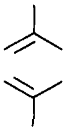
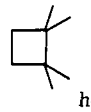
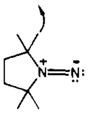
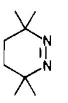
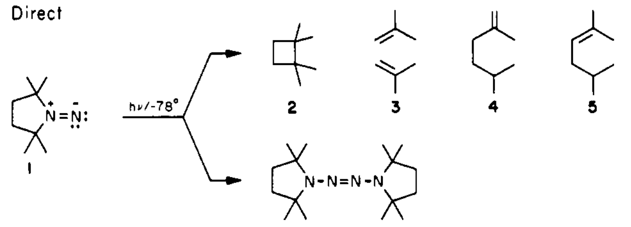
Table I

compd	conditions			hexenes
 1	0 °C, thermal[a]	47	49	4.0
	−10 °C, thermal[a]	53	44	3.5
	−20 °C, thermal[a]	59	39	2.0
	−78 °C, *hν* (direct)[a]	54	44	2.0
	−78 °C, *hν* (sens)[a]	74	24	2.0
 7	140 °C, thermal[b]	52	46	2.0
	−78 °C, *hν* (direct)[a]	56	42	2.0
	−78 °C, *hν* (sens)[c]	72	26	2.0

[a] $CFCl_3$. [b] Benzene. [c] CH_2Cl_2.

absorption spectrum is $1.3 \times 10^5\ s^{-1}$.[8]

For photochemical studies, the degassed chromatographed solution of **1** (~0.03 M in $CFCl_3$) was irradiated at 466–610 nm at −78 °C.[9] After 12 h of irradiation at −78 °C the red color had completely disappeared. Vapor-phase chromatography[10] and ^1H 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 $CFCl_3$ at −78 °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 S_0.

Triplet sensitization experiments were carried out at longer wavelengths at −78 °C. Irradiation of degassed chromatographed solutions of **1** (0.03 M in $CFCl_3$) 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/tetramethylcyclobutane ratios for the direct and sensitized photodecomposition of the 1,1-diazene **1** are 1.14 and 3.08, respectively. Importantly, the 2-methylpropene/tetramethylcyclobutane 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**.[17,18] 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 calcualted S_1–T_1 gap in the 1,1-diazene.[1f] 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 $S_1 \rightarrow T_1$ intersystem crossing, one can estimate an *upper limit* of $\leq 7 \times 10^7\ s^{-1}$[20] 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_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.

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(8) Turro, N. J. "Modern Molecular Photochemistry"; Benjamin/Cummings: Menlo Park, CA, 1978.

(9) Irradiation with 1000-W xenon lamp, Corning filters CS3-70, and CS4-96.

(10) Hydrocarbon products were analyzed by analytical VPC (Carbowax 400, 25 °C) and compared with authentic samples. Tetrazene/hydrocarbon ratios were determined by NMR spectroscopy.

(11) Irradiated with 1000-W xenon lamp, Corning filter CS-2-59.

(12) Murov, S. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973.

(13) 3,3,6,6-Tetramethyl-1,2-diazacyclohexene (**7**) was synthesized by the method of Greene.[14]

(14) Greene, F. D.; Gilbert, K. E. *J. Org. Chem.* **1975**, *40*, 1409

(15) Direct and triplet irradiation with 1000-W xenon lamp, Schott filter WG-335. The 1,2-diazene **7** has been shown to be effectively triplet sensitized by thioxanthone.[16]

(16) Porter, N. A. Ph.D. Thesis, Harvad University, Cambridge, MA 1969.

(17) Bartlett, P. D.; Porter, N. A. *J. Am. Chem. Soc.* **1968**, 90, 5317.

(18) For an excellent discussion and review of spin correlation effects in 1,2-diazenes, see: Engel, P. S. *Chem. Rev.* **1980**, *80*, 99.

(19) However, we cannot rule out that photoexcited **1** rearranges to photoexcited **7** which then undergoes reaction.

(20) Assuming $k(S_1 + S_0) \leq 9.3 \times 10^9\ M^{-1}\ s^{-1}$, concentration of $S_0 \leq 0.03$ M, and ratio of hydrocarbons/tetrazene products = 0.25.

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[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 [$H^+(H_2O)_n$ from ice,[3] $(N_2)_n^+$ and $N(N_2)_n^+$ from solid nitrogen,[2,4] $C^+(CO)_n$, $C_2^+(CO)_n$, and $(CO)_n^+$ from solid CO,[4] $C^+(CO_2)_n$ and $(CO_2)_n^+$ from solid CO_2[5]],

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(1) R. J. Day, S. E. Unger, and R. G. Cooks, *Anal. Chem.*, **52**, 557–72A (1980); B. L. Garrison, *J. Am. Chem. Soc.*, **102**, 6553–6555 (1980); N. Winograd and B. L. Garrison, *Acc. Chem. Res.*, **13**, 406–412 (1980).

(2) H. T. Jonkman and J. Michl, *Springer Ser. Chem. Phys.*, **9**, 292–294 (1979).

(3) G. M. Lancaster, F. Honda, Y. Fukuda, and J. W. Rabalais, *J. Am. Chem. Soc.*, **101**, 1951–1958 (1979).

(4) H. T. Jonkman and J. Michl, *J. Am. Chem. Soc.*, **103**, 733–737 (1981).

0002-7863/81/1503-1564$01.25/0

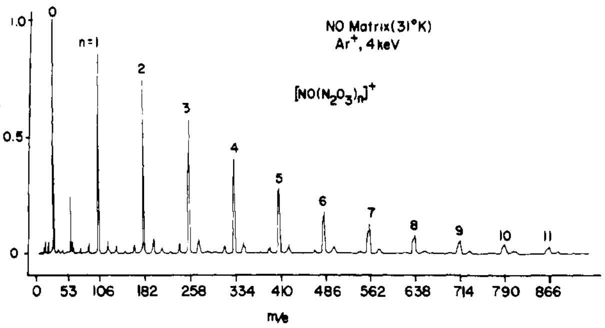

Figure 1. Positive SIMS of solid NO with Ar^+ at 4 keV.

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 N_2O, NO, N_2O_3, N_2O_4, and 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 (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 $[NO(N_2O_3)_n]^+$ up to the limit $n = 11$, imposed by our mass spectrometer. The series $[N_2O(N_2O_3)_n]^+$, $[NO_2(N_2O_3)_n]^+$, and $[N(N_2O_3)_n]^+$ are observed much more weakly. The solvating unit, N_2O_3, is richer in oxygen than the molecules of the solid itself.

The SIMS of solid N_2O, N_2O_3, and N_2O_4 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, $[NO(N_2O_3)_m(N_2O_4)_n]^+$, is observed to the instrumental limit. The relative abundance of the N_2O_4 solvating units increases in the order solid NO, N_2O_3, N_2O, and N_2O_4. It is noteworthy that the oxygen-rich solvating unit, N_2O_4, is so prominent in the solid with the oxygen-poor stoichiometry, N_2O. For solid N_2O_4, cluster ions $[NO(N_2O_4)_n(N_2O_5)]^+$, $n = 1,2$, are also observed.

The SIMS of solid O_2 is dominated by the peaks of O^+ and $O_2{}^+$, while $O_3{}^+$ is hardly observable. Clusters are again observed to the instrumental limit. The strongest series is $O_{3n+2}{}^+$, suggesting O_3 as the primary solvating unit.

The strange selectivity with which larger solvating units such as N_2O_3, N_2O_4, and O_3 are associated with a central positive ion in spite of the excess of the molecules of the solid, such as NO, N_2O, or O_2, present at first, suggests the initial formation of reactive charged and neutral fragments (O, N, O^+, etc.), which then react to produce N_2O_3, N_2O_4, or O_3 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[6] that clusters of type $[NO(N_2O_3)_n]^+$ 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 NO, one expects processes such as $N + NO \rightarrow N_2 + O$, $O + NO \rightarrow NO_2$, and $NO_2 + NO \rightarrow N_2O_3$. In N_2O, the expected processes are $N + N_2O \rightarrow N_2 + NO$, $O + N_2O \rightarrow 2NO$ or $N_2 + O_2$, $O + NO \rightarrow NO_2$, $NO_2 + NO \rightarrow N_2O_3$, and in N_2O_3, they are $N + N_2O_3 \rightarrow 3NO$ and $O + N_2O_3 \rightarrow N_2O_4$. In N_2O_4, reactions such as $N + N_2O_4 \rightarrow NO + N_2O_3$, $NO + N_2O_4 \rightarrow NO_2 + N_2O_3$, and $O + N_2O_4 \rightarrow N_2O_5$ appear probable. In many of these processes, the reactive species may actually be an ion rather than a neutral.

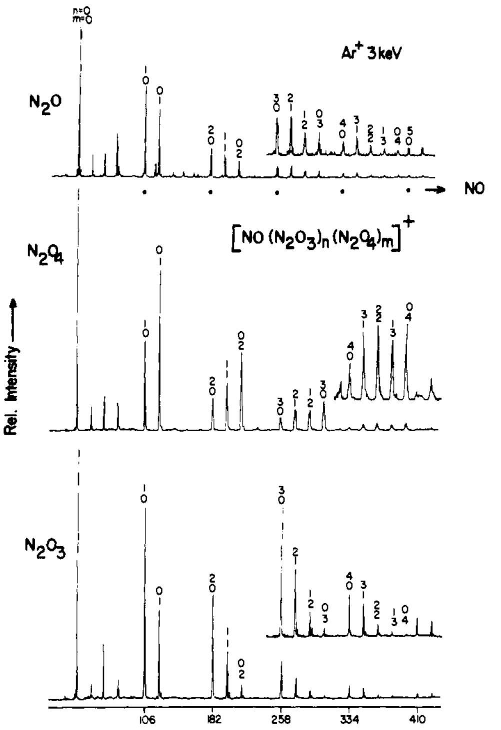

Figure 2. Positive SIMS of solid N_2O, N_2O_3, and N_2O_4 with Ar^+ at 3 keV (~18 K). The dots indicate the positions of intense peaks in the SIMS of solid NO.

In the SIMS of solid NO, NO_2 is likely to be converted into N_2O_3 efficiently by the excess NO present. In the SIMS of solid N_2O, this conversion should be less efficient since NO is scarce, accounting for the observed presence of N_2O_4 in the clusters. In solid N_2O_4, NO should be trapped efficiently to produce N_2O_3, while O can yield N_2O_5. The abundance of N_2O_4 present is reflected in the composition of the clusters. In the SIMS of O_2, initially formed O atoms can be expected to add to O_2 to produce O_3.

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 N_2O_3 and N_2O_4 which show intense peaks for $NO_3{}^-$, $N_2O_6{}^-$, and $N_3O_7{}^-$, 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,[2,8] surface adsorbate analysis[1,9]).

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

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(6) D. Golomb and R. E. Good, *J. Chem. Phys.*, **49**, 4176-4180 (1968).

(7) S. G. Lias and P. Ausloos, "Ion-Molecule Reactions. Their Role in Radiation Chemistry", American Chemical Society, Washington, D.C, 1975; K. Nishimura, O. Tokunaga, M. Washino, and N. Suzuki, *J. Nucl. Sci. Technol.*, **16**, 596-604 (1979), and references therein.

(8) H. T. Jonkman and J. Michl, *J. Chem. Soc., Chem. Commun.*, 751-752 (1978).

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