

## Two-Laser-Sensitized Decomposition of Carbon Tetrachloride: Photoacid Generation

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Laser flash photolysis (308 nm) of 2-acetylnaphthalene (ATN) in carbon tetrachloride (CCl<sub>4</sub>) solution yielded the ATN triplet, T<sub>1</sub>, state (T-T absorption:  $\lambda_{\text{max}}$  430 nm). Excitation of T<sub>1</sub> to an upper triplet state, T<sub>n</sub>, with a 445-nm pulsed dye laser (ca. 1  $\mu$ s after the 308-nm pulse) resulted in extensive permanent bleaching of the T-T absorption monitored at 430 nm. The bleaching quantum yield was determined by Aberchrome 540 actinometry,  $\Phi_{\text{Bleach}} = 0.03 \pm 0.006$ . While addition of 1  $\rightarrow$  3 M benzene did not effect the transient behavior at 430 nm, the extent of bleaching at 490 nm decreased with increasing benzene concentration, indicating the production of a new transient species concurrent with triplet bleaching. Dependence of the extent of bleaching on benzene concentration and the wavelength of this new absorption supports its assignment to the chlorine atom-benzene  $\pi$ -complex, confirming that sensitized CCl<sub>4</sub> decomposition occurs from the ATN triplet manifold, likely via energy transfer. One- and two-laser photolysis of ATN in 50:50 CCl<sub>4</sub>/methanol (MeOH) resulted in transient behavior similar to that observed in pure CCl<sub>4</sub>, but product analysis indicated production of acid (not observed in pure CCl<sub>4</sub>). The quantum yield for acid production under one-laser conditions was  $\Phi_{\text{Acid}}$  (one-laser, from ground state) =  $0.0044 \pm 0.0006$ . Two-laser irradiation resulted in a ca. 15-fold increase in the amount of acid produced. From the value of  $\Phi_{\text{Bleach}}$  and the ratio of moles triplet bleached to moles acid generated, the quantum yield for production of acid from the triplet state was calculated:  $\Phi_{\text{Acid}}$  (two-laser, from triplet state) =  $1.9 \pm 0.7$ .

### Introduction

The changes in polymer film solubility which are required for the manufacture of photoresists can be induced, in some systems, by acid catalysis. In such systems the presence of acid causes cross-linking or bond cleavage in the polymer substrate resulting in a change in solubility and, after development, a positive- or negative-tone resist. A convenient method of producing acid and thus, the desired solubility changes, with spatial selectivity, is by UV-visible irradiation.

In recent years, much effort has been expended to develop efficient photoacid generators (PAG's). Aryldiazonium and iodonium salts and a variety of sulfonic acid precursors have been used as PAG's in the production of both negative- and positive-tone resists.<sup>2-7</sup> However, these compounds have either suffered from poor thermal stability or inconvenient absorption characteristics ( $\lambda < 300$  nm).

More recently, halogen-containing compounds such as tris(2,3-dibromopropyl) isocyanurate (TRIS) and a variety of vicinal dibromides have been employed. TRIS, a dissociative electron acceptor undergoes photoinduced electron transfer with phenothiazine and derivatives. The production of bromide ion upon dissociation of TRIS is accompanied by deprotonation of the phenothiazine radical cation, giving HBr.<sup>8,9</sup>

In vicinal dibromides, homolytic C-Br bond cleavage yields bromine atoms (Br<sup>\*</sup>) which, in the presence of a H-atom donor, undergo abstraction to give HBr.<sup>10,12</sup> For most vicinal dibromides studied, the quantum yield for debromination is ca. 2.0, making these compounds efficient sources of acid.

By contrast with the growing body of work on photoacid derived from bromine-containing compounds and, in particular, vicinal dibromides, few studies have been reported on acid generation by irradiation of chlorine-containing compounds. This is surprising since Cl<sup>\*</sup> is a much better H-atom abstractor than Br<sup>\*</sup>.<sup>13</sup> One study of a chlorine-containing photoacid generating system involved UV lamp irradiation of naphthalene in mixtures of CCl<sub>4</sub> and MeOH. Production of HCl was proposed to take place by a multistep chain reaction involving H-atom abstraction by Cl<sup>\*</sup>.<sup>14</sup> However, in this study no direct evidence for Cl<sup>\*</sup> production was obtained, nor was the naphthalene excited state responsible for the sensitization identified. Furthermore, the sensitization mechanism itself was not determined, although the assumed presence of Cl<sup>\*</sup> would imply an energy transfer process between excited naphthalene and CCl<sub>4</sub>. We have utilized sequential two-laser flash photolysis in order to characterize the transient photoproducts formed following irradiation of an aromatic sensitizer (2-acetylnaphthalene (ATN)) in

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$\text{CCl}_4$ . In doing so we have determined that excitation of ATN to its upper triplet state causes production of  $\text{Cl}^\cdot$ . In addition, two-laser irradiation of ATN in  $\text{CCl}_4/\text{MeOH}$  mixtures results in acid generation. This two-laser upper triplet mechanism for  $\text{Cl}^\cdot$  production may prove to be a general method for generating acid since a wide variety of upper triplet states can be accessed with laser sources. Indeed, it should be possible to tune the absorption of the sensitizer triplet state to fit the specific absorption requirements of the photoresist material.

### Experimental Section

**Materials.** 2-Acetylnaphthalene ATN (Aldrich 99%) and benzophenone (Aldrich 99%) were recrystallized from methanol. Aldrich spectrophotometric grade carbon tetrachloride (99+%), methanol (99.9%), methylene chloride (99+%), and benzene (99+%) were used as received. Aberchrome 540 was used as received from Aberchromics Ltd. Azoxybenzene (Lancaster Synthesis 98+%) was used as received.

**Laser Flash Photolysis.** The laser flash photolysis system as used in the one- and two-laser experiments has been described in detail elsewhere.<sup>15</sup> Briefly, in the one-laser experiments, samples were irradiated by the UV pulses of a Lumonics EM510 XeCl excimer laser (308 nm; <40 mJ/pulse; 8-ns pulse duration). In the two-laser experiments the UV laser pulse was followed after a short (ca. 1  $\mu\text{s}$ ) delay by a pulse from a Candela SLL 250 flashlamp-pumped dye laser (504 nm; <150 mJ; 350 ns).

Samples were either static (ca. 3 mL) or were flowed through a specially constructed  $7 \times 7 \text{ mm}^2$  quartz cell which ensured that a fresh volume of sample was irradiated by each pulse. Unless otherwise indicated, samples were deoxygenated by bubbling with a stream of dry nitrogen for several minutes prior to irradiation.

The extinction coefficient for the triplet-triplet (T-T) absorption of ATN at 430 nm was determined by comparison with the T-T absorption of benzophenone ( $\lambda_{\text{max}}$  525 nm,<sup>16</sup>  $\epsilon = 7200 \text{ M}^{-1} \text{ cm}^{-1}$ ). The ground state absorbances for ATN and benzophenone were matched at the laser wavelength. Using this method,  $\epsilon$  (triplet ATN) =  $10500 \text{ M}^{-1} \text{ cm}^{-1}$ .

**Bleaching Quantum Yield of ATN Triplet.** The quantum yield of dye laser-induced bleaching of the ATN T-T absorption,  $\Phi_{\text{Bleach}}$ , was determined using Aberchrome 540 as an actinometric standard, according to the method outlined by Scaiano et al.<sup>17</sup> and represented in eq 1. In eq 1,  $\Delta\Delta \text{O.D.}^{430}$  represents

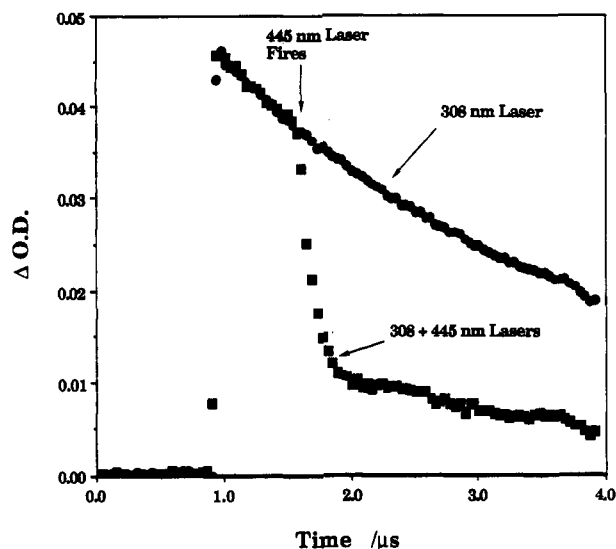
$$\Phi_{\text{Bleach}}^{\text{ATN}} = \frac{\Delta\Delta \text{O.D.}^{430}}{\Delta\Delta \text{O.D.}^{494}} \cdot \frac{\epsilon^{494}}{\epsilon^{430}} \cdot \Phi_{\text{Bleach}}^{\text{Aberch}} \quad (1)$$

the triplet absorbance, measured at 430 nm, which is bleached by the dye laser pulse;  $\Delta\Delta \text{O.D.}^{494}$  is the Aberchrome absorbance at 494 nm which is bleached under identical conditions, i.e. the Aberchrome and ATN T-T absorbances at the dye laser wavelength (445 nm) were matched at the time of the dye laser pulse;  $\epsilon^{430}$  and  $\epsilon^{494}$  are the extinction coefficients of the ATN triplet at 430 nm and Aberchrome at 494 nm respectively; and  $\Phi_{\text{Bleach}}$  for Aberchrome is calculated according to eq 2, where  $\lambda$  (dye laser

$$\Phi_{\text{Bleach}}^{\text{Aberch}} = 0.178 - [(2.4 \times 10^{-4}) \cdot \lambda] \quad (2)$$

wavelength) is expressed in nanometers.

**Quantum Yield of Photoacid Production.** Laser-irradiated samples of ATN in 50:50  $\text{CCl}_4/\text{MeOH}$  were washed with water several times, and the organic phase was discarded. The aqueous phase was then titrated with dilute solutions of NaOH which had been prepared immediately prior to use. In the preparation of the base, care was taken to avoid the formation of carbonates and silicates which would decrease the amount of base in solution.



**Figure 1.** Transient production and decay monitored at 430 nm following one-laser (308 nm; round symbols) and two-laser (308 + 445 nm; square symbols) flash photolysis of ATN in neat, degassed  $\text{CCl}_4$ .

Quantum yields for acid production were determined under one-laser (308 nm) conditions using azoxybenzene as an actinometer.<sup>18</sup> Sample and azoxybenzene ground-state absorbances were matched at the laser wavelength.

### Results and Discussion

**Two-Laser-Induced Decomposition of  $\text{CCl}_4$ .** Laser flash photolysis (308 nm) of degassed  $\text{CCl}_4$  solutions of ATN resulted in the production of the ATN triplet  $T_1$  state identified by its characteristic T-T absorption spectrum ( $\lambda_{\text{max}}$  430 nm).<sup>16</sup> The  $T_1$  state decayed by first-order kinetics over several microseconds. Under two-laser photolysis (308-nm pulse followed ca. 1  $\mu\text{s}$  later by the pulse from a flashlamp-pumped dye laser tuned to 445 nm), the T-T absorption was extensively bleached concurrent with the dye laser pulse. The decay profile observed at 430 nm under one- and two-laser conditions is shown in Figure 1. This bleaching indicates that some fraction of upper triplet  $T_n$  states initially produced by absorption of the 445-nm photons decay by a process that does not involve regeneration of  $T_1$ , i.e. a process that competes kinetically with rapid internal conversion. Triplet bleaching has been reported for several aromatic systems and is known to arise from a variety of mechanisms. For example, dye laser-induced bleaching of the benzil triplet is a result of "Reluctant" Norrish Type I bond cleavage occurring from an upper triplet state.<sup>19</sup> Benzophenone triplet is bleached during two-laser photolysis in aromatic solvents due to energy transfer from the upper triplet state to the triplet manifold of the solvent.<sup>20</sup> More recently it has been shown that bleaching of anthracene triplet in the presence of acrylonitrile results from [4 + 2] cycloaddition via the  $T_2$  state and that bleaching in the presence of dissociative electron acceptors is caused by electron transfer from  $T_2$ .<sup>15</sup> The intermolecular upper triplet state reactions reported, although to a certain extent

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limited by diffusion, were able to compete with fast internal conversion because in each case the quenchers were present in high concentrations or as solvent. In order to determine the role of CCl<sub>4</sub>, if any, in the observed bleaching of ATN triplet, similar two-laser experiments were performed in nonaromatic hydrocarbon solvents (e.g. cyclohexane) and in partially halogenated solvents such as methylene chloride. However, no triplet bleaching was observed in these cases, indicating that the presence of CCl<sub>4</sub> is required for bleaching.

The quantum yield for bleaching in CCl<sub>4</sub>,  $\Phi_{\text{bleach}}$  was determined by Aberchrome 540 actinometry using the two-laser technique described previously<sup>17</sup> and outlined in the Experimental Section;  $\Phi_{\text{bleach}} = 0.03 \pm 0.006$ . This result indicates that three out of every one hundred ATN T<sub>1</sub> states absorbing a 445-nm photon participate in the deactivation process with CCl<sub>4</sub>. Upon first inspection, the small value determined for  $\Phi_{\text{bleach}}$  is not consistent with the extensive (>50%) bleaching observed. However, it is likely that the majority of T<sub>1</sub> states undergo multiple excitation/relaxation cycles during the relatively long dye laser pulse, thus increasing the opportunity to interact with CCl<sub>4</sub>.

Given the ability of CCl<sub>4</sub> to quench excited states by acting as either an energy or electron acceptor, it is plausible that either mechanism is operative for the upper triplet state of ATN. In order to determine which process is occurring, we have attempted to detect the production of Cl<sup>•</sup> as a primary photoproduct following irradiation with the dye laser. (Production of Cl<sup>•</sup> would be a good indication that energy transfer is occurring.) In this investigation, we have used a transient probe for Cl<sup>•</sup>. In the presence of benzene, Cl<sup>•</sup> is scavenged to form the Cl<sup>•</sup> - benzene  $\pi$ -complex, a transient species with  $\lambda_{\text{max}} \sim 470$  nm.<sup>21,22</sup> Two-laser flash photolysis was carried out on degassed solutions of ATN in CCl<sub>4</sub> with 0 → 3 M benzene added. While the extent of triplet bleaching measured at 430 nm remained nearly constant at benzene concentrations up to 3 M, different transient behavior was observed at 490 nm (near  $\lambda_{\text{max}}$  for the  $\pi$ -complex). In the absence of benzene, the bleaching observed at 490 nm was similar to that at 430 nm. However, as the benzene concentration was increased, the magnitude of the bleaching decreased, until at 3 M there was virtually no bleaching observed. This two-laser behavior, which is shown in Figure 2, strongly suggests the production of the  $\pi$ -complex concurrent with the dye laser pulse. A two-laser experiment performed in neat benzene solvent resulted in bleaching of the T-T absorption similar at both 430 and 490 nm, i.e., no new product was observed. This result also supports the assignment of the  $\pi$ -complex since it indicates that both benzene and CCl<sub>4</sub> are required for the production of this transient absorption. As further confirmation, a transient absorption spectrum was obtained immediately following the dye laser pulse. While there was no clear indication of a new absorption peak produced, there was a definite increase in the transient absorption in the 440–510 nm region of the spectrum. This observation also strongly suggests the presence of  $\pi$ -complex. (The lack of a new peak can be attributed to the similar wavelength maxima of the ATN triplet and the  $\pi$ -complex ( $\lambda_{\text{max}} \sim 440$  and 470 nm, respectively.)) Thus, dye laser excitation of ATN T<sub>1</sub> leads to C–Cl bond cleavage.

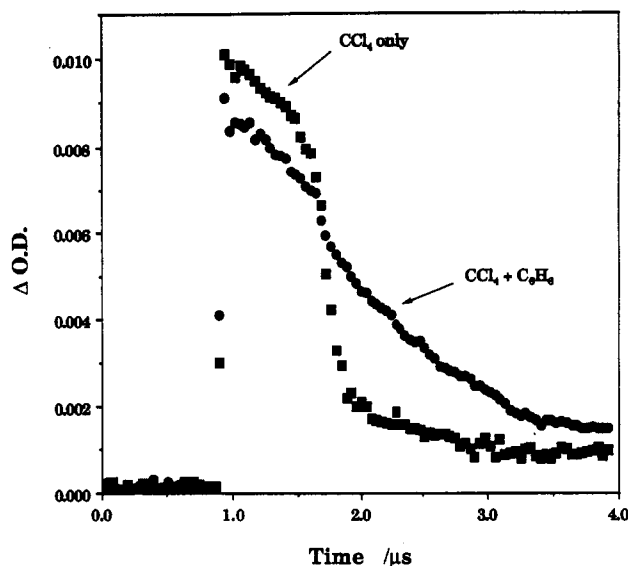


Figure 2. Transient production and decay monitored at 490 nm following two-laser (308 + 445 nm) flash photolysis of ATN in neat degassed CCl<sub>4</sub> (square symbols) and degassed CCl<sub>4</sub> with 3 M benzene.

While the production of Cl<sup>•</sup> itself is an indication of energy transfer from ATN to CCl<sub>4</sub>, that the sensitization process is not electron transfer is further indicated by the lack of bleaching observed when methylene chloride was used in place of CCl<sub>4</sub>. Both methylene chloride and CCl<sub>4</sub> have been reported to efficiently quench the excited state of diphenylmethyl radical by an electron transfer mechanism.<sup>23</sup> Thus, in the case of ATN, if CCl<sub>4</sub> quenching is by electron transfer, bleaching in the presence of methylene chloride would also be expected.

**Multiphoton Acid Generation.** Photogeneration of bromine atoms in a H-atom-donating solvent has been shown previously to lead to acid production.<sup>10–12</sup> For example, irradiation of vicinal dibromides in methanol or 2-propanol yields HBr. Since CCl<sub>4</sub> quenching of the upper triplet state of ATN leads to production of Cl<sup>•</sup>, and since Cl<sup>•</sup> is also known to undergo H-atom abstraction from hydrogen donors, this system could represent an efficient means of sensitizing acid production.

In order to determine the efficiency of photoacid generation following both one- and two-laser irradiation of ATN, product studies were carried out in 50:50 CCl<sub>4</sub>/MeOH. In the one-laser study, a 3-mL sample was exposed to 500 pulses from the excimer laser, while in the two-laser experiment, 500 pairs of excimer and dye laser pulses were used. (The dye laser pulse followed the excimer pulse by ca. 1 μs.) Following irradiation, the samples were treated as outlined in the Experimental Section and titrated with base. Both the one- and two-laser irradiated samples required more base to titrate than an identical unirradiated sample although significantly more base was required for the two-laser sample.

The quantum yield of acid production,  $\Phi_{\text{acid}}$ , was determined for the one-laser experiments by using azoxybenzene actinometry.<sup>18</sup> Samples of ATN in CCl<sub>4</sub>/MeOH and azoxybenzene in ethanol with matching ground-state absorbances at 308 nm were each irradiated by 500 excimer laser pulses. The ratio of acid ( $3.4 \times 10^{-3}$  M) to *o*-hydroxyazobenzene (obtained following treatment of the

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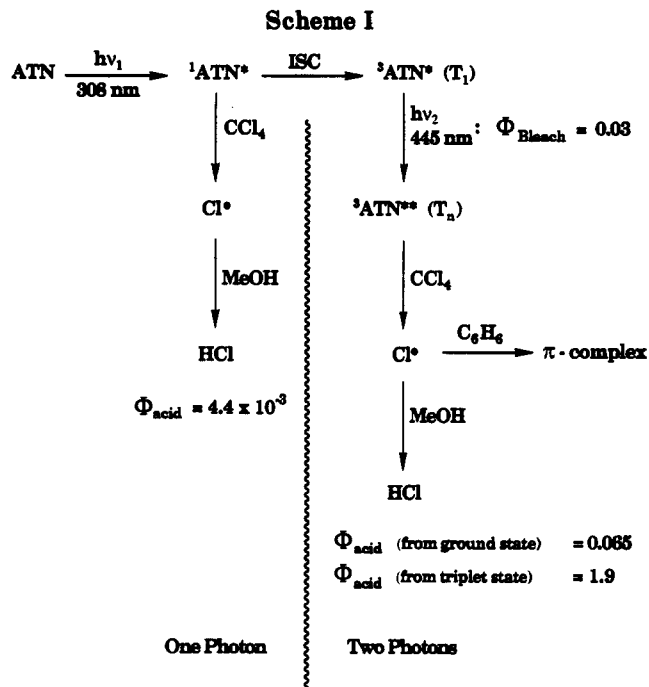
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irradiated azoxybenzene sample) yielded  $\Phi_{\text{acid}} = 4.4 \times 10^{-3} \pm 0.6 \times 10^{-3}$ . This value is considerably less than that reported previously for the 313-nm lamp irradiation of naphthalene in  $\text{CCl}_4/\text{MeOH}$ .<sup>14</sup> In the lamp irradiation, large (> 5) quantum yields were attributed to an efficient radical chain process which included a radical-radical termination step. The small yield in our experiments may be a result of very efficient chain termination, due to the large radical concentrations commonly produced by high flux laser sources. In addition, the quantum yield for acid production in the lamp experiments was reported to be very sensitive to the amount of  $\text{CCl}_4$  present, with the highest yield obtained at small  $\text{CCl}_4$  concentrations. In our experiments, however, it was necessary to maintain a larger ( $\sim 5$  M)  $\text{CCl}_4$  concentration in order to correlate triplet bleaching with enhanced acid production. (At low concentrations of  $\text{CCl}_4$  (<1 M) the extent of bleaching is small.)

The production of acid following one-laser excitation is likely due to sensitization via the singlet manifold of ATN. Since the ATN  $T_1$  lifetime is similar in  $\text{CCl}_4$  and benzene, it is improbable that  $T_1$  acts as a sensitizer.

In the two-laser experiment, ca. 15 times more acid was produced ( $5.1 \times 10^{-2}$  M) than in the one-laser experiment. Thus, the quantum yield for acid production from ground-state ATN under two-laser conditions is  $\Phi_{\text{acid}} = 0.065$ . However, the quantum efficiency for acid production from the triplet state of ATN is quite high, leading to a much larger quantum yield when the triplet state is considered as the primary absorbing species. This yield can be calculated from the value of  $\Phi_{\text{Bleach}}$  determined in the Aberchrome experiments and the quantum efficiency, which in turn is calculated from the ratio of moles of acid produced to moles of ATN triplet bleached by the dye laser. The moles of triplets bleached is determined from the T-T absorbance bleached and the ATN T-T extinction coefficient. Thus, the quantum yield of acid formation as a result of triplet excitation is  $\Phi_{\text{acid}} = 1.9 \pm 0.7$ .

The one- and two-laser photochemistry of ATN in  $\text{CCl}_4$  and  $\text{CCl}_4/\text{MeOH}$  is summarized in Scheme I.



Currently we are determining the two-laser bleaching and acid-generating efficiencies for a variety of other aromatic triplet states in  $\text{CCl}_4$ . Thus far we have observed that phenanthrene, acetylphenanthrene and benzophenone T-T absorptions are all efficiently bleached by dye laser excitation. These preliminary results indicate that the two-laser technique represents a tunable acid-generating method.

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