

Assignments were made by comparisons with the zero-point isotopic shifts observed for naturally abundant *s*-tetrazine in mixed molecular crystals<sup>2</sup> at 1.6 K and by their observed relative intensities in absorption (i.e., expect a ratio of 0.64:1.0 from natural abundances).

The Franck-Condon maximum of the  ${}^1B_{3u} \leftarrow {}^1A_g$  transition is at the  $6a_0^1$  band. Unlike the O-O band region, the rare (heavier) isotopic species absorb at lower energies than the more abundant species in the vibronic bands. The overall separations of the  $6a_0^1$  transitions of *s*-tetrazine- ${}^{15}N_1$  and *s*-tetrazine- ${}^{13}C_1$  from that of *s*-tetrazine in argon at 4.2 K are 5.9 and 12.2  $cm^{-1}$ , respectively. Dye laser excitation (spectral bandwidth 0.6  $cm^{-1}$ ) of a single isotopic species resulted in fluorescence exclusively from the particular single isotope originally excited.

The spectra of *s*-tetrazine in an argon matrix were bleachable by a few minutes of dye laser irradiation. Low temperature infrared experiments on photolyzed matrices demonstrated that the only infrared active photoproduct was HCN. Interestingly, the HCN was present exclusively as HCN dimers. This result indicates that there was very likely considerable motion of the HCN subsequent to its photochemical generation, as the stable dimer structure of HCN is known to involve head-to-tail hydrogen bonding (i.e., HCN...HCN).<sup>7</sup>

Finally, the results of the laser induced isotopic segregation are shown in Figure 2. Here, the origin region of *s*-tetrazine in argon at 4.2 K ( $M/R = 1000$ ) is shown in absorption at moderate resolution (ca. 0.8  $cm^{-1}$ ). The matrix sample containing 0.5 mg of *s*-tetrazine was irradiated at 17 928  $cm^{-1}$  ( $C_2N_4H_2$ ) with a 0.6  $cm^{-1}$  bandwidth dye laser (10 kW peak power, 50 Hz, 6 ns) for 5 min. The sample was probed in absorption for isotopic composition. Figure 2a represents a moderate resolution absorption spectrum of a virgin sample (i.e., natural abundances of nitrogen-15 and carbon-13) while Figure 2b demonstrates the isotopically selective photochemical removal of *s*-tetrazine ( $C_2N_4H_2$ ) thereby generating pure HCN and  $N_2$ . Identical procedures may be used to selectively photolyze *s*-tetrazine- ${}^{15}N_1$ , *s*-tetrazine- ${}^{13}C_1$ , or even less abundant isotopic species such as *s*-tetrazine- ${}^2H_1$ .

The principal result of this work is the demonstration that a photochemically unstable system can be deposited in an argon matrix with sufficient homogeneity that naturally abundant isotopic molecules can be clearly distinguished. The observed line widths of ca. 0.7  $cm^{-1}$  were sufficiently narrow that a tunable laser could be used to selectively decompose different isotopic species. This result has preparative implications since both the photolysis products (HCN and  $N_2$ ) and the inert lattice can be completely removed and purified from the unphotolyzed tetrazine.

A literature survey of optical spectra obtained from matrix isolated species reveals that the spectral line widths achieved here are not common. We, however, have found in a number of systems that when the deposition and annealing procedures and the vapor phase composition are systematically optimized, the spectral line widths obtained are a few tenths of  $cm^{-1}$  and are therefore perfectly suitable for isotopically selective chemistry. The technique of matrix isolation combined with tunable laser excitation offers a substantial practical advance over previous mixed crystal methods, since the search for appropriate organic host lattices is circumvented.

Additional examples of laser induced isotope separation at low temperature in rare gas matrices will be discussed in later reports.

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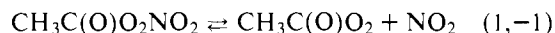
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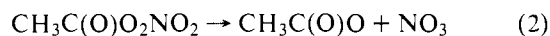
## Generation of Peroxy Radicals from Peroxy Nitrates ( $RO_2NO_2$ ). Decomposition of Peroxyacyl Nitrates

Sir:

The study of the chemistry of peroxy radicals has been largely limited to indirect sources such as autooxidation of hydrocarbons and generation of nonoxygenated radicals by photolysis in the presence of oxygen.<sup>1,2</sup> To develop a source of acylperoxy radicals suitable for studying reactions under atmospheric conditions, we have investigated the generation of acetylperoxy radicals ( $CH_3C(O)O_2$ ) from the corresponding peroxyacetyl nitrate according to the reversible reaction



However, the alternative homolysis mechanism cannot be excluded on an a priori basis:



In this report we demonstrate that reaction 1 is the predominant homolysis mechanism of peroxyacetyl nitrate (PAN). We also present our results on the use of PAN as a source of acetylperoxy radicals to determine the Arrhenius parameters for reaction -1 and for the reaction:



Estimation of the enthalpy changes for reactions 1 and 2 indicates that both reactions are endothermic by about the same amount,  $26 \pm 2$  kcal/mol. However, the entropy changes are calculated to be considerably different:  $\Delta S_1^\circ = 42 \pm 2$  and  $\Delta S_2^\circ = 30 \pm 2$  cal  $deg^{-1}$   $mol^{-1}$  (1 atm standard state). By analogy with other homolysis reactions, these entropy changes suggest a frequency factor of  $10^{16}$   $s^{-1}$  or greater for reaction 1 and about  $10^{14}$   $s^{-1}$  for reaction 2.<sup>3</sup> Therefore, reaction 1 would be expected to be considerably faster than reaction 2 (independent of temperature) if they do truly have similar heats of reaction.

To determine if the equilibrium in reaction 1 is important, we investigated the exchange of  ${}^{15}NO_2$  with PAN at 25 °C, using an IR technique. To minimize decomposition of PAN on the walls of the cell, it was necessary to expose the reaction cell to PAN until a constant rate of disappearance of PAN was obtained ( $\sim 1\%/h$ ). The conversion of unlabeled PAN to  ${}^{15}N$ -labeled PAN (PAN-15) was followed by the decrease of the 1735- $cm^{-1}$  band characteristic of unlabeled PAN<sup>4</sup> and the appearance of the 1696- $cm^{-1}$  band characteristic of PAN-15.<sup>5</sup> Similarly the bands at 1590 and 1570  $cm^{-1}$  from  ${}^{15}NO_2$  were replaced by bands at 1618 and 1600  $cm^{-1}$ , which are indicative of natural  $NO_2$ .<sup>6</sup> The expression for the loss of PAN in the case

where  $\text{CH}_3\text{C}(\text{O})\text{O}_2$  formed in reaction 1 reacts only with labeled and unlabeled  $\text{NO}_2$  in proportion to their concentrations is

$$-d[\text{PAN}]/dt = k_1\{[\text{PAN}] + [\text{PAN-15}]\} \{ [^{15}\text{NO}_2] / ([\text{NO}_2] + [^{15}\text{NO}_2]) \} - k_1[\text{PAN-15}] \quad (4)$$

From nine experiments at 25 °C where  $[^{15}\text{NO}_2]/[\text{PAN}]$  was varied from 1 to 3 at concentrations of PAN ranging from 0.8 to  $1.8 \times 10^{-4}$  M, a value of  $k_1 = (4.0 \pm 0.9) \times 10^{-4} \text{ s}^{-1}$  was obtained. This rate constant for exchange is 300 times faster than the apparent first order loss of PAN in the absence of added  $^{15}\text{NO}_2$  or NO.

A series of experiments was carried out to determine the effect of NO on the loss of PAN. The kinetic expression for the disappearance of PAN where reaction 3 is important is

$$-d[\text{PAN}]/dt = k_1 k_3 [\text{PAN}][\text{NO}] / \{ k_{-1}[\text{NO}_2] + k_3[\text{NO}] \} \quad (5)$$

At 25 °C in the presence of NO the decomposition of PAN was found to be first order in PAN and zero order in NO, consistent with eq 5 where  $k_3[\text{NO}] > k_{-1}[\text{NO}_2]$ . The average value for the initial apparent first-order rate constants obtained from five runs at PAN concentrations of 1.0 to  $3.60 \times 10^{-4}$  M and a ratio of  $[\text{NO}]/[\text{PAN}]$  ranging from 0.16 to 9.2 is  $(3.70 \pm 0.37) \times 10^{-4} \text{ s}^{-1}$ , experimentally identical with the rate constant obtained in the exchange experiments.<sup>7</sup> The rate constants for the disappearance of PAN in excess NO over the temperature range 25–40 °C follow the Arrhenius expression

$$\log(k_1/\text{s}^{-1}) = 16.29 \pm 0.60 - (26910 \pm 900)/\theta (\theta = 2.303RT \text{ in cal/mol}) \quad (6)$$

Expression 6 is in excellent agreement with the thermochemical estimates of the Arrhenius parameters for reaction 1. Furthermore, because the ratio of the forward and backward frequency factors,  $A_1/A_{-1}$ , equals  $e^{\Delta S^\ddagger/RT}$ ,<sup>3</sup> the value of  $k_{-1}$  is readily determined;  $k_{-1} = A_{-1} = 6.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , assuming no activation energy for this radical-radical reaction.

The rapid exchange of  $^{15}\text{NO}_2$  in PAN, the enhanced decomposition in the presence of NO, the agreement between the rates of these two experiments, and the agreement of estimated kinetic parameters for reaction 1 with the observed data, indicate that the reversible decomposition, reaction 1, is operative for PAN and undoubtedly for other peroxyacyl nitrates. Reaction 2 is ruled out because it would not lead to exchange; moreover, the rate of PAN decomposition by reaction 2 would not be enhanced by addition of NO because decarboxylation of acetoxy radicals is sufficiently fast<sup>8</sup> to preclude trapping of the radicals by NO.

To test the utility of PAN as a source of acetylperoxy radicals, we carried out a series of decompositions of PAN in the presence of mixtures of NO and  $\text{NO}_2$ . In these experiments, the rate of decomposition of PAN was related to the ratio  $k_3/k_{-1}$ , according to the expression

$$-dt.d[\text{PAN}] = (1 + k_{-1}[\text{NO}_2]/k_3[\text{NO}]) (k_1[\text{PAN}])^{-1}$$

Over the temperature range 25–45 °C, the ratio  $k_3/k_{-1}$  equals  $3.1 \pm 0.5$ , independent of temperature.<sup>9</sup> Combining these results with the data for  $k_{-1}$  gives  $k_3 = A_3 = 2.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ .

Thus, it is seen that PAN, which is easily prepared<sup>10</sup> and somewhat volatile,<sup>4</sup> is also a convenient source of free radicals because it decomposes rapidly ( $t_{1/2}$  for decomposition at 25 °C = 30 min) to yield acetylperoxy radicals and  $\text{NO}_2$ .<sup>11</sup> These factors recommend PAN as a gas-phase, free-radical initiator. Our results with the decomposition of PAN in the presence of

mixtures of NO and  $\text{NO}_2$  indicate that, in fact, PAN can be of considerable utility in probing reactions (e.g., reactions 1 and 3) that are relevant to the chemistry of polluted urban atmospheres.

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- (10) PAN can be prepared by a variety of photochemical techniques and purified by GLC.<sup>4,12</sup> Alternatively, as suggested by Stephens<sup>4</sup> and by Louw,<sup>13</sup> PAN can be obtained by the direct nitration of peracetic acid. We have prepared PAN in this manner, using 90%  $\text{HNO}_3$  and 30%  $\text{SO}_3$  in pentane solvent at 0 to  $-5$  °C. The yield of PAN (unpurified in pentane solution) was as high as 39% and GLC of PAN solutions provided samples of PAN containing <1% impurities.
- (11) The thermochemical analysis of the decomposition of peroxyalkyl nitrates by the reactions parallel to reactions 1 and 2 leaves little doubt that reaction 1 will also be considerably faster than reaction 2 in these cases, contrary to recent suggestions in the literature.<sup>14,15</sup> For example, for the decomposition of  $\text{CH}_3\text{O}_2\text{NO}_2$  the entropy change favors reaction 1 by 7 cal/mol and the enthalpy change favors reaction 1 by  $\sim 6$  kcal; in this case reaction 1 should be  $\sim 10^5$  times faster than reaction 2 at room temperature. Thus, peroxyalkyl nitrates, which have been synthesized,<sup>16</sup> should be suitable sources for studying the chemistry of alkylperoxy radicals.
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## Phyllanthocin, a Novel Bisabolane Aglycone from the Antileukemic Glycoside, Phyllanthoside<sup>1,2</sup>

Sir:

In the course of a continuing search for tumor inhibitors of plant origin, we have found that an ethanol extract of *Phyllanthus brasiliensis* Muell. (Euphorbiaceae)<sup>3</sup> showed significant activity in vitro against cells derived from human carcinoma of the nasopharynx (KB) and in vivo against the P-388 lymphocytic leukemia in mice (PS).<sup>4</sup> We report herein the structural elucidation of the novel bisabolane phyllanthocin (1), derived from the antileukemic glycoside, phyllanthoside (2).

Fractionation of the alcohol extract, guided by assay against the KB and PS systems, revealed that the inhibitory activity was concentrated, successively, in the chloroform layer of a chloroform-water partition and in the aqueous methanol layer of an aqueous methanol (1:9)-petroleum ether partition.