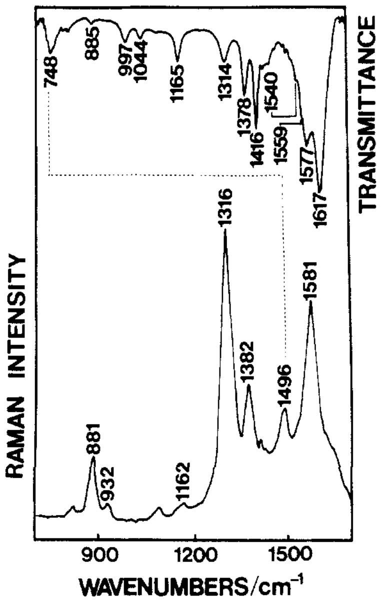

Figure 2. Infrared (upper) and Raman (lower) spectra of aqueous *N*-methylacetamide. Infrared: 1.6 M concentration, run in circle ATR cell (ZnSe rod), 1000 scans on Bomem DA3 at 4-cm^{-1} resolution, water spectrum subtracted. Raman: 0.4 M concentration with 0.2 M perchlorate. The spectral resolution is 7 cm^{-1}.

symmetric stretch does not indicate that an identical assignment is correct for resonance-enhanced bands in this region. As will be discussed in greater detail,[11] the positions of these bands and their shifts with isotopic substitution and conformation are completely consistent with their assignment to the overtone of amide V.[14-16]

This assignment is also consistent with the fact that this band occurs at a much higher frequency (1496 cm^{-1}) in aqueous NMA with 220-nm excitation (ref 4 and Figure 2). The amide V band in the infrared spectrum of neat liquid NMA[17] occurs at 725 cm^{-1}. In aqueous NMA, Figure 2, amide V shifts up to 748 cm^{-1} (an assignment confirmed by its disappearance in D_2O), to exactly half the frequency of the 1496-cm^{-1} Raman band. The 23-cm^{-1} increase in the amide V frequency from neat liquid to aqueous solution indicates that NMA forms a stronger hydrogen bond to the H_2O solvent than to another NMA molecule; this is consistent with the shifts in other amide modes. The assignment to a cis peptide group[9] can be easily excluded because of the expected cis amide frequencies[11] and because our experimental conditions prevent the observation of photochemically generated isomers.[10]

These experiments indicate that the overtone of amide V in the Raman spectra of peptides and polypeptides is selectively resonance-enhanced, even though little or no intensity is observed for the fundamental. Resonance Raman enhancement occurs for normal modes involving atomic displacements that distort the ground electronic state molecular geometry toward that of the resonant excited electronic state.[18,19] This accounts for the enhancement of the amide II and III and particularly the amide II′ modes,[5] which involve C–N bond stretching[12]; the C–N bond length is increased in the π^* excited state. The selective resonance enhancement of the overtone of amide V suggests that, as in ethylene[20] (where the overtone of the torsion is selectively enhanced by the twisted π^* state), the π^* state of the peptide group is twisted. The large CN torsion[12] component of amide V distorts the ground state toward that of the nonplanar excited state. However, as in the case of ethylene,[20] only overtone bands are expected to be enhanced (because of their symmetry). The local symmetry of the CONH fragment of NMA is formally C_s: we expect that this local symmetry will prevent out-of-plane vibrations from coupling efficiently (as fundamentals) to the in-plane $\pi \rightarrow \pi^*$ transition.

We expect that the frequency and intensity of the amide V overtone band will become an important monitor of protein secondary structure. This band is clearly evident in the 200 nm UV Raman spectra of cytochrome *c*,[7] tropomyosin,[8] and myoglobin[21] and shows a strong dependence upon conformation. It will be especially useful since it occurs in a spectral region free from overlap by the strong aromatic amino acid vibrations.

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A Reversible Photoredox Reaction: Electron-Transfer Photoreduction of β-Lapachone by Triethylamine

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Much attention has been focused on light-induced electron-transfer reactions, interest stimulated at least partially by possibilities that these reactions could be used in energy conversion or storage processes.[3-10] Despite much investigation, examples of recyclable systems based purely on solution photochemical processes and particularly those employing organic reagents are rare.[11-14] Herein, we describe a process based on a simple light-induced electron-transfer reaction and subsequent electron and atom-transfer processes which is at least partially reversible.

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These results offer some insights into both the problems and potentials inherent in these reactions.

The photoreaction under investigation involves the photooxidation of triethylamine by excited states of *o*-quinones (Q), in this case either β-lapachone (**1**) or phenanthrenequinone. Although *o*-quinones have been previously found to undergo cycloaddition reactions with alkenes and reductive additions with other reagents,[15-18] we have found that both **1** and phenanthrenequinone undergo clean conversion to the semireduced species, $QH^\bullet$, upon irradiation in the presence of tertiary amines, aminoalcohols, or alcohols such as 2-propanol or benzylalcohol.[19] Irradiation of **1** (5×10^{-4} M) with visible light ($\lambda > 400$ nm) in the presence of Et_3N (0.02 M) in degassed benzene leads to a bleaching of the quinone transition at 424 nm concurrent with an increase in absorption at 320 nm. The reaction can also be followed by ESR: concurrent with the bleaching of absorption due to **1**, there is a build-up of a single well-resolved five line ESR spectrum ($g = 2.0038$) which can be assigned to $QH^\bullet$ (or a mixture of $Q^{\bullet-}$ and $QH^\bullet$). The quantum efficiency for formation of $QH^\bullet$ under these conditions is 1.4.[20] Quantitative regeneration of **1** occurs rapidly on exposure to air; however, in a vacuum-degassed sample the ESR spectrum persists. For samples of **1** and Et_3N in wet (3% H_2O) benzene, the product $QH^\bullet$ appears indefinitely stable at room temperature. However, for rigorously dried and degassed solutions of **1** and Et_3N in benzene, there is a slow dark recovery of the absorption due to **1**, which is concurrent with and can be followed by the decay of the ESR signal. The extent of recovery is dependent on the total degree of conversion; in a typical experiment, photolysis of **1** (excess Et_3N, 13% conversion of **1**) results in 94.6% recovery after 15 h in the dark.

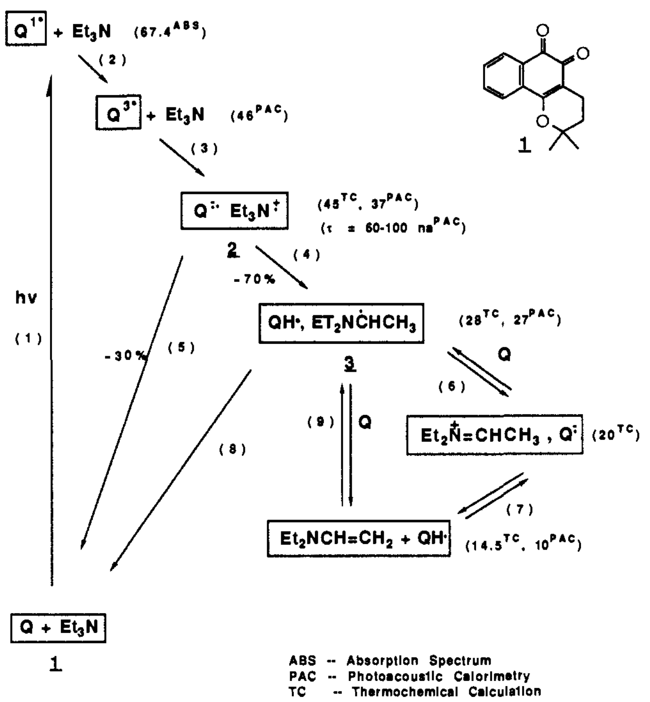
The thermal reversal of the photoreaction can also be observed by following the time evolution of the NMR spectrum of Et_3N. Irradiation of Et_3N:**1** (5:1 in degassed C_6D_6, 15% conversion of Et_3N, internal standard, cyclohexane) is followed by a dark recovery of Et_3N to 93%. Although the NMR of irradiated, degassed solutions shows as yet unidentified products,[21] the most prominent peaks (5.75 ppm, triplet, 1 H; 3.19 ppm, doublet, 2 H; 2.72 ppm, quartet, 4 H; 0.96 ppm, triplet, 6 H) can be assigned to the enamine, $Et_2N{-}CH{=}CH_2$.[22] In the dark, the resonances of the enamine decrease on the same timescale as the recovery of Et_3N and **1**. When the irradiation is carried out with 1-3% water present, no enamine is detected. However, both diethylamine and acetaldehyde are observed. Under these conditions there is no recovery of either Et_3N or **1**.

These results are consistent with photochemical and dark reactions according to reactions 1-9, shown in Scheme I, leading to reaction 10 as the overall process which goes as written with

$$2Q + Et_3N \underset{\Delta}{\overset{h\nu}{\rightleftharpoons}} 2QH^\bullet + Et_2N{-}CH{=}CH_2 \qquad (10)$$

light and reverses in the dark. The photoprocess is described by reactions 1-7 or alternatively by reactions 1-4 and 9 if the enamine is generated directly. Although iminium ion, $Et_2N^+ = CHCH_3$, is not detected directly via NMR, it should be rapidly formed via a favorable electron-transfer process (reaction 6), and it is the likely precursor to both the acetaldehyde formed by hydrolysis and the enamine (reaction 7).[23] The relatively slow thermal reversal is attributed to the reverse of reactions 6 and 7 (or 9) plus the H-atom transfer step 8; both mechanisms lead to similar rate expressions which predict the observed rapid fall-off in the recovery reaction with time.

Scheme I



The photoreaction has been studied by time-resolved photoacoustic calorimetry (PAC).[24] PAC permits the simultaneous determination of the energetics and dynamics of photoinitiated reactions. Deconvolution of the experimental waveforms measures the magnitude and time evolution of heat deposition. The details of this method have been previously reported.[24c-e] The results of this study together with some thermochemical data permit an approximate energetic assessment of the process as shown in Scheme I.[25] Excitation of **1** ($\sim 2 \times 10^{-4}$ M) at 405 nm in degassed benzene yields a transient having a lifetime onto the μs time scale in which 46 ± 3 kcal/mol are stored. This agrees well with the value obtained by quenching studies of **1** (42-48 kcal/mol)[26a] and is similar to the reported (48.8 kcal/mol) triplet energy of phenanthrenequinone.[26b] Addition of Et_3N (0.1 M) results in the immediate formation (<10 ns) of an initial intermediate which stores 37 ± 3 kcal/mol. This intermediate decays, 60-100 ns, to give a second intermediate, which stores 27 ± 4 kcal/mol.[27] Excitation of **1** ($\sim 2 \times 10^{-3}$ M) at 505 nm in degassed benzene with Et_3N (0.1 M) produces an initial intermediate with the same energy and lifetime as that found at lower [**1**]. However, its decay gives a different second intermediate, which stores only

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[20] The sample containing **1** and TEA was degassed. The quantum yield of photoreduction of **1** was determined by measuring the absorption spectrum of **1** as a function of irradiation time. Photolysis was taken by using a 200-W mercury lamp with appropriate Corning glass filters to isolate the peak at 420 nm. The system was calibrated by ferrioxalate actinometry.

[21] Other products, possibly resulting from either further photolysis or thermolysis (i.e., $Et_2N\dot{C}HCH_3$ + enamine or $Et_2N^+ = CHCH_3$ + enamine) are formed as large amounts of Et_3N are reacted.

[22] (a) Rowland, R.; Dinnocenzo, J. P. Unpublished results. (b) The enamine $Et_2N{-}CH{=}CH_2$ has been previously implicated both in the photooxidation of TEA by substituted benzophenones[32a] and the chemical oxidation of TEA by iodine[32b] and independently synthesized.[32c]

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[25] Photolysis is initiated by a nitrogen pumped dye laser (405 nm). The heat deposited is detected by a PZT transducer. The signal is amplified, digitized, and transferred to a laboratory computer. An average of 50-100 laser pulses are analyzed by a deconvolution program.[24a] The optical densities of the calibration compound, ferrocene, and the sample are adjusted to within 2% of each other. Sample absorbances did not change during the experiment.

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8–10 kcal/mol.[27]

Although the precise assignment of these species must await further experiments, the initially formed intermediate at both [**1**] could be assigned to the ion-radical pair **2** formed in reaction 3.[28] The energy of **2** can be estimated from redox potentials to be ~45 kcal/mol.[29] At low [**1**], the second intermediate produced could be assigned to the radical pair (**3**) formed in reaction 4. At high [**1**], the α-amino radical could further react with **1**, reactions 6 and 7. The energy of the ion pair generated by secondary electron transfer from α-amino radical to **1** (reaction 6) is estimated to be about 20 kcal/mol.[29,30] By using thermochemical cycle calculations, the enthalpies of reaction to produce the radical pair **3** and products according to reaction 10 are estimated to be 28 and 14.5 kcal/mol, respectively.[31]

These results indicate that for the present two-component system a combination of electron, proton, and/or H-atom transfer steps permits the efficient accumulation of reactive but metastable products which persist long enough to be usable as reagents in other dark processes without the necessity for sacrificial reagents or complex catalysts. The energy stored in the overall reaction (reaction 10) is modest (at most 20% of the threshold excitation energy of **1**), and the degree of reversibility is limited by the reactivity of the amine oxidation products. Nonetheless, the results suggest attractive possibilities exist for fashioning fairly simple organic reagents in homogeneous solution into potentially powerful systems for energy transduction and associated application.

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(27) Although the maximum quantum efficiency for QH$^\bullet$ production is 2, the observed value is ~1.4. As observed in the reductions of quinones by amines and aromatic hydrocarbons,[31] this inefficiency can be attributed to the partitioning of the ion-radical pair between back-electron transfer, reaction 5, and proton transfer, reaction 4. Consequently, the PAC values are calculated assuming the quantum yields for back-electron transfer and formation of the radical pair are 0.3 and 0.7, respectively. These quantum yields are unaffected by [**1**].

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(29) This estimate uses the equation[33]

$$\Delta E(\mathbf{2}) = E_{1/2}(\mathrm{TEA}/\mathrm{TEA}^+) - E_{1/2}(\mathbf{1}^-/\mathbf{1}) + 0.2\ \mathrm{eV}$$

and the redox potentials of **1** ($E = -0.78$ ev vs SCE) and triethylamine ($E = 0.96$ ev vs SCE)[19] in acetonitrile. The 0.2 eV term is the empirical correction value obtained by Weller for exciplexes.[33] It is assumed that the energetics of the ion pair in benzene is quite similar to that of the exciplex. In addition, studies on the quenching of quinones by amines provide support for this equation.[28]

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Cross Polarization Magic Angle Spinning Proton NMR Spectroscopy of Solids

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Recently, proton magic angle spinning (^{1}H MAS)–NMR spectroscopy of solids has been used to probe the surface sites of silica gel[1] and silicaalumina catalysts[2] as well as hydrogen environments in calcium phosphates[3] and hydrous minerals.[4] Relatively narrow ^{1}H MAS spectra can be obtained with rapid spinning alone[5] or with slower spinning speeds in conjunction with either multiple-pulse averaging[6] or isotopic dilution[7] with ^{2}H. Since ^{1}H chemical shift assignments are frequently controversial for inorganic solids and surface species and scalar couplings typically cannot be resolved, the most important problem in ^{1}H MAS–NMR spectroscopy is the development of new experiments for the assignment of resonances to specific proton environments. *We have found that cross polarization[8] from low-γ nuclei to protons provides a convenient means of identifying resonances corresponding to relatively immobile protons closely associated with the low-γ nuclei.*

This experiment may at first seem counterintuitive in that cross polarization is normally performed by transferring magnetization from abundant, high-γ nuclear spins (γ_I, usually ^{1}H) to the isotopically or chemically dilute low-γ nuclear spins (γ_S) which are to be observed. Since the maximum theoretical enhancement in a cross polarization experiment[8] is γ_I/γ_S, cross polarization from a low-γ nucleus to ^{1}H will result in an *attenuation* of the observable ^{1}H magnetization. Furthermore, the recycle time will be dependent on the (typically long) T_1 of low-γ, spin-1/2 nuclei, so a potentially large reduction in sensitivity could occur in the proposed experiment. Fortunately, ^{1}H MAS–NMR is so intrinsically sensitive that typically only a few dozen scans are taken, and large penalties in sensitivity will be tolerable in return for information that will facilitate spectral assignments.

Our first experiments have involved cross polarization from ^{31}P to ^{1}H (^{1}H{^{31}P} CP/MAS–NMR), reflecting our interest in phosphorus chemistry,[9] the favorable properties of ^{31}P for the first demonstration of the experiment, and the availability of assignments for ^{1}H MAS–NMR spectra of a number of solid calcium phosphates.[3] All spectra were obtained on a Chemagnetics M-100S spectrometer equipped with a home-built magic angle spinning probe double tuned for ^{1}H and ^{31}P. The observation and decoupling channels of the probe are interchangeable. Contact times of 2 ms were used for the ^{1}H{^{31}P} CP/MAS spectra reported below, and the ^{1}H and ^{31}P 90° pulse lengths were each 6.5 μs. Spinning speeds on this probe are limited to 4 kHz, so we sometimes do not obtain the ^{1}H resolution reported for spinning speeds of 8 kHz or higher. Therefore, we sometimes use isotopic dilution with ^{2}H to reduce the ^{1}H–^{1}H homonuclear dipolar couplings to manageable levels.[7] Our probe has a broad ^{1}H background signal centered at 0 ppm which is noticeable only in spectra of dilute samples. The ^{1}H{^{31}P} CP/MAS spectra have all of the characteristics of true cross polarization spectra including sensitivity to the Hartmann–Hahn match, ^{31}P T_1, ^{31}P flip angle, and cross polarization contact time. We have not observed any improvement in the resolution of ^{1}H MAS or CP/MAS spectra by

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