← RAMAN SHIFT/cm⁻¹

Figure 2. RR spectra of compound I (A) and compound II (B) of HRP obtained by subtracting the contribution of the ferric enzyme from the transient spectra shown in Figure 1: spectrum A = spectrum e – (0.23 × spectrum d); spectrum B = spectrum f – (0.25 × spectrum d).

note that the relative intensity of Raman lines at 1640 and 1379 cm⁻¹ is distinctly different between parts A and B in Figure 2, although their frequencies are unexpectedly close.

Previously Van Wart and Zimmer[8] observed the spectrum of compound I in frozen solution with low laser power, but due to its similarity to the spectrum of compound II, they attributed their observations to a photoreduced species of compound I, that is, compound II. As noted above, the present sample does not contain compound II. If compound I was photoreduced to the ferrous state and it reacted with O_2, then compound III with λ_{max} = 417 nm might be formed.[12] However, such a possibility is ruled out from the absence of an absorption band around 417 nm in trace b in Figure 1. These considerations lead us to propose that spectrum A in Figure 2 arises from compound I of HRP and to admit that our cryogenic measurements reported previously yielded the photoreduced ferrous species.

HRP compound I has been considered to contain the a_{2u} porphyrin π-cation radical on the basis of the absorption spectra of M(OEP) derivatives (OEP = octaethylporphyrin).[13] Recently, Spiro and co-workers[14] succeeded in categorizing the RR spectra of cation radicals of M^{II}(OEP); the a_{1u} radical exhibits positive (14 to 21 cm⁻¹) and negative (–19 to –38 cm⁻¹) shifts for the ν_4 and ν_2 modes, respectively, whereas the a_{2u} radical exhibits negative (–12 to –22 cm⁻¹) and positive (20 to 23 cm⁻¹) shifts for them upon formation of a cation radical. Accordingly, it was expected that the ν_4 band around 1380 cm⁻¹ of compound II exhibited a negative shift in compound I. Nevertheless, there is no prominent frequency shift between parts A and B in Figure 2. One likely reason for this insensitivity is that a clear cation-radical state as seen for M^{II}(OEP) is not generated for compound I. This would mean that the oxidative equivalent is extensively delocalized through iron and axial ligands. An alternative explanation assumes that the shifts expected for the formation of the cation radical of Fe^{IV} porphyrin are much smaller than those for M^{II}(OEP). This possibility arised from the facts that the amount of frequency shifts upon the formation of cation radicals are noticeably metal-dependent[14] and that there has been no experimental data for iron porphyrins. Thus the RR spectra cannot distinguish between the a_{1u} and a_{2u} radicals for compound I. However, it has been dem-

onstrated that the device presented here is very useful in a general sense and rather necessary for discussing the RR spectra of a transient species of enzymic reactions.

A Two-Photon Study of the "Reluctant" Norrish Type I Reaction of Benzil[1]

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During the last few years the applications of pulsed lasers in industry and in research have increased dramatically. It is now recognized that in some cases laser and conventional (e.g., lamps or sunlight) irradiation can lead to different chemical consequences, even when the total energy and wavelength used may have been the same. A few studies have been concerned with the transient phenomena associated with these differences,[2–8] and occasionally the "laser vs. lamp" effects on products have been examined.[3a,7,9] There are, however, few examples where products and transient phenomena have been examined as part of the same study.[3a,7]

The laser vs. lamp differences are frequently related to the involvement, directly or indirectly, of multiphoton processes under laser irradiation. In our work we have found it desirable to identify systems where two-photon processes would take place, but where no monophotonic chemistry occurs. Compounds with these characteristics could find wide application as laser-photosensitive materials, but where no protection from normal illumination (e.g., room lights or sunlight) is necessary.

In this paper we report preliminary results on the photochemistry of benzil (Ia), which has been reported to be essentially photostable at room temperature[10] but which under conditions of laser irradiation undergoes the Norrish type I cleavage, reaction 1.

Irradiation of benzil (5 × 10⁻⁴ M in benzene) with the 308-nm pulses from an excimer laser (~5 ns, ≤50 mJ/pulse)[11] leads to

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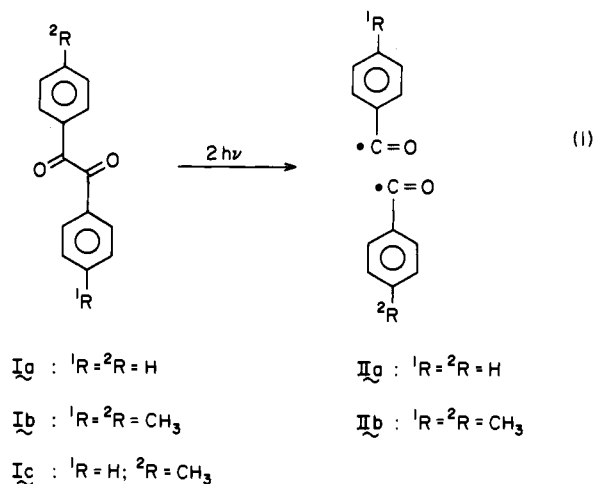(7) Johnston, L. J.; Scaiano, J. C. *J. Am Chem. Soc.* **1986**, *108*, 2349.
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$$Ia : {}^1R = {}^2R = H$$
$$Ib : {}^1R = {}^2R = CH_3$$
$$Ic : {}^1R = H; {}^2R = CH_3$$
$$IIa : {}^1R = {}^2R = H$$
$$IIb : {}^1R = {}^2R = CH_3$$

the generation of its readily detectable triplet state (λ_{max} = 480 nm).[12] When the intensity of the transient absorption signals is monitored as a function of the laser dose (adjusted with neutral density filters calibrated and tested for laser use), one observes a nonlinear dependence of the detectable triplet yield on the laser dose (see insert in Figure 1). This curvature is not due to ground-state depletion, since under our conditions ≤5% of the benzil molecules are excited. The effect is most likely due to the involvement of two-photon processes resulting from laser irradiation of transient intermediates produced during the early part of the laser pulse. Both singlet (τ = 2.6 ns)[13] and triplet states are candidates for this effect. The extinction coefficient of the latter is 4 times larger than that of the ground state at 308 nm, and toward the end of the laser pulse, it competes for absorption with the ground state.

The effect of triplet-state irradiation on the transient phenomena was studied by using the pulses from a dye laser ($\sim$250 ns, 100–500 mJ/pulse), tuned in the 420–520-nm range. Figure 1 shows a comparison of triplet-decay traces under conditions of one- and two-laser irradiation. In the latter, the dye laser pulse (at 517 nm where ground-state benzil is transparent) followed the excimer laser after 0.75 μs. The traces were monitored at 470 nm, where the intense light from the dye laser does not interfere, and show extensive triplet-state depletion. These observations suggest that extensive changes take place upon laser photolysis of benzil; however, product studies are somewhat deceiving. UV–vis spectroscopy shows virtually no permanent change, while GC analysis only reveals the formation of traces of biphenyl, some of which is also formed under lamp irradiation at $\sim$300 nm.

In order to test whether triplet excitation provides an alternate route to the ground state[14] or if reversible photochemistry involving reaction 1 followed by radical recombination was taking place, we examined the photochemistry of mixtures of Ia and Ib.[15] A preliminary examination of the transient phenomena in this system showed it to be essentially the same as for Ia, and UV–vis spectroscopy again did not reveal any detectable chemical change. However, GC analysis showed formation of substantial yields of Ic under laser irradiation, but not from a comparable dose from lamps.[16] In the one-laser experiment (308 nm only) the yield
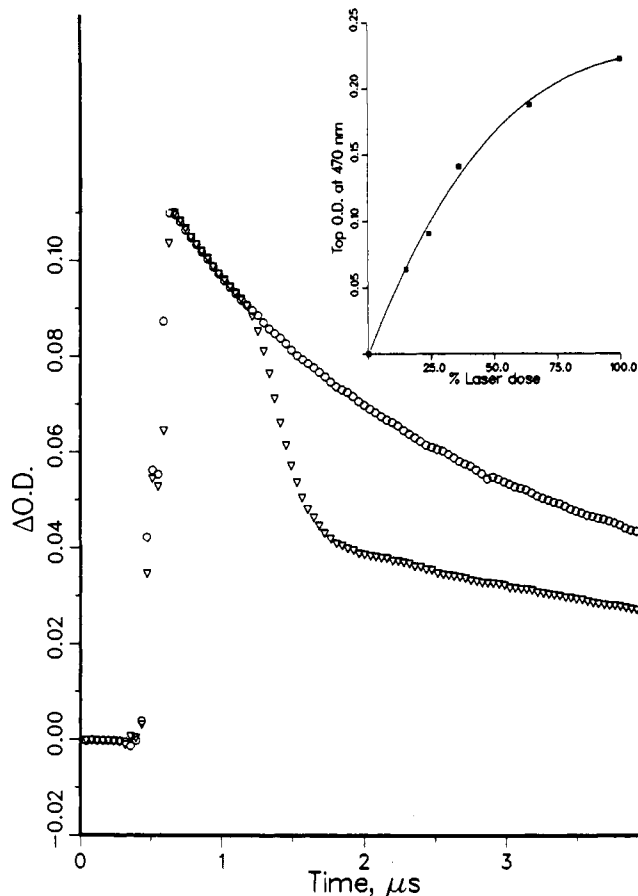
Figure 1. One- (O) and two-laser (▽) irradiation of a deaerated 0.5 mM solution of benzil in benzene. In the two-laser experiment the 308-nm pulse was followed by a 517-nm pulse after 0.75 μs. Insert: Power dependence of the yield of benzil triplets monitored at 470 nm. The full dose corresponds to ca. 20 mJ/pulse.

of Ic decreased when the laser was attenuated or when the volume of sample irradiated was increased, as expected for a multiphoton process. Under the conditions of Figure 1, the relative yields of Ic formed in the two-laser, one-laser, and lamp experiments were 1.0:0.25:undetected (detection limit is 2 × 10^{-4}). Typical conversions were ca. 4% for the two-laser experiment. We attribute the formation of Ic to the combination of IIa and IIb produced in the photolysis of the appropriate precursor. In addition, we observed traces of biphenyl and of 4–methylbiphenyl, but no 4,4'-dimethylbiphenyl. Irradiation of Ib alone in benzene gave traces of 4-methylbiphenyl as the main diaryl derivative as well as an even smaller yield of biphenyl. These results (which are not unprecedented)[10b] suggest that at least two minor processes involving the solvent take place. Under conditions of lamp irradiation no benzil consumption was detected.

In a few experiments in hydrogen-donating solvents, such as cyclohexane, laser irradiation led to permanent change, as expected from the trapping of benzoyl radicals by the solvent.

In conclusion, laser excitation of benzil leads to symmetric Norrish type I cleavage, which does not take place upon lamp irradiation. In the two-laser experiment, reaction 1 results from photolysis of benzil triplets, while in the case of the one-laser results, two-photon processes may occur within the singlet manifold, in addition to the triplet photoprocesses characterized by using two lasers. A rather interesting observation is that in the one-laser experiments we were unable to prevent the occurrence of two-photon processes (as measured by the formation of Ic from mixtures of Ia and Ib) even when the energy per unit volume was reduced by about a factor of 50 as compared with that normally

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(14) Deactivation via triplet excitation would be a distinct possibility if the upper excited triplet generated by absorption of a second photon undergoes energy transfer to the benzene solvent or intersystem crossing to the upper levels of the singlet manifold followed by relaxation to S_1 and incomplete intersystem crossing back to T_1.

(15) A sample containing $\sim$5 × 10^{-4} M each of benzil and 4,4'-dimethylbenzil, stirred by a stream of small nitrogen bubbles, was subjected to a series of 600 pairs of pulses at 308 and 517 nm; the latter followed each 308-nm pulse after a 0.75-μs delay. The 308-nm pulse was defocused and attenuated to 24% of the available power. A control experiment was run in which only the 308-nm laser pulse was used.

(16) Lamp irradiations were carried out by using Rayonet RPR-3000 lamps. The irradiation times (typically a few minutes) were adjusted so as to match the irradiation dose used in the laser experiments.

used for laser flash photolysis at NRC and elsewhere. As the beam quality and power of modern lasers improve over the next few years, it will become increasingly important to be aware of these effects if typical flash data are to be reliably interpreted. Further, two-photon processes resulting from transient excitation may play an important role in laser ablation techniques if the reactive intermediates generated can compete with the starting material for light absorption.

Benzil and its derivatives may find applications as readily available laser-specific free-radical sources. Some of these applications to vinyl polymerization are currently being explored in our laboratory.

Finally, we mentioned in earlier studies the difficulties associated with the determination of quantum yields in two-laser experiments. Work is now in progress trying to develop actinometers for two-photon, two-color processes. Preliminary data suggest that efficient chemical processes, such as that illustrated in Figure 1, may actually reflect low (<10%) quantum yields. This is likely to be the case in this system.

An Acidity Scale, [H+]hν, for Proton Quenching of Excited States

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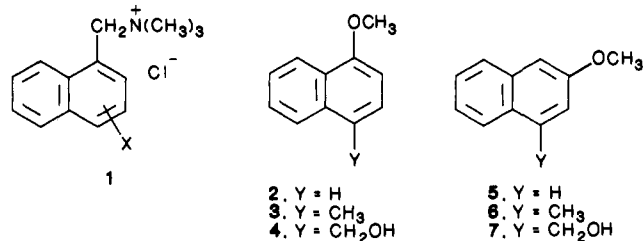Halifax, Nova Scotia, Canada B3H 4J3
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Recently, several groups have reported on photochemical reactions that occur because many functional groups have increased basicity in their excited singlet state.[1] For instance, Wan and Turro[2,3] studied the photocleavage of benzyl alcohols and the Yates Group has examined photohydrations of alkenes and alkynes.[4,5] In these cases reaction resulted from excited-state protonation which was monitored by the quenching of the substrate fluorescence. Analysis by Stern–Volmer methods and lifetimes is simple provided the quenching occurs in the region where the concentration of protons by titration is a reasonable estimate of the proton activity. At higher acidities, curved plots were observed.

Acidity scales for ground-state equilibria and their application to acid-catalyzed reactions have been extensively studied.[6,7] Ground-state acidity scales are usually established by application of the Hammett proposal for the cancellation of indicator activity coefficient ratios. Excited-state kinetic scales are inherently different since the quantity measurable is always a ratio relative to other processes of the same excited state. Thus, the activity of the substrate excited state cancels. Moreover, these photochemical protonations are assumed to be irreversible[8] so that the activity of the protonated form can be ignored. For fluorescence quenching by protons, the Stern–Volmer relationship will be given by $I^0/I = 1 + k_q\tau[H^+]^{h\nu}$ where $[H^+]^{h\nu}$ is the kinetic protonating ability of the medium. Determination of these values requires an indicator whose fluorescence quenching can be measured over a range of acidities that can be anchored in the pH region. We

have chosen 1-cyanonaphthalene because quenching of its fluorescence ($\phi_f = 0.37^9$) begins at pH 1 and yet the cyano group has such a low ground-state basicity that it will remain unprotonated in quite concentrated acid solutions.

Stern–Volmer fluorescence quenching data for 1-cyanonaphthalene in 20% ethanol/80% aqueous sulfuric acid[10,11] are plotted in Figure 1 where the horizontal axis indicates titratable protons. The inset shows the linear regeion of the quenching from which the slope $k_q\tau = 0.555 \pm 0.006$ is established. On the graph, this line is then extrapolated well beyond values for titratable protons. Evaluation of $[H^+]^{h\nu}$ at any given $[H^+]$ involves a simple extrapolation from the quenching curve. This is shown graphically[12] for two experimental determinations of I^0/I vs. $[H^+]$. Values of $[H^+]$ and derived $[H^+]^{h\nu}$ obtained this way are 2.44, 3.03; 2.95, 4.39; 5.30, 12.1; 6.63, 22.3; 8.58; 50.7; and 9.81, 85.1.[13] The two are identical below $[H^+] = 2.0$ M. At high acidities the extrapolations required are large and the obvious concern is that they could be unreliable. However, our first test of the $[H^+]^{h\nu}$ scale is successful.

We have previously examined the effect of substituents on the photocleavage of (1-naphthylmethyl)trimethylammonium chlorides (**1**) and found that the 4-methoxy substrate gives a faster rate of heterolytic cleavage than the 3-methoxy isomer.[14] In contrast, for the proton-catalyzed cleavage of benzyl alcohols the 3-methoxy isomer reacts faster than the 4-methoxy one,[2] which is a quantitative confirmation of the "meta" effect postulated by Zimmerman in the 1960s.[15,16] To analyze the difference between the two systems, we now report on the proton fluorescence quenching of a series of 1-methoxy- (**2–4**) and 2-methoxynaphthalene derivatives (**5–7**).


```
      +
  CH2N(CH3)3              OCH3                    OCH3

        Cl-

        X

   1                  2. Y = H          5. Y = H
                      3. Y = CH3        6. Y = CH3
                      4. Y = CH2OH      7. Y = CH2OH
```

Proton quenching of the fluorescence of the 1-methoxy derivatives **2–4** occurs in the range pH 2–0. Linear Stern–Volmer plots are obtained and the $k_q\tau$ values are reported in Table I. The quenching of the 2-methoxy derivatives occurs at higher acidities (2–10 M); the Stern–Volmer plots obtained by using titratable $[H^+]$ curve upward. Attempt to evaluate the $k_q\tau$ values for **6** and **7** from the linear part of these curves at acidities lower than $[H^+] = 2$ M are unreliable, as indicated by standard deviations and correlation coefficients (Table I), because the extent of quenching is small. For **5**, even this becomes impossible. Attempts to use the ground-state $H_0{}^{10}$ scale also failed. However, all three plots are gratifyingly linear vs. $[H^+]^{h\nu}$. The calculated $k_q\tau$ values given in the table and the improved standard deviations show this to be a much more reliable method than trying to use the weak fluorescence quenching at low acidities.

The generality of this procedure for analyzing excited-state protonations awaits further testing. The simpliticy of constructing a Stern–Volmer plot with 1-cyanonaphthalene as the indicator for any conditions (solvent, acid, temperature, etc.) will make this a very useful method. Such studies are in progress.

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