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The Laser-Drop Method: A New Approach To Induce Multiple Photon Chemistry with Pulsed Lasers. Examples Involving Reactions of Diphenylmethyl and Cumyloxyl Radicals

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Abstract: A new method, described as the laser-drop technique, is presented which allows preparative experiments in laser-induced multiphoton chemistry. The technique shares most of the advantages of the successful laser-jet technique but allows the use of pulsed lasers that are readily available in many laboratories. The laser-drop method has been tested with two photochemical systems. The well-studied diphenylmethyl radical system allows a direct comparison of results from laser-drop, laser-jet, lamp, and two-color two-laser studies. The laser-jet and laser-drop techniques show comparable performance for two-photon processes, but the latter has advantages in reactions of higher order in light intensity. The photolysis of dicumyl peroxide has been used to demonstrate for the first time laser-induced β-cleavage of alkoxyl radicals. Photolysis of dicumyl peroxide in methanol leads to dramatically different product distributions under conditions of lamp and laser-drop photolysis.

Introduction

Over the past decade, the solution photochemistry of organic reaction intermediates has been the subject of considerable attention. The approach used in our laboratory has concentrated on laser flash photolysis techniques utilizing two pulsed lasers: these *two-laser two-color* experiments use one laser to produce the transient to be studied (*the synthesis laser*) and a second laser to excite the transient (*the photolysis laser*).[1] This technique is extremely valuable for mechanistic and kinetic studies and has proven useful in studies of free radicals,[2] carbenes,[3] triplet states,[4] xylylenes,[5] ylides,[6] etc. While the technique has been occasionally used to characterize two-photon products,[7] its major drawback is that isolating significant amounts of reaction products is difficult.

An alternate approach that greatly facilitates product studies has been developed by Adam, Wilson, and co-workers.[8,9] Described as the *laser-jet technique*, this technique frequently employs a continuous wave argon ion laser focussed onto a thin microjet of the solution to be irradiated. It has been suggested that the microjet serves as a light intensifying device and that the light intensity within the jet approaches that of pulsed lasers. This technique allows relatively large volumes of solution to be processed and recycling of the solution as many times as necessary to bring the reaction to completion. This makes it possible to isolate significant quantities of multiple photon products which can then be characterized by conventional spectroscopic methods. The laser-jet technique is limited in the mechanistic insights it provides and for practical purposes cannot yield any kinetic information.

It is clear that the two-laser two-color and laser-jet techniques could be used in a symbiotic fashion to elucidate the reaction mechanisms from which multiple photon products are derived. In a recent paper,[10] we provided a rare comparison of the two techniques, in a system involving reactions of α,α-dialkoxylbenzyl radicals. To the best of our knowledge there is no laboratory that is currently well set up to carry out both types of experiments "in house".

For the numerous laboratories that use pulsed lasers for transient studies, setting up the laser-jet technique would represent a major investment. We reasoned that what the laser-jet technique achieves by using a continuous laser and a continuous flow could perhaps also be achieved with a pulsed laser by using it in conjunction with a "pulsed" flow, thus the idea of employing pulsed lasers to irradiate small droplets of solution. This article describes our successful implementation of this rather simple idea.

In order to illustrate the capabilities of the laser-drop technique, we report results on two reaction intermediates. Our first example deals with diphenylmethyl radicals which have been extensively studied by two-laser two-color and related techniques[11-16] and more recently by the laser-jet technique[17] and under ablative conditions.[18] The results of laser-drop experiments can be readily compared with literature data obtained using other techniques. Our second example deals with cumyloxyl that slowly cleaves thermally to yield acetophenone and methyl radicals. We show that under laser-drop conditions this cleavage occurs far more efficiently, leading to a dramatic change in product distribution.

Results

Description of the Experiment. One of our earlier ideas, that one could run a pulsed laser at high frequency and focus it onto a microjet, did not prove useful. Even if an excimer laser with 10-ns pulses was operated at 100 Hz, the light beam would

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[1] Scaiano, J. C.; Johnston, L. J.; McGimpsey, W. G.; Weir, D. *Acc. Chem. Res.* **1988**, *21*, 22.

[2] Scaiano, J. C.; Johnston, L. J. *Pure Appl. Chem.* **1986**, *58*, 1273.

[3] Scaiano, J. C. In *Kinetics and Spectroscopy of Carbenes and Biradicals*; Platz, M. S., Ed.; Plenum Press: New York, 1990; p 353.

[4] McGimpsey, W. G.; Scaiano, J. C. *Chem. Phys. Lett.* **1987**, *138*, 13.

[5] Scaiano, J. C.; Wintgens, V.; Netto-Ferreira, J. C. *Pure Appl. Chem.* **1990**, *62*, 1557.

[6] Scaiano, J. C.; McGimpsey, W. G.; Casal, H. L. *J. Am. Chem. Soc.* **1985**, *107*, 7204.

[7] Johnston, L. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 2349.

[8] Wilson, R. M.; Adam, W.; Schulte-Oestrich, R. *The Spectrum* **1991**, *4*, 8.

[9] Wilson, R. M.; Schnapp, K. A.; Hannemann, K.; Ho, D. M.; Memarian, H. R.; Azadnia, A.; Pinhas, A. R.; Figley, T. M. *Spectrochim. Acta* **1990**, *46A*, 551.

[10] Banks, J. T.; Scaiano, J. C.; Adam, W.; Schulte Oestrich, R. *J. Am. Chem. Soc.* **1993**, *115*, 2473.

[11] Bromberg, A.; Schmidt, K. H.; Meisel, D. *J. Am. Chem. Soc.* **1984**, *106*, 3056.

[12] Bromberg, A.; Schmidt, K. H.; Meisel, D. *J. Am. Chem. Soc.* **1985**, *107*, 83.

[13] Scaiano, J. C.; Tanner, M.; Weir, D. *J. Am. Chem. Soc.* **1985**, *107*, 4396.

[14] Redmond, R. W.; Scaiano, J. C. *J. Phys. Chem.* **1989**, *93*, 5347.

[15] Redmond, R. W.; Scaiano, J. C.; Johnston, L. J. *J. Am. Chem. Soc.* **1990**, *112*, 398.

[16] Weir, D. *J. Phys. Chem.* **1990**, *94*, 5870.

[17] Adam, A.; Oestrich, R. S. *J. Am. Chem. Soc.* **1992**, *114*, 6031.

[18] Arnold, B. R.; Scaiano, J. C. *Macromolecules* **1992**, *25*, 1582.

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effectively be on one millionth of the time. Depending on beam and jet size, only 1–5% of the solution would be irradiated under these extreme conditions.

The idea of irradiating free-falling drops of solution proved to be, while feasible, very impractical. The simplest approach proved to be to excite the drop shortly before it was ready to fall from the tip of a needle. The output pulses from an excimer laser (308 nm, ~6 ns, 60–130 mJ/pulse) were focussed onto a drop suspended from a nearly-horizontal syringe needle. Care must be taken to ensure that the laser beam is incident on the lower half of the droplet, just below the needle, and that *it does not actually hit the needle tip* (refer to cautionary note in the Experimental Section). Irradiations should also be performed under an inert gas atmosphere for safety reasons. During the course of an experiment in cyclohexane under an air atmosphere, the laser pulse hit the needle tip and ignited the solvent mist. All experiments should be performed under a nitrogen or argon inert atmosphere. The syringe pump is set at a solution flow which would lead to a spontaneous droplet rate slightly lower than the laser frequency. Additional details are provided in the Experimental Section. We note that ablation of quartz is not uncommon under these irradiation conditions and that the cell design must take this into account to minimize this problem.[19]

Excitation of droplets causes them to burst, presumably as a result of a shock wave generated within the drop, since thermal changes are not sufficient to induce this effect (see Experimental Section). Cell design is also important in ensuring that ejected portions of the solution are collected efficiently.

Photochemistry of 1,1-Diphenylacetone (I). Diphenylmethyl radicals (II) were selected for this study since they meet several criteria. Their photochemistry is well-established,[11-16,20] the extinction coefficients for ground and excited radical are known or can be estimated,[18] their absorptions at 308 nm are very large, and at this wavelength it is possible to produce *and* excite the radical within a single laser pulse.

In order to fully characterize our excitation conditions, a few laser flash photolysis experiments were carried out on the same solutions employed for the laser-drop experiments. Figure 1 shows the transient spectra recorded upon 308-nm laser excitation of a deaerated solution of I (2 mM) in acetonitrile. Figure 1 gives the spectrum immediately after excitation (a) and after a delay of 0.5 μs (b). The short-lived species (see insert in Figure 1) has a lifetime of 232 ns and λ_{max} 355 nm and can be confidently assigned to excited diphenylmethyl radicals (II*).[11-13] The long-lived species that has a half-life in excess of 10 μs under our experimental conditions and λ_{max} 334 nm is due to the ground state radical (II).

When drops of a deaerated 10 mM solution of I in carbon tetrachloride were irradiated by the focussed output from a 308-nm excimer laser, a strong green fluorescence was readily visible. This can be attributed to fluorescence from excited II, II*.[21] The products of the laser-drop photolysis of I show benzhydryl chloride (III) as the main (>98%) reaction product. In contrast lamp photolysis yields very little III, while tetraphenylethane (IV) and 1,1,1,-trichloro-2,2-diphenylethane (V) are now the main products. Product distributions for the photolysis of I in CCl_4 are given in Table I. While the acetyl radical products were not quantified, it is evident that V results from the combination of II with trichloromethyl radicals, which under lamp irradiation would be the expected product of reactions of acetyl radicals with the solvent according to reaction 1.

$$CH_3\dot{C}O + CCl_4 \rightarrow CH_3COCl + CCl_3^{\bullet} \qquad (1)$$

Recent reports employing time-resolved infrared spectroscopy have demonstrated the reactivity of acyl radicals toward the C–Cl bond.[22] We note that the absence of V under laser-jet and laser-drop excitation conditions cannot be due to failure to produce $CCl_3^{\bullet}$, since in fact excited diphenylmethyl provides an additional source of these radicals under these conditions (*vide infra*).[13]

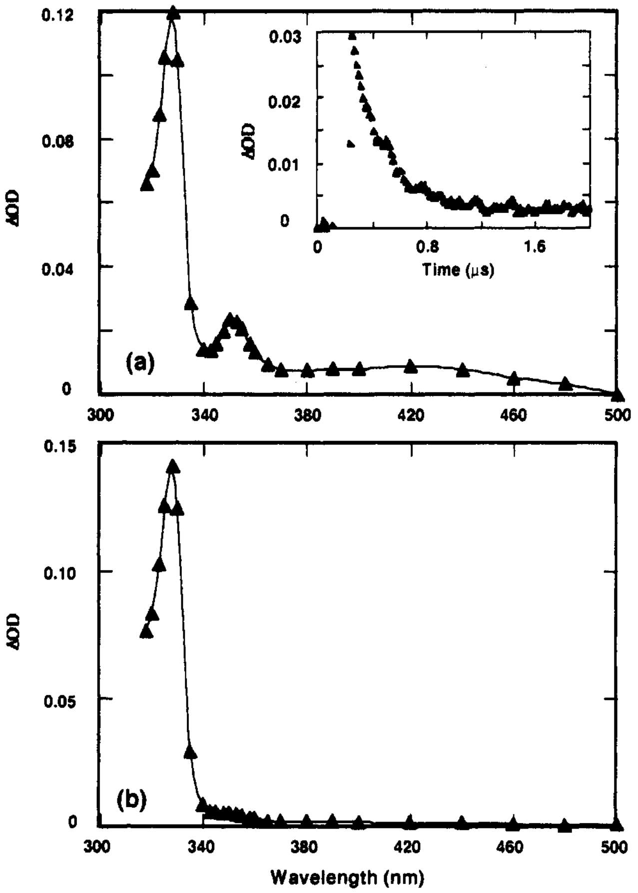

Figure 1. Transient spectra recorded upon 308-nm excitation of a 2 mM solution of I in acetonitrile recorded immediately (a) and 0.5 μs (b) after excitation. The increase in peak intensity in part b is due to decay of excited redical (II*) leading to ground state repopulation. Inset: Decay of II* monitored at 355 nm.

Table I. Photolysis of Diphenylmethyl Radical Precursors in Carbon Tetrachloride[a]

method	precursor	% conv	III	IV	V
Rayonet[b]	I	87	10	38	52
laser jet[c]	XI	22	96	4	
laser-drop	I	15	>98	<2	

[a] Product yields ±5%. [b] Lamp irradiation at 300 nm. [c] Data from ref 17.

The photolysis products of I (10 mM) in methanol again showed a strong dependence on light intensity. Under lamp irradiation the major product (>98%) is 1,1,2,2-tetraphenylethane (IV), formed by the combination of radicals II, while under laser-drop conditions the ether VI accounts for 92% of the products. Product distributions for the photolysis of I in methanol are given in Table II. Solutions of I in methanol-d_1 were also irradiated under lamp-drop conditions and analyzed by GC-MS. The products contained ether VI but not VI-d_1.

Photochemistry of Dicumyl Peroxide (VII). Cumyloxyl radicals (VIII) have been recently reported to have absorption bands in the UV and visible (λ_{max} 485 nm) regions.[23] Figure 2 shows the spectrum recorded upon 266-nm laser flash photolysis of a

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(19) Ihlemann, J. *Appl. Surf. Sci.* **1992**, *54*, 193.

(20) Bohne, C.; Boch, R.; Scaiano, J. C. *J. Org. Chem.* **1990**, *55*, 5414.

(21) Weir, D.; Scaiano, J. C. *Chem. Phys. Lett.* **1986**, *128*, 156.

(22) Neville, A. G.; Brown, C. E.; Rayner, D. M.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1991**, *113*, 1869.

(23) Avila, D. V.; Lusztyk, J.; Ingold, U. *J. Am. Chem. Soc.* **1992**, *114*, 6576. Avila, D. V.; Brown, C. E.; Ingold, K. U.; Lusztyk, J. *J. Am. Chem. Soc.* **1993**, *115*, 466.

Table II. Photolysis of Diphenylmethyl Radical Precursors in Methanol

method	precursor	% conv	IV	VI
Rayonet[a]	I	98	>98	
laser jet[b]	XI	27	59	34
laser-drop	I	19	8	92

[a] Lamp irradiation at 300 nm. [b] Data from ref 17.

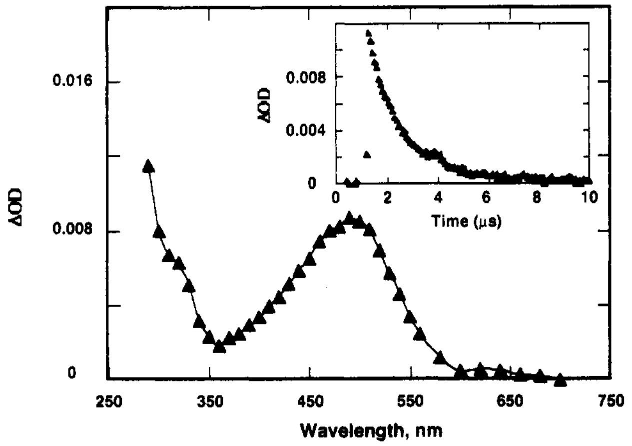

Figure 2. Transient spectrum recorded upon 266-nm laser excitation of dicumyl peroxide in acetonitrile. Inset: Decay trace in acetonitrile monitored at 500 nm.

1 mM solution of VII in acetonitrile. Typical lifetimes under these conditions were around 1.5 μs, and they agree well with recently reported values.[23] When the solvent is methanol the lifetimes of cumyloxyl radicals (VIII) are reduced to ca. 165 ns. Addition of methanol concentrations in the 0–1 M range to solutions of VII in acetonitrile led to a shortening of the lifetime of VIII (monitored at 500 nm). The decay traces follow excellent first-order kinetics, and a plot of the experimental rate constant for cumyloxyl decay as a function of methanol concentration leads to a rate constant of $(3.0 \pm 0.2) \times 10^5$ M^{-1} s^{-1} for reaction of VIII with methanol. For comparison the reported value for reaction of *tert*-butoxyl with methanol is 2.9×10^5 M^{-1} s^{-1}.[24]

Lamp irradiation (300 nm) of a 10 mM solution of VII in acetonitrile gave acetophenone (IX) as the only major aromatic product (98%). The β-scission of cumyloxyl radical in the absence of readily abstractable hydrogens is well-documented.[25,26] When the photolysis is carried out in methanol as solvent, cumyl alcohol (X) becomes the only major aromatic product (>98%), with only a small amount of acetophenone (IX < 2%). We attribute this behavior to hydrogen abstraction by VIII from the solvent, as expected from the reactivity observed in the laser flash photolysis experiments (*vide supra*).

Cumyloxyl radicals have significant absorption at 308 nm (see Figure 2). In contrast, the precursor peroxide (VII) absorbs very weakly at this wavelength ($\epsilon_{308} \sim 5.7$ M^{-1} cm^{-1}, corresponding to $A = 0.04$ for a 10 mM solution in a cell with 7 mm optical path). It was possible to use the 308-nm excimer laser for these laser-drop experiments by recycling the solution several times until a sufficient concentration of products had accumulated. Five cycles of laser-drop irradiation of 10 mM solutions of VII in methanol lead to an almost equimolar mixture of IX and X. At this point the conversion was ca. 10%. Table III gives the corresponding product distributions.

In a series of experiments we also tested the effect of varying the drop size (5 to 25 μL/drop). Within this range size had little effect on product distribution as long as the laser energy was kept constant, although the percent conversion tends to decrease with increasing drop size. The question of drop size was not pursued any further other than to keep the drops slightly larger than the laser cross section at the focal point. Typically 130 to 150 drops per milliliter proved adequate (see Experimental Section).

Table III. Photolysis of Dicumyl Peroxide in Acetonitrile and in Methanol

method	solvent	% conv	IX	X
Rayonet[a]	acetonitrile	39	>98	
Rayonet[a]	methanol	48	<2	>98
laser-drop[b]	methanol	10	46	54

[a] Lamp irradiation at 300 nm. [b] 5 cycles.

Discussion

Laser excitation of small absorbing droplets leads to the rapid ejection of material in an apparent explosion of the drop. One may question whether this process is the result of a thermal effect (leading to rapid boiling) or a shock wave type of effect similar to that occurring in ablation processes.[27-30] A simple calculation shows that the ejection of material cannot be due to thermal effects. If 100 mJ are deposited and converted into heat in a 10-μL droplet the temperature change would be 4 deg in methanol (specific heat, $C = 0.60$ cal/(K·g)) and 12 deg in carbon tetrachloride ($C = 0.20$ cal/(K·g)). In practice temperature changes are expected to be smaller, since not all the energy is absorbed within the droplet, and a significant fraction is used to induce chemical change, and not to generate heat. Further, specific heats for common solvents are unlikely to be lower than for carbon tetrachloride. Under most conditions, the actual temperature change should be between 2 and 6 deg. Thus, we conclude that drop "explosion" occurs as a result of ablative-type processes initiated by a shock wave within the drop. We assume that ejection of material probably occurs in the microsecond time scale, although further studies employing nanosecond photography will be required to solve this question.

Another question of interest relates to the actual concentration of intermediate that could be generated under laser-drop conditions. At 308 nm the energy corresponds to approximately 93 kcal/mol. A simple calculation indicates that a 100 mJ pulse incident on a 10-μL droplet would lead to a transient concentration of 0.025 M if it was totally absorbed and the process occurred with a quantum yield of one. While these criteria may not be always met,[31] one can anticipate that initial transient concentrations could approach 10^{-2} M.

The Diphenylmethyl Radical System. In a recent paper Adam and Schulte Oestrich[17] examined the high-intensity photochemistry of benzhydryl phenyl ketone (Ph$_2$CHCOPh, XI) in carbon tetrachloride and in methanol. The process involves the intermediacy of excited electronic states of the diphenylmethyl radical, II*. Adam's results[17] on the laser-jet photolysis of XI are very similar to those recorded by us for the laser-drop photolysis of I (see Table I). In CCl$_4$ the formation of III can be readily explained by the reaction of II* with the solvent, reaction 2.

$$\mathrm{Ph_2\dot{C}H^* + CCl_4 \rightarrow Ph_2CHCl + CCl_3^{\bullet}} \qquad (2)$$

It has been reported that reaction 2 occurs with a rate constant of 1.6×10^8 M^{-1} s^{-1} at room temperature and that the lifetime of II* in CCl$_4$ is less than 5 ns.[13] We proposed several years ago that quenching of II* by CCl$_4$ probably involved charge transfer

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(24) Paul, H.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520.

(25) Baignée, A.; Howard, J. A.; Scaiano, J. C.; Stewart, L. C. *J. Am. Chem. Soc.* **1983**, *105*, 6120.

(26) Neville, A. G.; Brown, C. E.; Rayner, D. M.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1989**, *111*, 9269.

(27) Srinivasan, R. *Science* **1986**, *234*, 559.

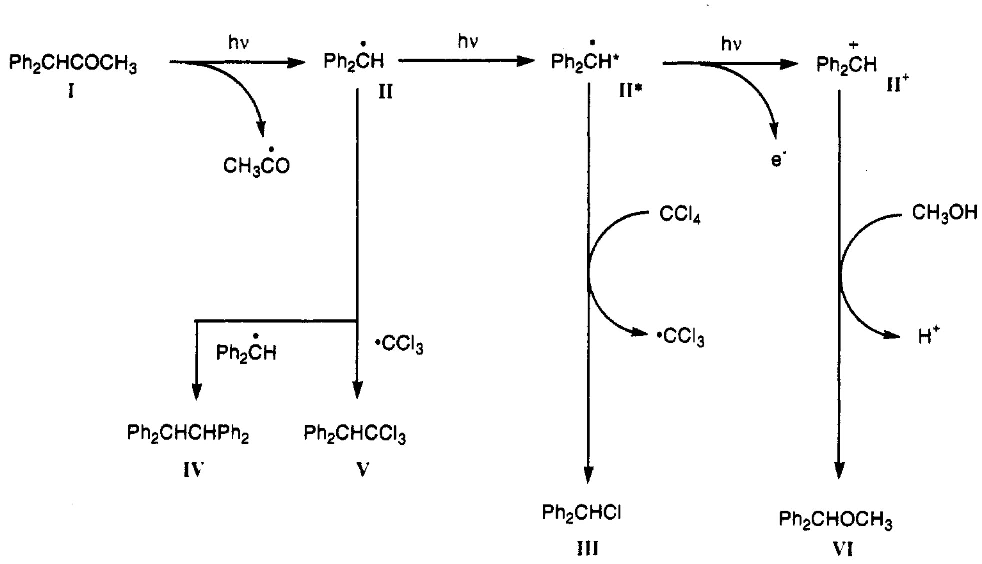
(28) Srinivasan, R.; Braren, B. *Chem. Rev.* **1989**, *89*, 1303.

(29) Srinivasan, R.; Braren, B.; Casey, K. G. *Pure Appl.Chem.* **1990**, *62*, 1581.

(30) Yeh, J. T. C. *J. Vac. Sci. Technol. A* **1986**, *4*, 653.

(31) In the case of peroxides quantum yields of alkoxyl radical formation frequently exceed one. See for example: Lissi, E. *Can. J. Chem.* **1974**, *52*, 2491.

Scheme I



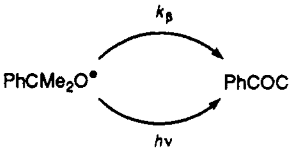
interactions.[13] We have recently been able to prove unequivocally this mechanism by characterizing the corresponding carbocation, Ph_2CH^+, as an intermediate in the reaction in acetonitrile.[32] In nonpolar media (e.g. in CCl_4 solvent) geminate recombination of the ions (Ph_2CH^+ and Cl^-) may predominate and account for the high yield of III (>98%).

When the solvent is methanol, the charge transfer mechanism is no longer efficient for II*, and its lifetime is 236 ns, a value quite close to those typically observed in inert solvents.[12,13] Under high-intensity excitation conditions (laser-jet or laser-drop) a significant yield of ether VI was formed (see Table II). Meisel et al.[12] and later Arnold et al.[32] showed that II* can be further excited to II**. Meisel[12] suggested that II** may lose a hydrogen atom to form diphenylcarbene. In this case one would expect the carbene to insert into the OH bond of methanol to form ether VI. However, no deuterium incorporation in VI was detected under either laser-jet[17] or laser-drop excitation of precursors of II* in methanol-d_1. This suggests that the ether is formed by the nucleophilic trapping of the cation, II^+, by methanol. That this is the case is further supported by Steenken's report on the photoionization of aryl-substituted methyl radicals.[33,34]

Adam was also able to show that the ratio of products VI/III increased as a function of laser intensity when the laser-jet photolysis of XI was carried out in a 1:99 mixture of CCl_4 and methanol.[17] This, combined with Meisel's observation of irreversible photobleaching of II* in methanol, suggests that the formation of VI results from the successive absorption of three photons. Thus, we find that the photochemistry of I under laser-drop conditions parallels that observed by Adam[17] for XI under laser jet conditions. The origin of the products of laser-drop photolysis of I is outlined in Scheme I.

Ether VI accounted for 92% of the diphenylmethyl radical products under laser-drop irradiation of I, compared with 34% reported for the photolysis of XI under laser-jet conditions (see Table II). We note that the conversion of the 10 mM solution of starting material is similar for both laser-drop and laser-jet experiments, suggesting at least comparable efficiencies for both the laser-drop and laser-jet techniques in producing multiple-photon products. In fact, the conversion to three-photon products is much higher in the laser-drop technique, probably suggesting that this method should be preferred for processes requiring more than two photons. In this sense, the photolysis conditions are reminiscent of those encountered in laser ablation experiments.

The Cumyloxyl Radical System. Once it was established that the laser-drop technique was a viable method to induce multiple photon chemistry, we decided to explore the photochemistry of a new system, specifically of dicumyl peroxide. Photolysis of this peroxide yields two cumyloxyl radicals (VIII). These radicals undergo β-scission in the microsecond time scale to give acetophenone and methyl radicals. We were interested in establishing if a similar cleavage could occur from an excited state of the radical, reaction 3.



$$PhCMe_2O^\bullet \underset{h\nu}{\overset{k_\beta}{\rightleftharpoons}} PhCOCH_3 + CH_3^\bullet \qquad (3)$$

In order to carry out this experiment we decided to use a good hydrogen donor solvent, so that the spontaneous decay of the radical would not be dominated by β-scission. Methanol proved to be an adequate choice.

Radical VIII has suitable absorption properties for multiphoton work using the laser-drop method. Lusztyk et al.[23] estimated $\epsilon_{485} = 1300\ M^{-1}\ cm^{-1}$. From the spectrum of Figure 2 we estimate the extinction coefficient at 308 nm to be $\sim 1000\ M^{-1}\ cm^{-1}$. In contrast, the extinction coefficient of the peroxide precursor is $\epsilon_{308} \leq 5.7\ M^{-1}\ cm^{-1}$.

Our results show that the IX/X ratio changes dramatically when the irradiation method is changed from lamp to laser-drop irradiation. In particular, the relative yield of IX increases over 23-fold under laser-drop conditions. To the best of our knowledge, this is the first report on the photoinduced cleavage of alkoxyl radicals in solution.

In order for the laser-drop method to induce significant transient photochemistry, it is necessary that the transient in question compete favorably with its own precursor for the incident photons. This also requires that the transient be formed within the irradiation of the laser pulse ($\sim$6 ns in our case). Peroxides are believed to cleave from a dissociative state, implying that for practical purposes 0–0 cleavage occurs instantaneously.[35]

Given our earlier calculation indicating that transient concentration of up to 10^{-2} M can be achieved, it is surprising that only 10% conversion of a 10 mM solution was achieved after five irradiation cycles (*vide supra*). This is due to the very low absorption of the peroxide at the laser wavelength. Scheme II shows the main reaction paths taking place in the laser-drop photolysis of dicumyl peroxide. The photocleavage of cumyloxyl

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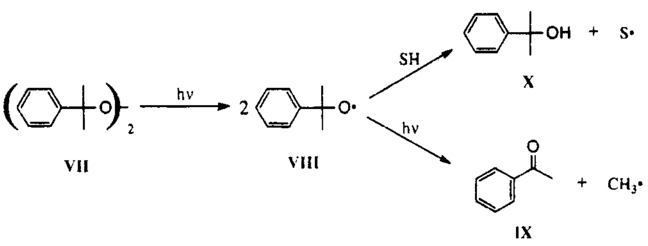
(32) Arnold, B. R.; Scaiano, J. C.; McGimpsey, W. G. *J. Am. Chem. Soc.* **1992**, *114*, 9978.

(33) Faria, J. L.; Steenken, S. *J. Am. Chem. Soc.* **1990**, *112*, 1277.

(34) Indeed other types of radicals, such as Ph_2COH, also undergo electron photoejection upon photolysis in polar solvents.[15]

(35) Scaiano, J. C.; Wubbels, G. G. *J. Am. Chem. Soc.* **1981**, *103*, 640.

Scheme II



radicals parallels the cleavage of α,α-dialkoxylbenzyl radicals recently reported by us[10] and studied previously by Fischer et al.[36,37]

Conclusion

The laser-drop and laser-jet techniques offer similar, if certainly not identical, capabilities for the preparation of multiphoton products. One may wonder if there is an obvious reason why one or the other should be preferred. The most obvious answer is that the choice should reflect the availability of lasers on-site. Given an available laser, the cost of either technique is minimal compared with the cost of the lasers. We feel this should be the main reason for choice.

We have already indicated that for multiphoton processes to occur the intermediates must be produced within the duration of the laser pulse. If the drop survives more than $\sim$100 ns after excitation, then the laser-drop technique offers the possibility of overcoming this problem by employing two laser pulses in sequence, in much the same way in which they are employed in the two-laser two-color technique.[1] Naturally, this would also allow the possibility of using two different laser wavelengths.

In summary, the laser-drop technique offers the possibility of carrying out preparative multiphoton chemistry in a simple way with equipment readily available in laboratories that routinely carry out laser flash photolysis experiments. Our results for the diphenylmethyl radical system are in line with those reported using the laser-jet technique. In the case of cumyloxyl radicals, we have demonstrated for the first time efficient β-photocleavage of this radical.

Experimental Section

Materials. 1,1-Diphenylacetone (I) and dicumyl peroxide (VII) were recrystallized twice from methanol. All solvents were spectral grade (BDH, Omnisolv) and used as received.

General Techniques. UV–visible spectra were recorded on a Hewlett-Packard Model 8451 diode array spectrometer. Products of photolysis of I were identified by GC-MS, and quantified with a Perkin-Elmer Model 8320 capillary gas chromatograph equipped with a DB-5 bonded phase column of 15-m length (from J&W Scientific) employing 1,4-di-*tert*-butylbenzene as an internal standard.

Products from the photolysis of VII were identified by HPLC (Varian 9010 pump with Model 9065 autosampler, and a Model 9090 diode array detector interfaced to a 386 computer equipped with Star Workstation software) employing a 25-cm Techsphil C-18 column. Products were identified against authentic samples and benzene was used as an internal standard; we estimate analytical errors at $<5\%$.

Low-Intensity Photolysis. Irradiations were carried out in 7 × 7 mm^2 cells made from Suprasil quartz tubing. The samples were deaerated by purging with a slow stream of nitrogen for 20 min. They were irradiated in a reactor equipped with nine RPR-300 lamps. The temperature of the irradiation chamber was in the 30–35 °C range.

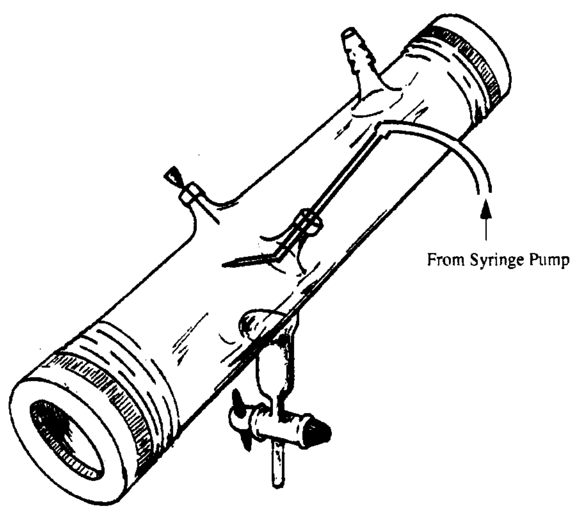


Figure 3. Outline of the cell employed for laser-drop experiments. The overall length is 12 in. and the cell is equipped with removable quartz windows.

Laser-Drop Irradiations. The beam from a Lumonics EX-530 excimer laser (Xe/HCl/Ne, 308 nm, $\sim$6 ns, 80–130 mJ/pulse) was focussed by means of a quartz lens ($F = 200$ mm) onto a drop of a solution suspended from the tip of a 6-in. syringe needle (20 gauge). The flow rate of the solution was controlled by a Sage Instruments Model 355 syringe pump. Shortly before the drop would fall spontaneously as a result of its increasing weight, it is irradiated by one laser pulse, which causes it to disintegrate into smaller droplets and a mist which are collected at the walls of the irradiation cell. With the laser-induced removal of the irradiated drop, a new drop starts to form. The size of the drop can be controlled by either changing the repetition rate of the laser or changing the flow rate of the syringe drive. We found it best to run the laser at a constant repetition rate (usually 1–5 Hz) and to adjust the flow rate with the syringe pump controller, so that the drop would be slightly bigger than the area excited by the laser. The irradiation cell was constructed from an Ace Glass Ltd. photochemical cell (12 in. in length and 50 mm in diameter, with removable quartz windows at both ends). Two septa inlets were placed near the top, in the center of the cell, to insert the solution input needle and the inert gas relief needle. A gas inlet was placed at the top of the cell near the front window. The input needle was bent at $\sim$135° so that the end was horizontal. Figure 3 shows a schematic display of the irradiation setup. Losses of solution during handling and irradiation are similar to those of the laser jet technique. Typical loses after several cycles are usually in the 10–20% range. *Caution: These irradiations must be carried out in an inert atmosphere. If the laser beam hits the tip of the syringe air-saturated mixtures can explode readily. At least one rubber septum must be employed in the cell to provide a safety pressure release should these precautions fail.* Finally, the long cell design of Figure 3 is important so that the windows are located away from the focal point of the laser beam. When this is not the case, repetitive irradiation causes ablation of the quartz windows and eventually leads to perforations. Ablation of quartz with concentrated laser beams is not unprecedented.[19]

Laser Flash Photolysis. These experiments were carried out using a Lumonics EX-510 excimer laser operated with Xe/HCl/He mixtures (308 nm, $\sim$6 ns, $\leq$60 mJ/pulse). Transient signals were captured with a Tektronix-2440 digital scope which was interfaced to a Macintosh IIci computer which also controlled the experiment. The system was operated under LabVIEW 2.2 software from National Instruments. Other aspects of this instrument are similar to those described earlier.[13,38]

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(36) Jent, F.; Paul, H.; Fischer, H. *Chem. Phys. Lett.* **1988**, *146*, 315.

(37) Fischer, H.; Baer, R.; Hany, R.; Verhoolen, I.; Walbiner, M. *J. Chem. Soc., Perkin Trans. 2* **1990**, 787.

(38) Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747.