High Intensity, Argon Ion Laser-Jet Photochemistry

R. Marshall Wilson, Karlyn A. Schnapp, Klaus Hannemann, Douglas M. Ho, Hamid R. Memarian, Ardeshir Azadnia, Allan R. Pinhas and Timothy M. Figley

Department of Chemistry, University of Cincinnati Cincinnati, Ohio 45221-0172, USA

Abstract – A new technique for the study of high intensity solution photochemistry has been developed. With this laser-jet technique, a high velocity microjet is irradiated with the focussed output of an argon ion laser. Under these extremely high intensity conditions, photochemically generated transient species with suitable absorption properties are excited further and produce relatively large amounts of photoproducts which are not observed under low intensity of radicals, biradicals, photoenols and the higher excited states of carbonyl and polycyclic aromatic compounds is described.

High intensity photochemistry and the mechanisms by which conventional photochemical processes may be altered under high intensity conditions have become topics of great interest to photochemists. A successful strategy for the study of high intensity photo-chemical processes is to examine systems that are known to give rise to strongly absorbing photochemical transients. The study of the photochemistry of these transient inter-mediates has conventionally been conducted in low temperature matrices. In this environment, the lifetime of the target species is prolonged to the extent that it is sometimes possible to further excite the transient with a second photon delivered by a conventional low intensity light source [1]. Unfortunately this matrix method does not readily afford substantial quantities of multiple-photon products. Thus, these products often are not isolated, but only characterized spectroscopically in the matrix where they are formed.

More recently, Scaiano and coworkers have developed an exciting new method for the study of multiple-photon photochemistry [2]. This approach employs two pulsed lasers, one laser to generate the transient and the second laser to excite the transient and produce the multiple-photon photo-products. The forte of this technique is that it provides excellent spectroscopic information about the time sequence of the formation of the various transients produced in a photochemical reaction. Thus, by varying the time delay of the second laser pulse and its wavelength, it becomes possible to irradiate selected transients and observe their photochemistry. However, while the multiplephoton products can be isolated in favorable cases using this technique, it can be a very tedious process and the products are only obtained in very small quantities ($\sim 1 \text{ mg.}$).

The Laser-jet Technique

In our laboratory, an alternative method for the study of high intensity photochemistry based upon a C-W argon ion laser has been developed. In this laser-jet technique, a high velocity microjet (~100 μ m in diameter) of a solution of the material to be irradiated is injected into the focal region of an argon ion laser beam as illustrated in Fig. 1. Since typical microjet flow rates are about 1-2 mL-min-1, relatively large volumes of solution can be processed and the solution recycled as many times as necessary to bring the reaction to completion. Consequently, it becomes possible to isolate significant quantities of the multiple-photon products and to characterize these materials by spectroscopic methods used in more conventional organic chemistry.

The most significant attribute of this irradiation configuration is that the microjet serves as a light intensifying device. Irradiation of microbodies, such as the microjet used in this laser-jet apparatus, trap a significant portion of the light in modes or standing waves within the microbody [3]. These surface waves or whispering gallery modes, as they are sometimes called, occur as concentric cylinders of high light intensity within the outer 30% of the microjet cross section. Thus, the microjet becomes a resonance cavity within which light intensities are obtained far in excess of those generated by simply focussing the laser beam in a homogeneous medium. For example it has been estimated that for 600 nm light focussed on a lossless dielectric cylinder with a refractive index of 1.53 and a diameter of about 9 µm the first order mode has an intensity of more than 10⁶ times that of the background light [3c]. Simple calculations for the laser-jet device used in this work indicate that intensities in the range of 0.1 - 1 Einsteins-cm-2-s-1 might be expected



Fig. 1. Laser-jet apparatus: 1) jet nozzle, 2) 2-way valve, 3) pulse-dampener, 4) medium-pressure LC pump, 5) filter, 6) 4-way valve, 7) imaging screen, 8) demountable windows, 9) 75 mm lens, 10) x-y-z microtranslators, 11) optical bench, 12) electronic translator controls, and 13) viewing telescope.

within the jet. However, if the development of modes within the jet is taken into consideration, this intensity might be increased to values approaching 10^5 - 10^6 Einsteins-cm⁻²-s⁻¹.

At these intensity levels, the laserjet technique should provide access to C-W light intensities approaching those obtained from high power pulsed laser sources such as excimer lasers. While no direct quantitative measure of the light intensities produced within the microjet have been obtained as yet, photochemical results indicate that these estimates are qualitatively correct intensity. Thus, Scaiano and Johnston have reported that the deep-seated photochemical rearrangement of the bisdiphenylmethyl biradical 1 to the indene 2 via the dihydrofluorenyl biradical 3 occurs in about 12% yield relative to the single-photon products when the ketone 4 is irradiated with an excimer laser source (Scheme 1) [2]. In order to obtain about 1 mg. of 2 it was necessary to irradiate multiple samples of 4 with about 9000 laser pulses. In contrast

about 40-50 mg of 2 (ca. 40% yield relative to the single-photon products) were obtained in a single afternoon by means of argon ion laser-jet irradiation of about 100 mg of 4 [2e].

Double-beam Laser-jet Irradiation

The versatility of the laser-jet technique is further demonstrated in the photochemical transformation of omethylbenzophenone (5) to anthrone (6) as shown in Fig. 2. This reaction is known to proceed through the photoenol 7 which undergoes photocyclization to the dihydroanthrone 8. The dihydroanthrone 8 can either revert to the 7 or be irreversibly oxidized to 6. Under low intensity conditions and in the absence of an oxidizing agent, formation of 6 is extremely inefficient [4]. However, under laser-jet conditions the yields of are enhanced greatly. This apparently is due in part to the enhanced efficiency for the cyclization of 7 to 8, but probably in greater part due to the generation of high concentrations of oxidizing transients such as triplets of 5 which



Scheme 1



Fig. 2. Crossed laser beams in the sequential excitation of transient photochemical intermediates.

serve to efficiently oxidize 8 to 6 [5]. This conversion is enhanced further if two laser beams of different wavelengths are focussed on the same volume element of the jet. An ultraviolet beam (all of the ultraviolet lines of an argon ion laser) efficiently transforms 5 ($\lambda_{max} = 340$ nm) to 7 and a visible beam (all of the visible lines of a second argon ion laser) effectively cyclizes 7 ($\lambda_{max} = 430$ nm) to 8.

Delayed Trapping Using the Laser-Jet

Photochemical reactions that afford long-lived transients with lifetimes greater than about one millisecond provide ideal candidates for study with this delayed trapping technique. Inter-mediates of this type can be formed in the jet and rapidly quenched in solutions of trapping agents that would be incompatible with the formation of the intermediate. This partitioning of a photochemical reaction from a dark reaction also can provide valuable mechanistic information that is not readily available by other means.

Again the photoenol 7 of omethylbenzophenone (5) provides an excellent example of how this delayed trapping, laser-jet technique can be used to establish the mechanistic sequence of a photochemical reaction (Scheme 2) [6]. When 5 and N-phenyltriazolinedione (PTAD) are irradiated together, a good yield of the substitution product 9 is obtained. This material might be formed by either of two general mechanisms: 1) 7 might undergo reaction with ground state PTAD, or 2) an excited PTAD molecule might abstract a hydrogen atom from the methyl group of 5, and the resulting radicals combine. Since both 5 and PTAD absorb light at the irradiating wavelength, there is no simple, con-ventional method to distinguish between these two mechanistic alternatives. However, if 5 is irradiated in the jet and rapidly injected into a fountain contain-ing PTAD, 9 is obtained, albeit in reduced yield. If the roles are reversed and PTAD is irradiated in the jet and quenched in a fountain containing 5, the formation of 9 is not observed. Thus, these delayed trapping results clearly demonstrate that this reaction proceeds through the reaction of 7 with ground state **P**TAD.



In another example of delayed trapping, Fe(CO)5 can be irradiated in the presence of triphenylphosphine in the jet to form both the mono- and diphosphine adducts, $Fe(CO)_4PPh_3$ and $Fe(CO)_3(PPh_3)_2$, respectively [7]. While the obvious exploration for this the obvious explanation for this observation is that $Fe(CO)_4$ and $Fe(CO)_3$ are being formed in the jet and trapped by the triphenylphosphine, these processes do not fully account for this chemistry. Thus, if Fe(CO)₅ is irradiated by itself in the jet using a nonligating solvent such as cyclohexane and the irradiated jet injected into a solution of triphenylphosphine, the same two phosphine adducts are formed, albeit in reduced yields. In fact, the quenching can be delayed by 15 minutes and the same two phosphine adducts are still formed! Clearly long-lived and reactive iron species are being formed upon irradiation. While the exact nature of these species are not yet known, it would seem that they are not simply $Fe(CO)_4$ and $Fe(CO)_3$ or some form of these species ligated by the solvent. Presently, the best working hypothesis is that some

highly reactive iron complex is formed and survives for quite long times after its photochemical generation. That this species is not $Fe_2(CO)_9$ is indicated by the fact that little if any $Fe_2(CO)_9$ can be detected in the absence of phosphine and triphenylphosphine reacts much more slowly with $Fe_2(CO)_9$ then it does with the photochemically generated species. Similar observations have been made with other metal carbonyls and the structures of these reactive metal species is under active investigation.

The Photochemistry of Diphenylmethyl Radicals and Related Biradicals

The photochemistry of triphenylmethyl radicals has been observed, although not mechanistically defined, early in this century [8]. Subsequently, the photocyclization of triphenylmethyl radical itself (10) to dihydrofluorenyl radical (11) and its disproportionation with 10 to form 9-phenylfluorene (12) and triphenylmethane (13) was proposed (Scheme 3) [9].



Scheme 3



More recently, Meisel and coworkers have examined the photochemical behavior of substituted diphenylmethyl radicals using modern transient spectroscopic techniques [10]. They observed that 10 and 1,1diphenylethyl radical (14) undergo irreversible photochemistry; while the parent diphenylmethyl radical (15) is stable photochemically (Scheme 6). On the basis of these spectroscopic observations, they speculated that substituted diphenylmethyl radicals undergo photocyclization to the corresponding dihydrofluorenyl radicals, but that the unsubstituted diphenylmethyl radical was inert towards this cyclization. This behavior was ascribed to the steric congestion between the phenyl groups which should be enhanced through the introduction of a substituent on the central carbon atom.

We have sought a source of substituted diphenylmethyl radicals that might be accessed with the argon laser-jet technique and used to test these spectroscopic observations. Such a source has been found in α -substituted α,α -diphenylacetophenones. Thus, for example, when benzopinacolone (16) is irradiated at low light intensities, the major photochemical process is the migration of an α -phenyl group to the carbonyl oxygen to form the enol ether 17 (Scheme 4) [11]. Under these low intensity conditions, very little Norrish Type I cleavage occurs to form 10 and associated products. However, under high intensity, laser-jet conditions, the relative importance of these two competing triplet processes [12] is inverted with the virtually complete suppression of the phenyl migration mode and predominance of the Norrish Type I cleavage.

A working hypothesis which rationalizes these observations is outlined in Scheme 5. Phenyl migration apparently occurs with relatively higher efficiency from the first excited triplet state of 16 (18). While Norrish Type I cleavage seems to be much more efficient from higher excited triplet states (19). Scaiano has observed that ketones which exhibit reluctant Norrish Type I cleavage from their first excited triplet states can undergo efficient cleavage from higher triplet states [13]. Unfortunately, attempts to observe 18 and determine its lifetime have been unsuccessful, since its absorption apparently is masked by the very intense absorption of 10 which is formed rapidly upon excitation of 16 [14]. Furthermore, Wagner and Zhou have reported triplet lifetimes in the subnanosecond range for closely related diarylacetophenones [12]. Since species with subnanosecond lifetimes would seem to be too short-lived to present viable targets for the absorption of a second photon, the exact nature of the target transient that gives rise to the intensity dependence of this reaction still remains in question.



Scheme 5



Nevertheless, when laser-jet conditions were applied to a series of α , adiphenylacetophenones (Scheme 6), benzopinacolone (16) and α , a-diphenylpropiophenone (20) were found to yield 9phenylfluorene (12) and 9-methylfluorene (21), respectively, as the major products. While α , a-diphenylacetophenone (22) did not yield fluorene, but afforded only 1,1,2,2-tetraphenylethane (23) instead. These results are in complete accord with the spectroscopic observations of Meisel [10].

Since the biradical 1 (Scheme 1) incorporates two substituted diphenylmethyl radicals into its structure, its photochemical cyclization to the dihydrofluorenyl biradical 3 is consistent with the photochemical behavior of the simpler substituted diphenylmethyl radicals described above. In order to see if this photochemical reaction pattern would be followed with other biradicals containing diphenylmethyl radical termini, the laser-jet photochemistry of the unsymmetrical 1,3-biradical 24 was examined (Scheme 7) [15]. Under low intensity conditions, 24 collapses to the unsymmetrical cyclopropane 25. However, under laserjet conditions, no indication of diarylmethyl radical terminus was observed. Instead, if 24 was generated via pathway A, 1,1-diphenylethylene (26) and the symmetrical cyclopropane 27 were formed in addition to the low intensity product 25. In contrast, generation of 24 via pathway B yielded 1,1-di-pmethoxyphenylethylene (28) and the symmetrical cyclopropane 29 as the major, high intensity products. These products are consistent with the photochemical cleavage of the pivotal biradical 24 into an olefin and a carbene as outlined in Scheme 7.

In order to gain further information about the regiochemistry of this carbene extrusion reaction, the unsymmetrical cyclopropane 30 was irradiated under laser-jet conditions (Scheme 8). In this case, the generation of the triplet 1,3-biradical 31 is internally sensitized through the initial excitation of the anthronyl chromophore. Since the diphenylmethyl radical is known to absorb at about 330 nm [10], and the anthronyl radical absorbs at about 500 nm [16], excitation of biradical 31 will afford an excited anthronyl terminus. The only high intensity products formed upon laser-jet irradiation of 30 were 10-methylene-anthrone (32) and tetraphenylethylene (33) which would be the expected product from the dimerization of diphenyl-carbene. These products are those that would arise from the cleavage of the σ -bond β to the excited anthronyl moiety. Had the cleavage occurred at the σ -bond α to the anthronyl unit, bianthrone (34) and 1,1-diphenylethylene (26) should have been produced and these



Scheme 7



products were not detected. Thus, this carbene extrusion reaction from excited 1,3-biradicals provides a second example β -cleavage of an excited radical center [17].

Further examples of biradical photochemistry have been sought in the laser-jet irradiation of quinone-olefin systems. Detailed studies of the *p*benzoquinone-tetraphenylallene system have been conducted in hopes of observing high intensity photochemistry of the Paterno-Büchi, preoxetane biradical 35 (Scheme 9) [18]. However, transient spectroscopy in concert with oxygen and proton trapping studies [19] indicate that the intermediate is not the preoxetane biradical 35, but the chargetransfer exciplex 36. In accord with these findings, the *p*-benzoquinonetetraphenylallene system affords only the indene 37 upon both conventional and laser-jet irradiation.

The Photochemistry of Phenanthrene Analogs

The photoaddition of phenanthroquinone to tetraphenylallene has been sity dependent photochemistry. Thus, while 38 and 39 are photochemically inert under low intensity conditions, 38 rearranges to 40 and 39 to 41 under high intensity, laser-jet conditions. The efficient [2+2] photocycloaddition of related 1,4-dioxins has been reported, and apparently stems from the π,π^* excited state of the phenanthrene ring system [21]. Consequently, the rearrangements of 38 to 40 and 39 to 41 probably originate from higher π,π^* excited states of this type of substituted phenanthrene. While the mechanistic details of these extensive molecular reorganizations remain to be determined, these observations do suggest that the excited states of polycyclic aromatic hydrocarbons might be suitable target species for further laserjet studies.

Conclusions

The development of the C-W, argon ion, laser-jet technique makes it possible to routinely isolate and characterize the photoproducts of transient photochemical species. To date, this approach has been successfully applied in the study of the photochemistry of such transients as



Scheme 9

examined in the search for new high intensity photoreactions (Scheme 10) [20]. While phenanthroquinone adds readily to tetraphenylallene to form the mono- and diadducts 38 and 39, respectively, these addition reactions are not intensity-dependent under present laser-jet conditions. However, the adducts 38 and 39 both display intenphotoenols, biradicals, and higher excited states of carbonyl compounds and polycyclic aromatic hydrocarbons. When coupled with the more established techniques of transient spectroscopy, the laser-jet provides a most valuable tool for the mechanistic study of high intensity photochemical processes.



Acknowledgement – We would like to thank the National Science Foundation for their support of this reseach (NSF CHE-8409628) and for funds used to help establish the NMR and mass spectro-metry facilities used in this work (CHE-8102974 and PCM-8219912). K.A.S. would like to thank the Center for Laser Chemistry and the University of Cincinnati for fellowship support.

REFERENCES

- a) D. E. Seeger, P. M. Lahti, A. R. Rossi, J. A. Berson, J. Am. Chem. Soc. 108, 1251 (1986). b) I. R. Dunkin, J. G. MacDonald, *Tetrahedron Letters* 23, 5201 (1982). c) S. P. Schmidt, A. R. Pinhas, J. H. Hammons, J. A. Berson, J. Am. Chem. Soc. 104, 6822 (1982). d) H. Nakanishi, A. Yabe, K. Honda, Chem. Commun. 86 (1982). e) R. J. McMahon, O. L. Chapman, R. A. Hayes, T. C. Hess, H.-P. Krimmer, J. Am. Chem. Soc. 107, 7597 (1985). f) G. W. Griffin, Angew. Chem., Int. Ed. Engl. 10, 537 (1971). g) J. F. Muller, D. Muller, H. J. Dewey, J. Michl J. Am. Chem. Soc. 100, 1629 (1978).
- [2] a) McGimpsey, J. C. Scaiano, J. Am. Chem. Soc. 110, 2299 (1988). c) J. C. Scaiano, L. J. Johnston, W. G. McGimpsey, D. Weir, Acc. Chem. Res. 21, 22 (1988). d) J. C. Scaiano, L. J. Johnston in Organic Photo-chemistry, Vol. 10, A. Padwa, Ed., Dekker, New York, p. 309, 1989. e) We thank J. C. Scaiano for his generous gift of ketone 4.) L. J. Johnston, J. C. Scaiano, J. Am. Chem. Soc. 108, 2349 (1986). b) W. G.
- [3] a) A. Ashkin, J. M. Dziedzic, *Phys. Rev. Letters* 38, 1351 (1977). b) A. Ashkin, J. M.Dziedzic, *Applied Optics* 20, 1803 (1981).
 c) J. F. Owen, R. K. Chang, P. W. Barber, *Optics Letters* 6, 540 (1981). d) H.-M. Tzeng, K. F. Wall, M. B. Long, R. K. Chang, *Optics Letters* 9, 499 (1984). e) S.-X. Qian, J. B. Snow, H.-M. Tzeng, R. K. Chang, *Science* 231, 486 (1986).
- [4] a) E. F. Ullman, K. R. Huffman, Tetrahedron Letters 1863 (1965). b) N. D.

Heindel, J. Molnar, M. Pfau, J. Chem. Soc., Chem. Commun. 1373 (1970).

- [5] R. M. Wilson, K. Hannemann, K. Peters, E.-M. Peters, J. Am. Chem. Soc. 109, 4741 (1987).
- [6] R. M. Wilson, K. Hannemann, W. R. Heineman, J. R. Kirchhoff, J. Am. Chem. Soc. 109, 4743 (1987).
- [7] T. M. Figley, A. R. Pinhas, R. M. Wilson, unpublished results.
- [8] a) Gomberg, L. H. Cone, Ber. 37, 3545 (1904).
 (1904).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
 (1912).
- [9] R. L. Letsinger, R. Collat, M. Magnusson, J. Am. Chem. Soc. 76, 4185 (1954).
- [10] A. Bromberg, K. H. Schmidt, D. Meisel, J. Am. Chem. Soc. 107, 83 (1985).
- [11] H. G. Heine, Tetrahedron Letters 1473 (1971).
- [12] P. J. Wagner, B. Zhou, J. Am. Chem. Soc. 110, 611 (1988).
- [13] a) W. G. McGimpsey, J. C. Scaiano, J. Am. Chem. Soc. 109, 2179 (1987). b) L. J. Johnston, J. C. Scaiano, J. Am. Chem. Soc. 109, 5487 (1987). c) B. Guerin, L. J. Johnston, T. Quach, J. Org. Chem. 53, 2826 (1988).
- [14] We thank Professor J. Wirz for his efforts to observe the triplet state of 16.
- [15] R. M. Wilson, K. A. Schnapp, J. Am. Chem. Soc. 110, 982 (1988).
- [16] H.-D. Becker, T. Elebring, J. Org. Chem. 10, 1319 (1985).
- [17] J. C. Scaiano, P. J. Wagner, J. Am. Chem. Soc. 106, 4626 (1984).
- [18] K. A. Schnapp, R. M. Wilson, D. M. Ho, R. A. Caldwell, D. Creed, unpublished results.
- [19] R. M. Wilson in Organic Photochemistry, Vol. 7, A. Padwa, Ed., Dekker, New York, p. 339, 1985.
- [20] K. A. Schnapp, R. M. Wilson, D. M. Ho, unpublished results.
- [21] S. Farid, D. Hess, Ber. 102, 3747 (1969).