Table I. Yield of Excited States from the Thermolysis of 1, 2, and 3 under Various Conditions

Compound	Solvent	Acceptor	Triplet yield, %
2	CH_3CN	DBA	0.07[a]
2	CH_3CN	DBN	0.06
2	CH_3CN	Biacetyl	0.04
3	CH_3CN	DBA[b]	0.08
3	CH_3CN	DBA[c]	0.06
1	CH_3CN	DBA	0.08
2	Hexane	DBA	0.06

[a] Yields calculated assuming tetramethyldioxetane efficiency is 50%. Estimated error ±50% of the reported value. [b] Compared to 2. [c] Compared to tetramethyldioxetane.

nation of the triplet multiplicity of the chemiproduced excited xylene. From the near identity of these yields we can conclude that (1) the yields of excited xylenes are comparable from **2** and **3** and (2) the yield of Dewar xylene(s) from **1** is very high and rearrangement of **1** to Dewar xylene possibly occurs with unit efficiency.

In conclusion we provide evidence that identifies Dewar xylene as the key chemiluminescent intermediate in the thermolysis of biscyclopropenyls to benzenes.[13] It is, of course, possible that **1** passes inefficiently through a highly efficient chemiluminescent species that exhibits the exact same chemielectronic characteristics as Dewar xylenes. The thermolysis of **2** represents the first clear cut case of an energy sufficient Dewar benzene rearrangement; i.e., one in which the sum of reaction enthalpy and activation enthalpy (~60 + 28 = 88 kcal/mol) is greater than the energy of the final excited state (E_T of xylene ~82 kcal/mol). The observation that the excited state yield from **2** is no higher than from the parent system lays to rest the idea that the low yield of excited states results from unfavorable energetics.

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Isotopically Selective Photochemistry in Molecular Crystals

Sir:

We wish to report here the first low temperature (1.6-10 K) *isotopically selective photochemical reaction* performed in a molecular crystal. We in addition document the feasibility of selective optical excitation of molecules rich in naturally abundant isotopes, in this example ^{13}C, ^{15}N, and ^{2}H, using available tunable dye lasers, and demonstrate that such excitations can be readily used for (a) the total enrichment of isotopes, (b) the exploration of photoprocesses and their intermediates, and (c) the study of the optical emission spectra of specific isotopically substituted molecules.

In molecular crystals at low temperature it is invariably possible to discern optical transitions corresponding to organic molecules containing ^{13}C and ^{15}N atoms in natural abundance because the zeropoint or vibronic isotope shifts are in the range 1-10 cm^{-1} whereas the inhomogeneous zerophonon optical line widths[1] are usually between 0.1 and 3 cm^{-1}. However, in the gas phase[2,3] isotopic selectivity in moderate size molecules is not so clear cut because of overlapping rotation envelopes. The isotopic processes resulting from selective excitation depend on the effectiveness of energy transfer, but isotopic scrambling can be eliminated (or studied!) in suitably dilute mixed crystals. In systems where a photochemical process occurs faster than the excitation energy is channeled into the various photophysical pathways, one can perform isotopically selective photochemistry. In this communication we present a resumé of our results on the dye laser induced photochemical decomposition of *sym*-tetrazine ($C_2N_4H_2$) in neat and mixed crystals at low temperature.

Two excited states of *sym*-tetrazine known[4-10] to have transitions in the 5000-7000 Å region are $^1B_{3u}$ and $^3B_{3u}$. Both states correspond to $n \rightarrow \pi^*$ electronic promotions but are unusual in that the observed lifetimes are very short ($\tau_S \lesssim 500$ psec, $\tau_T \simeq 80\ \mu sec$[8,9]) compared with other heteroaromatic $n\pi^*$ transitions, and substantially no intersystem crossing $^1B_{3u} \rightsquigarrow {}^3B_{3u}$ occurs in this molecule. Phosphorescence can be studied by directly exciting the triplet state.[8-10] In a neat or in mixed crystal at 1.6 K *sym*-tetrazine undergoes efficient photochemical decomposition following excitation into either $^1B_{3u}$ or the $^3B_{3u}$ states. The $^1B_{3u} \leftarrow {}^1Ag$ radiative transition displays mainly a progression in ν_{6a} (ca. 700 cm^{-1}) and each vibronic transition in the spectrum shows naturally abundant isotopic side bands that can be selectively excited using a dye laser. The fol-

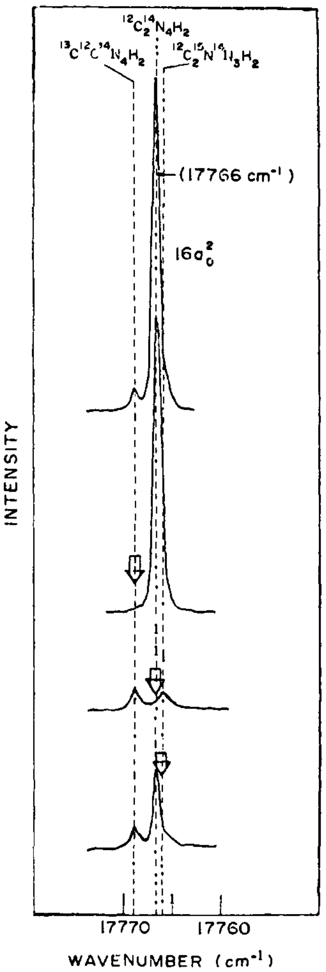
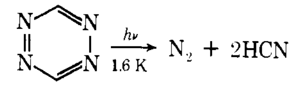


Figure 1. Excitation spectra of the isotopically selective photodecomposition of *sym*-tetrazine in benzene at 1.6 K. Four suitably dilute crystals showing the natural abundances of ^{13}C and ^{15}N containing tetrazine, in benzene, were placed in an optical helium dewar and cooled to 1.6 K. The $16a^2_0$ transition of the $^1B_{3u}$ ($n\pi^*$) state of tetrazine was observed in excitation by monitoring the total fluorescence intensity as a function of exciting dye laser wavelength. The excitation and photolysis source was a narrow band (~0.8 cm⁻¹) tunable dye laser pumped by a 100-KW nitrogen superradiator and using fluorescein as the active medium. The transition energies for each isotopic species of tetrazine were established in the first sample. Each of the subsequent samples was irradiated at a specific isotope transition as indicated by the arrows. The respective excitation spectra of the photolyzed samples demonstrate the high degree of isotopic selectivity achieved in the decomposition reaction in this system. The situations depicted in the figure (corresponding to an enrichment of 10^4-fold for ^{15}N and ^{13}C) were achieved by a few minutes irradiation.

lowing experiments have been performed. (i) The zeropoint and several vibronic transitions due to the natural abundance of $^{12}C_2{}^{14}N_4H_2$, $^{13}C^{12}C^{14}N_4H_2$, $^{12}C_2{}^{15}N^{14}N_3H_2$, and $^{12}C_2{}^{14}N_4HD$ were observed in the dye laser fluorescence excitation spectra of mixed crystals, and identified by studying the isotopically unique fluorescence resulting from each excitation. (ii) The fluorescence excitation spectra of $^{12}C_2{}^{14}N_4$, ^{13}C, and ^{15}N containing molecules, in suitably dilute mixed crystals at 1.6 K, exhibited relative intensities in accordance (±10%) with their natural abundances indicating that the effects of these isotopic substitutions on the photoprocesses are small. (iii) The isotopic compositions as determined by the excitation (or absorption) spectra of *sym*-tetrazine in mixed crystals, could be modified photochemically to exclude any of the species listed in (i) above by tuning the dye laser to the appropriate transition energy. Some of these results are summarized in Figure 1, and additional experimental details are given in the caption. (iv) The infrared spectrum at 4.2 K, of neat *sym*-tetrazine irradiated (at 4.2 K) either in the singlet or triplet states confirmed that the *sym*-tetrazine is destroyed by light and established that HCN is thereby formed. The only other prevalent products that are stable at 4.2 K are atoms and/or homonuclear diatomics. N_2 was detected on warming the sample to 77 K.

We therefore suggest that the reaction at 1.6 K is



The quantum yield for this monophotonic process appears to be high, since the gas phase and condensed phase lifetimes are each very short compared with the radiative lifetime, and the gas phase decomposition yield is near unity.[10] The effective unimolecular rate constant is at least 2×10^9 sec⁻¹ and it is consistent with all data that the reaction occurs at least 2×10^5 times faster in the singlet than in the triplet state. The reaction can be readily carried out with isotopic impurity selection in the condensed phase yielding isotopically pure *sym*-tetrazine and specific isotopic mixtures of N_2, HCN, and DCN. *sym*-Tetrazine represents just one example (analogous systems have been studied by Chapman and coworkers[11,12]) of a number of photoreactions for which isotopic selectivity via a monophotonic process should be possible in crystals or mixed crystals at very low temperatures.[13] Such experiments open up new possibilities for studying isotope effects in photoreactions and for the synthesis in situ of significant quantities of rare isotopically substituted thermally unstable molecules. The dye laser excitation method is an extremely sensitive spectroscopic tool as is evidenced by our observation of optical spectra of molecules containing deuterium in natural abundance—to our knowledge for the first time. This technique can obviously be used to study the optically detected magnetic resonance and ENDOR of ^{13}C, ^{15}N, and D containing heteroaromatic molecules in natural abundance.

Obviously potential mixed crystal systems used for condensed phase isotope separation could involve any appropriate host, including rare gases and other media that are readily moved between low temperature traps in an open-ended system. Thus economic barriers to the generation of significant quantities of rare isotopically substituted molecules may not prove unsurmountable using these principles.

A more detailed account of these experiments is being prepared for publication.

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Theoretical Calculations of the Hydrolysis Energies of Some "High Energy" Molecules. I. The Phosphoric and Carboxylic Acid Anhydrides

Sir:

In view of a recent proposal by Boyer et al.[1] that much of the free energy change associated with the formation of certain biologically important P-O-P bonds (e.g., that of ATP) occurs when the product is released from the enzyme into the aqueous environment rather than during actual bond formation, we felt it would be timely to reexamine the nature of these and other "high energy" molecules. We have carried out ab initio molecular orbital calculations using a STO-3G basis set[2] on phosphoric acid (H_3PO_4), pyrophosphoric acid ($H_2PO_3OPO_3H_2$), methyl dihydrogen phosphate ($CH_3OPO_3H_2$), acetic anhydride [$(CH_3CO)_2O$], and their hydrolysis products as an approach to the description of the electronic structure of molecules with high group-transfer potential.

Complete geometrical optimization of these molecules would have been prohibitive, so we carried out a limited search,[3] optimizing the geometries at a comparable level for all the compounds involved. First, we examined the energy of H_3PO_4 as a function of the O=P—O—H dihedral angles, $\phi_1 = \phi_2 = \phi_3$, with $R(\mathrm{P{=}O}) = 1.5$ Å, $R(\mathrm{P—O}) = 1.7$ Å, and $R(\mathrm{O—H}) = 0.99$ Å. Since $\phi = 0$ was the lowest energy, we optimized $R(\mathrm{P{=}O})$ and $R(\mathrm{P—O})$ at this angle, and then varied the ϕ's once again, but this time independently, on a 60° grid. The energy minimum is at $\phi_1 = 180$, $\phi_2 = 0$, and $\phi_3 = 0$. Then we carried out calculations on $CH_3OPO_3H_2$ and $H_2O_3POPO_3H_2$ reoptimizing[4] only the P-O and C-O bond distances and bond angles of the P-O-P and C-O-P linkages. Using the optimal geometries of Lathan et al.[5] we calculated the energies for both CH_3OH and H_2O. This enabled us to calculate ΔE values for the prototypal "high" and "low energy" hydrolysis reactions (eq 1 and 2) (see Table I).

$$H_2O_3POPO_3H_2 + H_2O \rightarrow 2H_3PO_4 \qquad (1)$$

$$CH_3OPO_3H_2 + H_2O \rightarrow CH_3OH + H_3PO_4 \qquad (2)$$

The energies (ΔE) for the hydrolysis of the "high energy" P-O-P bond in reaction 1 and "low energy" C-O-P bond in reaction 2 are calculated to be −2.71 and −0.94 kcal/mol, respectively.

Since the predominant phosphate species in aqueous solution at neutral pH are charged, we also carried out calculations on ${}^-HO_3POPO_3H^-$, $CH_3OPO_3H^-$, and $H_2PO_4^-$ to study the energetics of reactions 3 and 4.

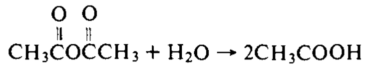
$${}^-HO_3POPO_3H^- + H_2O \rightarrow 2H_2PO_4^- \qquad (3)$$

$$CH_3OPO_3H^- + H_2O \rightarrow CH_3OH + H_2PO_4^- \qquad (4)$$

Using the minimum energy dihedral angles determined by Newton[6] for the dimethyl phosphate anion, we optimized both the P-OH and P—O$^-$ bond lengths in $H_2PO_4^-$ and used these geometrical parameters in $CH_3OPO_3H^-$ and ${}^-HO_3POPO_3H^-$. We reoptimized only R(P-O) of the POP and POC linkages and R(C-O) for the POC linkage (see Table I). The energies for reactions 3 and 4 are calculated to be −75.3 and +0.7 kcal/mol, respectively.[7] To determine the role of electrostatics in these reactions, we also calculated the energy of hydrolysis of ${}^-HO_3POPO_3H_2$ (reaction 5),[8] and found it to be +10.2 kcal/mol.

$${}^-HO_3POPO_3H_2 + H_2O \rightarrow H_3PO_4 + H_2PO_4^- \qquad (5)$$

To test the reliability of these results for a "high energy" bond whose gas phase thermodynamics are known, we calculated the energy of the molecules involved in reaction 6. Using Hess's law and experimental heats of formation,[9] the enthalpy of reaction 6 is found to be −11.6 kcal/mol. Using our calculated total energies for acetic anhydride, acetic acid,[10] and water, the ΔE of reaction 6 is predicted to be −17.2 kcal/mol. Although this agreement is only fair, it is clear that our calculations show a qualitative difference between the acetic anhydride "high energy" bond and those of the neutral and singly charged phosphates. Similarly, the calculations on the pyrophosphate dianion indicate that, in the gas phase, hydrolysis of this molecule is even more exothermic than the carboxylic acid anhydrides.



$$CH_3\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}CH_3 + H_2O \rightarrow 2CH_3COOH \qquad (6)$$

Table I. Summary of Geometry and Energy Results[a]

Molecule	R(P—OH)	R(P=O)	ϕ	R (C—O)	R- (O—H)	θ(POP), deg	R(P—OR)[d]	θ(POC), deg	E_T
H_2O					0.99				−74.96590
CH_3OH				1.433	0.99				−113.54919
H_3PO_4	1.657 (1.57)[b]	1.575 (1.52)[b]	0, 0, 180		0.99				−633.896804
	1.657	1.575	0, 0, 0		0.99				−633.894514
$CH_3OPO_3H_2$	1.657	1.575	0, 0, 0	1.445	0.99		1.655	109.5[f]	−672.472448
	1.657	1.575	0, 0, 180	1.445	0.99		1.655	115.6	−672.478593
$H_2O_3POPO_3H_2$	1.657	1.575	(0, 0, 0 0, 0, 180)[c]		0.99	117.0	1.685		−1192.823393
$H_2PO_4^-$	1.714	1.607	*e*		0.99				−633.14333
$CH_3OPO_3H^-$	1.714	1.607	*e*	1.440	0.99		1.740	109.5	−671.727694
${}^-HO_3POPO_3H^-$	1.714	1.607	*e*		0.99	109.5	1.730		−1191.200828

[a] Distances in angstroms, and energies in hartrees. [b] Experimental values in parentheses; see ref 17. [c] One phosphate group had 0, 0, 0 dihedral angle; the other 0, 0, 180. The conformation with all $\phi = 0$ brought the two P=O bonds too close together. [d] P—O bond length for POP or POC linkage. [e] We used RO—P—O—R' dihedral angles of 60° which are near the calculated optimum angles reported in ref 6 for dimethyl hydrogen phosphate anion. [f] This angle was assumed tetrahedral for only the ϕ = 0, 0, 0 conformation, and optimized for ϕ = 0, 0, 180.