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Multiple-Photon Chemistry in the Laser-Jet: Photochemistry and Time-Resolved Laser-Flash Spectroscopy of the 1-Naphthylmethyl Radical

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In the laser-jet (LJ) photolysis (λ_{exc} 333, 351, and 364 nm, high intensity) of 1-[(4-benzoylphenoxy)methyl]naphthalene (**1**), a two-photon process is observed in CCl_4 to yield 1-(chloromethyl)naphthalene (**3a**) as the main product, while the one-photon products of the conventional photolysis (low intensity) are 1,2-di(1-naphthyl)ethane (**2**), 1,1,1-trichloro-2-(1-naphthyl)ethane (**3b**), and 1-naphthaldehyde (**5**). In MeOH or EtOH, however, our results suggest even a three-photon reaction in which 1-naphthylmethyl methyl ether (**4c**) and 1-naphthylmethyl ethyl ether (**4b**) are produced in addition to the one-photon product **2**. The three-photon mechanism is based on a competition experiment in which ether **1** was irradiated in mixtures of CCl_4 and methanol. The ratio of the two high-intensity products ether **4c** and 1-(chloromethyl)naphthalene (**3a**) showed a strong intensity dependence. We propose that the electronically excited 1-naphthylmethyl radical **1-NpCH$_2^{\bullet *}$** is photochemically ionized to 1-naphthylmethyl cation **1-NpCH$_2^{+}$** under the high-intensity LJ photolysis conditions and the latter trapped by the respective alcohols to give the 1-naphthylmethyl ethers **4c** and **4b**. With the help of time-resolved laser flash photolysis (248 nm) of 1-[(4-benzoylphenoxy)methyl]naphthalene (**1**), it was established that homolysis of the C−O bond to yield 1-naphthylmethyl (**1-NpCH$_2^{\bullet}$**) and 4-benzoylphenoxy (**ArO$^{\bullet}$**) radicals takes place. The authentic **1-NpCH$_2^{\bullet}$** and **ArO$^{\bullet}$** radicals were generated independently by pulse radiolysis of 1-(bromomethyl)- or 1-(chloromethyl)naphthalene in 2-propanol and of 4-hydroxybenzophenone (**6**) in water (1% *t*BuOH); in the latter case, $SO_4^{\bullet -}$ was used as oxidant. In the LJ photolysis, the triplet state of the 1-naphthylmethyl moiety is probably further excited to yield the observed products.

Introduction

The 1-naphthylmethyl radical (**1-NpCH$_2^{\bullet}$**) has been the subject of recent photophysical and photochemical studies.[1−6] Thus, its first excited state **1-NpCH$_2^{\bullet *}$** can be generated upon pulsed-laser photolyses with 337-nm light.[1] While the ground-state radical **1-NpCH$_2^{\bullet}$** has a strong, sharp band at 365 nm,[1,2] the electronically excited radical **1-NpCH$_2^{\bullet *}$** exhibits an absorption at 430 nm.[1] Furthermore, upon irradiation of arylmethyl derivatives with two pulsed lasers (two-color experiments), excited arylmethyl radicals and even aryl cations were detected by UV spectroscopy.[7] The fluorescence from **1-NpCH$_2^{\bullet *}$** has been reported by Rentzepis *et al.*,[3,4] who used this property to monitor the formation of the ground-state radical in the photochemistry of (halomethyl)naphthalenes. **1-NpCH$_2^{\bullet *}$** was reported to have a lifetime of 13 ± 3 ns in hexane at room temperature and to fluoresce at a λ_{max} of ca. 600 nm. Scaiano[1] explored the reactivity of **1-NpCH$_2^{\bullet *}$** in CCl_4 and showed that it does not abstract a chlorine atom nearly as well as the excited diphenylmethyl radical. In fact, the excited **1-NpCH$_2^{\bullet *}$** radical was found to be an excellent electron donor toward the efficient electron acceptor methylviologen.

The ground-state **1-NpCH$_2^{\bullet}$** radical is an ideal substrate for laser-jet experiments since its absorption characteristics match optimally the available lines of the argon ion laser (333, 351, 364 nm). Furthermore, the lifetime of the excited **1-NpCH$_2^{\bullet *}$** radical is about 35 ns in methanol,[1] which fulfills the requisite to be sufficiently long-lived for further electronic excitation under the high-intensity LJ conditions.[8]

We report herein results on the products formed from the excited **1-NpCH$_2^{\bullet *}$** radical, namely the 1-naphthylmethyl cation (**1-NpCH$_2^{+}$**), in the laser-jet photolysis of 1-[(4-benzoylphenoxy)methyl]naphthalene (**1**). Furthermore, we present spectral evidence for **1-NpCH$_2^{\bullet}$** by time-resolved laser-flash spectroscopy of the ether **1** and the generation of the 4-benzoylphenoxy radical (**ArO$^{\bullet}$**) by pulse radiolysis of 4-hydroxybenzophenone. In this study, we demonstrate that the LJ mode of operation constitutes a valuable complementary technique for the time-resolved laser flash photolysis with pulsed lasers and pulse radiolysis by making available for the first time quantitative product data.

Results

Product Studies and Control Experiments of the Laser-Jet and Conventional Laser Photolyses. The

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Scheme 1. Products of Photolyses of the Naphthyl Ether 1 in Various Solvents

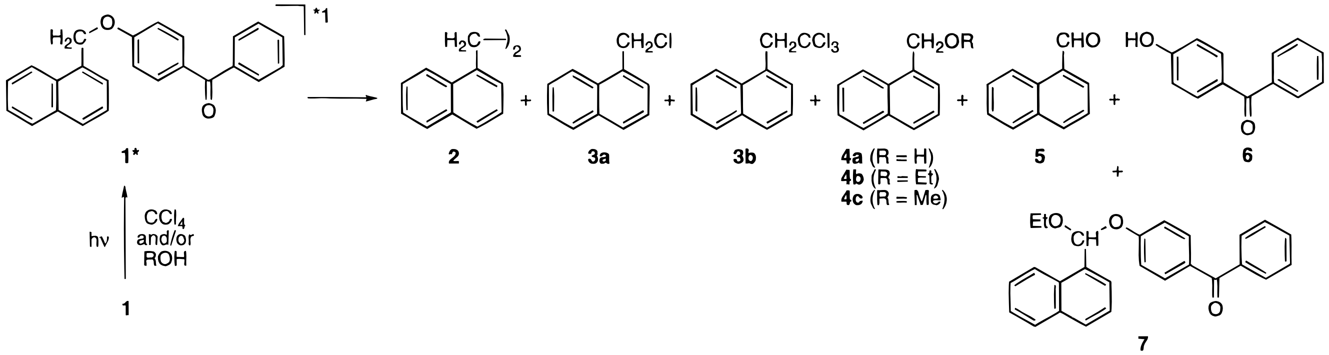

Table 1. Product Studies of the Conventional (Low Intensity) and Laser-Jet (High Intensity) Photolyses of Naphthyl Ether 1 in Carbon Tetrachloride and in Ethanol

				product distribution[a,b] (%)						
mode	solvent	convn[a] (%)	mb[a] (%)	**2**	**3a**	**3b**	**4a**	**4b**	**5**	**7**
laser, widened beam[c]	CCl_4	9	76	29		13	10		48	
laser, widened beam[d]	CCl_4/EtOH (10:1)	11	81	27		18	traces		traces	54
laser-jet[e]	CCl_4	22	77		26	3	3		68	
laser, widened beam[f]	EtOH	23	88	100			traces	traces		
laser-jet[g]	EtOH	16	78	46			traces	54		

[a] Conversion (convn) of ether **1**, mass balance (mb) of products, and product distribution were determined by ^{1}H NMR spectroscopy, error 5% of stated value; benzoylphenoxy-derived products are not listed; ketone **6** was formed quanititatively. [b] Normalized to 100%. [c] $c = 2.94 \times 10^{-3}$ M, all UV lines (333, 351, and 364 nm), 3.0 W, 5 min. [d] $c = 2.94 \times 10^{-3}$ M, all UV lines (333, 351, and 364 nm), 3.0 W, 10 min. [e] $c = 2.94 \times 10^{-3}$ M, 100-μm capillary, flow rate of 1.2 mL/min, all UV lines (333, 351, and 364 nm), 4.3 W, 1 cycle. [f] $c = 2.94 \times 10^{-3}$ M, all UV lines (333, 351, and 364 nm), 3.0 W, 15 min. [g] $c = 2.94 \times 10^{-3}$ M, 100-μm capillary, flow rate of 1.2 mL/min, all UV lines (333, 351, and 364 nm), 4.2 W, 1 cycle.

photolysis products, which are derived mainly from the naphthylmethyl (**1-NpCH$_2^•$**) and the 4-benzoylphenoxy (**ArO$^•$**) radicals generated on CO homolysis of ether **1** (*vide infra*), are outlined in Scheme 1 and the product studies in Table 1. On photolysis of the ether **1** in CCl_4 as solvent, the following products were observed: the dimer **2**, the chlorides **3a** and **3b**, the alcohol **4a**, and the aldehyde **5**. A strong dependence of the product distribution was found on the light intensity for the dimer **2** and 1-(chloromethyl)naphthalene (**3a**). The dimer **2** was formed at the low intensity of the conventional photolysis (Table 1, entry 1) but not at the high intensity of the LJ photolysis experiment (Table 1, entry 3), while the chloro derivative **3a** was absent at the low but appreciable amounts were found at the high intensities. These results indicate that multiple-photon chemistry is operating under the laser-jet conditions (high intensity). The remaining products in CCl_4, namely chloride **3b**, alcohol **4a**, and aldehyde **5**, were observed both under the low- as well as high-intensity conditions but were formed in different amounts (Table 1, entries 1 and 3). Hexachloroethane was detected by GC analysis of ether **1** photolysate in CCl_4 both at the low and the high light intensities.

When the conventional photolysis of ether **1** was conducted in a 10:1 mixture of CCl_4 and ethanol (Table 1, entry 2), only traces of the aldehyde **5** were observed, but the acetal **7** (54% yield) was detected as new product and spectrally characterized. Unfortunately, all efforts to isolate the hydrolytically labile acetal **7** by chromatographic techniques failed.

To assess the origin of the aldehyde **5**, the major product under both the low- and high-intensity conditions, the potential influence of molecular oxygen was checked by photolyzing the ether **1** under the low-intensity conditions in CCl_4 solutions saturated with oxygen gas or rigorously degassed (three freeze−pump−thaw cycles) with argon gas. Unfortunately, molecular oxygen efficiently quenches the photolysis as evidenced by less than 3% conversion, so that no definitive answer was acquired in this experiment. Also, the possible hydrolysis of the chloride **3a** to its alcohol **4a** and subsequent oxidation to the aldehyde **5** was excluded by control experiments. However, evidence that electron-transfer chemistry may be responsible for the formation of aldehyde **5** was obtained by treating ether **1** with the chemical one-electron oxidant bis(4-bromophenyl)(2,4-dibromophenyl)aminium hexachloroantimonate, known as "Magic Green" (E_0 = 1.42 V),[9] in $CDCl_3$ and a dry argon gas atmosphere. At 20% conversion, the aldehyde **5** was the exclusive naphthalene-derived product besides 4-hydroxybenzophenone (**6**).

In ethanol solution, the product composition for the photolysis of ether **1** is considerably simpler (Table 1, entries 4 and 5) than in CCl_4. Now the dimer **2** is formed under low- as well as high-intensity conditions. It is essentially the only product in the conventional photolysis (Table 1, entry 4), while in the LJ experiment the ether **4b** is formed as the major product (Table 1, entry 5). The latter is observed only in traces during irradiation at low intensities of the widened laser beam (Table 1, entry 4). Ketone **6** was formed quantitatively (relative to the extent of conversion), independent of the solvent and the light intensity used.

Of mechanistic relevance in the LJ photolysis is the influence of the light intensity on the product distribution as a function of the laser power (Table 2). In a 1:4 mixture of CCl_4 and MeOH, the ratio of 1-naphthylmethyl methyl ether (**4c**) *versus* 1-(chloromethyl)naphthalene (**3a**) increases with laser power. Again, this implies multiple-photon chemistry.

Since in the CCl_4/MeOH solvent mixture the methyl

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Table 2. Laser-Jet Photolyses of Naphthyl Ether 1 in a 1:4 Mixture of Carbon Tetrachloride and Methanol

entry	laser power[a] (W)	product ratio[b] **4c/3a**
1	3.0	1.9
2	3.5	3.4
3	4.0	4.6

[a] $c = 3.00 \times 10^{-3}$ M, 100-μm capillary, flow rate of 1.0 mL/min, all UV lines (333, 351, and 364 nm), 1 cycle. [b] ^{1}H NMR spectroscopy, error 5% of stated value.

ether **4c** may arise also from methanolysis in the dark or photosensitized methanolysis of 1-(chloromethyl)naphthalene (**3a**) produced from the ether **1**, it was necessary to run control experiments in the laser-jet photolyses. Fortunately, the methanolysis of 1-(chloromethyl)naphthalene (**3a**) in the dark and the photolysis of a 1:1 mixture of the ether **1** and 1-(chloromethyl)naphthalene (**3a**) gave only low amounts (ca. 3%) of the 1-naphthylmethyl methyl ether (**4c**) product.

Time-Resolved Spectral Studies of the Transients by Laser-Flash Photolysis and Pulse-Radiolysis and Control Experiments. On photolysis of a deoxygenated 0.2 mM solution of ether **1** in acetonitrile with the 20-ns pulses of 248-nm laser light, a spectrum was observed after the pulse that was characterized by peaks at ca. 241, 336, 366, 395, and 419 nm and a broad absorption between 450 and 700 nm (see Figure 1). In the 280−310 nm region, in which the ether **1** possesses a strong absorption band, the optical density decreased (negative ΔOD) immediately after the excitation pulse. Thereafter, the negative signal partly decreased (which is assigned to the recovery of the ground-state parent ether **1** by the decay of its triplet), with a rate similar to that of the decay of the positive signals at 241, 395, or 419 nm (see below).

Whereas the peaks at 241, 395, and 419 nm were fully developed after the excitation pulse and started to decrease in intensity thereafter, those at 336 and 366 nm showed “delayed” formation, which extended over 100 ns ($k \approx 2 \times 10^7$ s^{-1}).[10] The decay of the absorptions at 241, 395, and 419 nm and the recovery of the absorption at 280−310 nm followed a first-order rate law with about equal rates ($k \approx 7 \times 10^5$ s^{-1}). In contrast, the decays at 336 and 366 nm followed second-order kinetics. When O_2 was admitted to the solution, at all wavelengths the decay of the transient absorptions was accelerated, from which it may be concluded that the transient species have radical or triplet character. The rate constant for quenching of the ether **1** triplet by O_2 was determined as 2×10^9 M^{-1} s^{-1}, a value that is characteristic for reaction of triplet ketones.

Solutions of the ether **1** in acetonitrile were also photolyzed at 308 nm, and the spectrum observed was the same as that with 248-nm light, except for the peaks at 336 and 366 nm, which were absent. The decay rates at 241, 395, and 419 nm and those for the recovery at 280−310 nm were the same as on excitation at 248 nm. At 10−20 μs after the 308-nm pulse, all the absorption changes had essentially disappeared and the recovery of parent as monitored at 280−310 nm was more or less quantitative, which indicates that the effects of excitation with 308-nm light are to a large extent reversible, in contrast to excitation with 248-nm light.

To identify the transients produced from ether **1**, the model compounds 1-methylnaphthalene, 1-(hydroxymethyl)naphthalene (**4a**), and 1-(ethoxymethyl)naphthalene (**4b**) were studied. Instead of bond homolysis to radical products, these compounds are expected to generate triplet states on irradiation. With acetonitrile as solvent, in all cases spectra were observed characterized by peaks at ca. 240, 395, and 420 nm with depletion of the OD at 290 nm, at which the parent compounds absorb. The transients could be effectively quenched by O_2 with quantitative recovery of the starting material. These observations are interpreted in terms of formation of the triplet states of these naphthalene derivatives, followed by relaxation (with or without O_2) to the respective ground states (eq 1). Therefore, by analogy it is concluded that in the case of ether **1** the peaks at 241, 395, and 419 nm are due to the triplet of ether **1**, an assignment that is in agreement with the known spectrum of the unsubstituted naphthalene triplet.[11a] In this respect, it is interesting that even immediately after the pulse (20 ns) there was no evidence for the triplet of the benzophenone chromophore in the ether **1**, although this moiety also absorbs light at 248 or 308 nm. This indicates rapid ($k \geq 5 \times 10^7$ s^{-1}) and efficient intramolecular energy transfer from the benzophenone to the naphthalene moiety. Such intramolecular energy migration is expected to be energetically downhill, since for comparison, the triplet energy (E_T) of 4-methoxybenzophenone is 64.9 kcal/mol[12] *versus* 60.8 kcal/mol[13−16] for 1-methylnaphthalene.

$$\mathrm{Np(S_0)} \xrightarrow{h\nu} \mathrm{Np(S_1)} \xrightarrow{<20\ \mathrm{ns}} \mathrm{Np(T_1)} \rightarrow \mathrm{Np(S_0)} \qquad (1)$$

To identify the peaks at 336 and 366 nm observed on photolysis of ether **1** at 248 nm, 1-(bromomethyl)naphthalene in acetonitrile was photolyzed. The spectrum observed at the end of the pulse showed depletion at 290 nm and peaks at 337 and 366 nm, but none at 395 or ca. 420 nm and only very weak absorption at ca. 240 nm. These results are explained in terms of 1-naphthylmethyl radical (**1-NpCH$_2^\bullet$**) formation by photoinduced homolysis of the C−Br bond. The identification of the radical was confirmed by producing the **1-NpCH$_2^\bullet$** radical in an alternative way, i.e., by allowing 1-NpCH$_2$Br or 1-NpCH$_2$Cl in 2-propanol as solvent to react with radiation-chemically generated solvated electrons. As expected, the observed spectrum was independent of the nature of the halogen and displayed the same peaks as in the case of the photolyses. The 336- and 366-nm peaks obtained in the 248-nm photolysis of ether **1** are, therefore, due to the **1-NpCH$_2^\bullet$** radical generated under these conditions. Consequently, in addition to triplet formation, the 248-nm photolysis of ether **1** also leads to C−O bond homolysis to afford the naphthylmethyl and phenoxy radicals. By measuring the optical density at 336 nm as a function

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(10) The “delayed” formation of the absorption in the wavelength range 310−380 nm (see Figure 1) is an artifact, caused by the decay of the fluorescence of the naphthalene moiety ($k \approx 2 \times 10^7$ s^{-1}) in this region.

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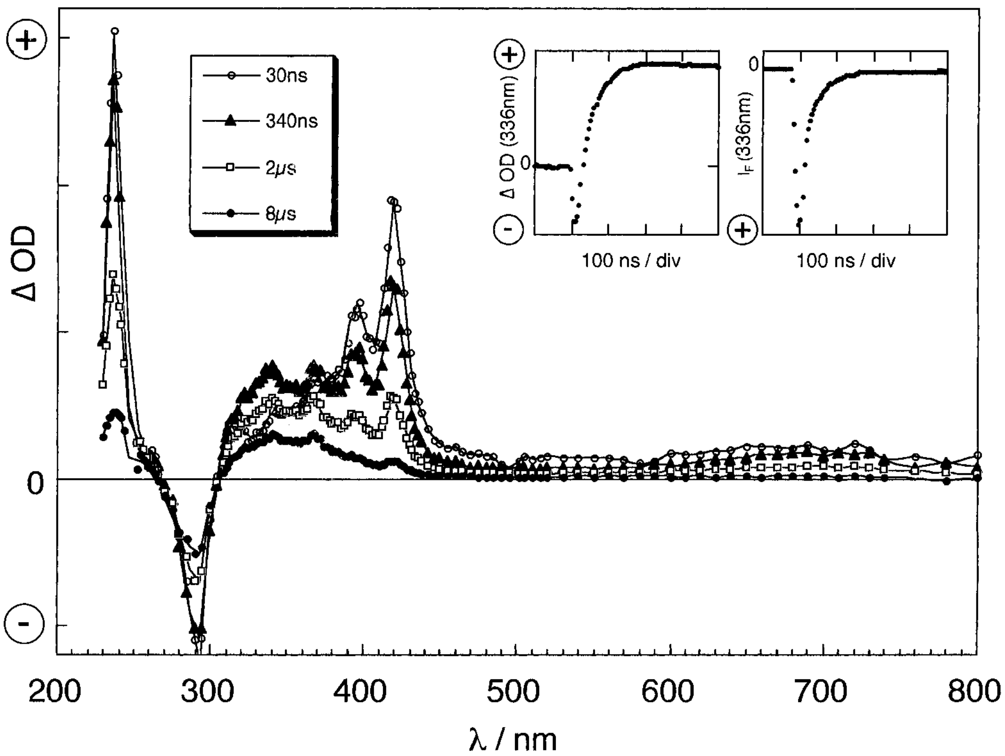

Figure 1. Time-resolved absorption spectra observed on 248-nm photolysis of a deoxygenated 0.14 mM solution of ether **1** in acetonitrile. Spectra recorded at 30 ns, 340 ns, 2 μs, and 8 μs after the 20-ns pulse. In the insets contain kinetic traces that show the apparent buildup of OD (left trace) and the decay of fluorescence (right trace) at 336 nm. The peaks at 336 and 366 nm (maximum OD reached at 340 ns after the pulse) are due to the **1-NpCH$_2$$^•$** radical and those at 241, 395, and 419 nm to the triplet of ether **1**.

of laser power, it was found that the formation of the 1-naphthylmethyl radical (**1-NpCH$_2$$^•$**) from ether **1** requires only one photon.

The question arises whether C−O homolysis occurs exclusively from the excited singlet state or whether the triplet state is also a precursor to the radicals. On the basis of the results obtained in the 308-nm excitation, for which only the triplet state was seen without radical formation during its decay, the answer is that C−O bond cleavage does *not* occur from the triplet state of ether **1**. This observation appears to be in agreement with the thermochemistry of the process since the triplet energy of the naphthalene chromophore is 60.8 kcal/mol, while C−O bond homolysis requires 68 kcal/mol (not considering the stabilization energy of **1-NpCH$_2$$^•$**).

If the naphthylmethyl radical (**1-NpCH$_2$$^•$**) is formed, the PhC(O)C$_6$H$_4$O$^•$ (**ArO$^•$**) radical is produced as partner. To obtain spectral data on the authentic **ArO$^•$**, this radical was produced independently by allowing radiation-chemically generated $SO_4^{•-}$ to react with 4-hydroxybenzophenone, for which the pulse radiolysis technique was employed (0.4 mM 4-hydroxybenzophenone, 20 mM $S_2O_8^{2-}$, and 0.1 M 2-methyl-2-propanol in aqueous solution). Under these conditions, the hydrated electrons produced in the pulse radiolysis are scavenged by $S_2O_8^{2-}$ to yield the strongly oxidizing species $SO_4^{•-}$, while the hydroxyl radicals (derived from the radiolysis of water) are intercepted by 2-methyl-2-propanol to give the inert and invisible $(CH_3)_2C(OH)CH_2^•$ radicals. Subsequently, the $SO_4^{•-}$ oxidant reacts with the phenol (**ArOH**) to give the corresponding phenoxyl radical (eq 2), for which the

$$SO_4^{•-} + PhC(O)C_6H_4OH \rightarrow HSO_4^{-} + PhC(O)C_6H_4O^{•} \qquad (2)$$

observed absorption spectrum consisted of a symmetric peak centered at 395 nm ($\epsilon_{395\ nm}$ = 1550 M^{-1} cm^{-1}). In addition, uncharacteristic absorption was exhibited at higher wavelengths, which extended beyond 700 nm. As expected for a phenoxyl-type radical, there was only a low reactivity with O_2. On inspection of the absorption spectrum recorded in the photolysis of ether **1** (see Figure 1), there is no definitive evidence for the phenoxyl radical **ArO$^•$**. This is probably due the low ϵ of **ArO$^•$** (see above) and the severe spectral overlap in the 390-nm region with the strong 395-nm band of the naphthalene triplet and also with that of the 1-naphthyl-methyl radical (366 nm).

As a further naphthylmethyl derivative, the ether 1-NpCH$_2$OPh was studied. On 248-nm photolysis in CH$_3$CN, its triplet state (λ_{max} at ca. 240, 400, and 420 nm) and the 1-naphthylmethyl radical (**1-NpCH$_2$$^•$**) were seen. The formation of the **1-NpCH$_2$$^•$** radical required one photon; thus, the 1-NpCH$_2$OPh ether undergoes the same type of photochemistry as does the ether **1**. For the model ether, the ratio of optical densities (at 420 nm) of the triplet state *versus* the naphthylmethyl radical (at 335 nm) was somewhat lower than for ether **1**.

Mechanistic Discussion

As shown in the time-resolved laser-flash photolysis (Scheme 2), the singlet excited ether **1*** suffers C−O bond homolysis (path a) to afford the 1-naphthylmethyl (**1-NpCH$_2$$^•$**) and aryloxy (ArO$^•$) radicals. Under the conditions of LJ photolysis, it is likely that the additional pathways b and c (Scheme 2) for C−O bond homolysis operate, which involve the triplet state of ether **1** on the absorption of further photons. As seen from Table 3, the extinction coefficients of the chromophore components of

Scheme 2. Photolysis Pathways of Ether 1 by Time-Resolved Transient Spectroscopy

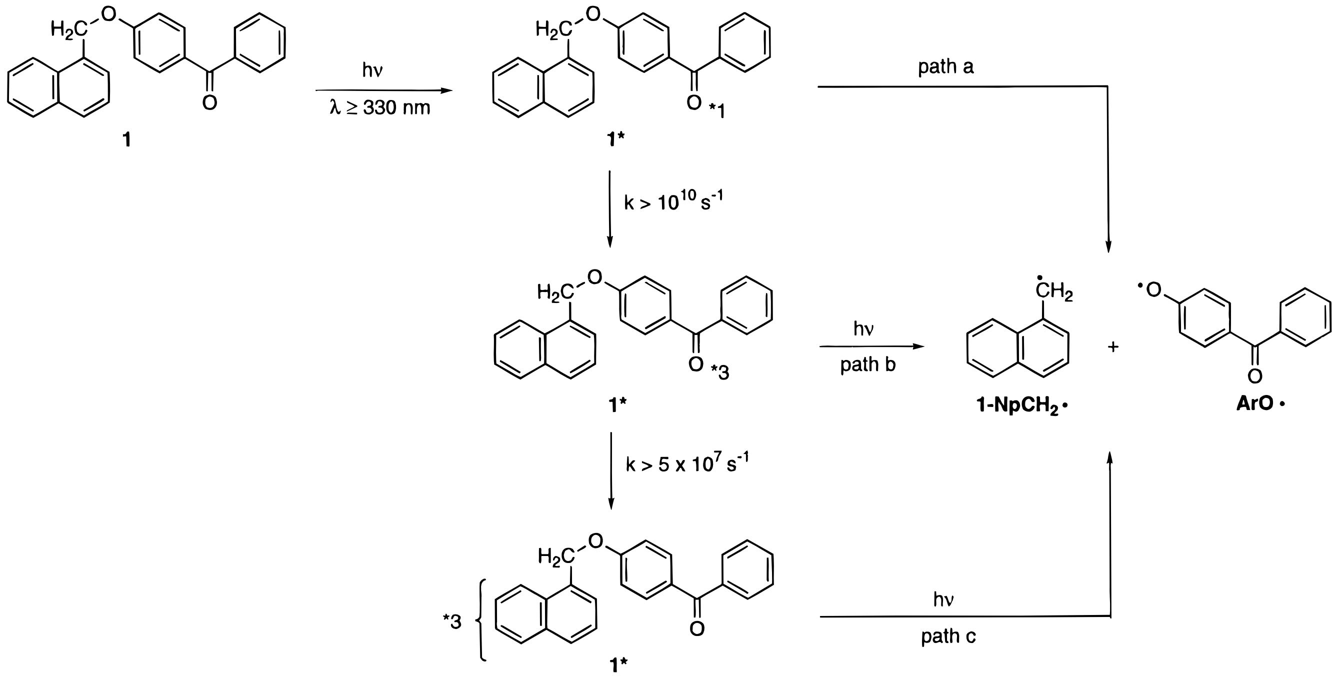

Table 3. Molecular Extinction Coefficients of the Ether 1 and of Its Chromophore Components

molecular extinction coefficients (log ε)[a] λ (nm)	**1**	**6**	benzophenone	**4a**
248	3.31	3.76	4.19	3.08
308	3.07	3.52	2.01	2.86
333	2.50	2.80	2.47	b
351	2.12	2.70	2.08	b
364	1.54	2.58	1.78	b

[a] In acetonitrile. [b] $\epsilon \leq 10^{-1}$ cm^2 mol^{-1}.

the ether **1**, i.e., 4-hydroxybenzophenone (**6**) and 1-(hydroxymethyl)naphthalene (**4a**), are such that at $\lambda \geq 333$ nm essentially all the light is absorbed by the benzophenone chromophore. As is evident from the time-resolved experiments, in a period of 20 ns the excitation energy is funneled into producing the triplet state of the naphthalene moiety. This triplet state has absorptions at the emission wavelengths of the argon ion laser (see Figure 1) and is, thus, subject to further excitation, and C−O homolysis becomes feasible. As to the chemical fate of **1-NpCH$_2^{\bullet}$**, in the low-intensity experiments under conventional laser photolysis in CCl_4 as solvent, the expected ground-state reaction of the **1-NpCH$_2^{\bullet}$** radical is its dimerization to the hydrocarbon **2** (Scheme 3, path a). Furthermore, the halogenated product **3b** derives from coupling of **1-NpCH$_2^{\bullet}$** with trichloromethyl radicals. As to the source of the latter, they certainly do not derive from the photolysis of CCl_4 under the widened laser beam (low intensity) and laser-jet (high intensity) conditions, since control experiments confirmed that CCl_4 is photostable under these conditions. Their generation appears to be connected with the formation of 1-naphthaldehyde (**5**) and the 1-naphthylmethyl alcohol (**4a**), which shall be discussed later on in that context.

In contrast to the usual radical reactions observed in the conventional photochemistry, for the high-intensity photolysis, novel phototransformations of the intermediary 1-naphthylmethyl radical (**1-NpCH$_2^{\bullet}$**) can be witnessed, which suggest multiple-photon processes. Thus, in the LJ photolysis (Scheme 3, path b), 1-(chloromethyl)naphthalene (**3a**) is observed exclusively as the multiple-photon product of ether **1** in CCl_4 (Table 1, entry 3), rather than the dimer **2** (Scheme 3, path a), the single-photon product of the conventional photolysis (Table 1, entry 1). This underscores the efficiency of the LJ technique for such multiple-photon reactions so that high conversions can be achieved to afford sufficient multiple-photon product for isolation and complete characterization.

To rationalize the novel laser-jet results, we recall the fact that in the pulse radiolysis of 1-(bromomethyl)naphthalene, the authentic **1-NpCH$_2^{\bullet}$** radical is conveniently generated, as spectroscopically confirmed herein. This radical shows high absorption in the region of the emission wavelengths of the argon ion laser (λ_{max} at 333, 351, and 364 nm); therefore, the formation of the excited **1-NpCH$_2^{\bullet *}$** radical in the laser-jet photolysis is very likely. In Scaiano's[1] time-resolved laser flash photolyses it was reported that the excited **1-NpCH$_2^{\bullet *}$** radical is quenched by CCl_4 with a rate constant k_q of ca. 4×10^6 M^{-1} s^{-1}, and its lifetime was estimated to be ca. 15 ns. The propensity of the excited **1-NpCH$_2^{\bullet *}$** radical to engage in electron-transfer reactions was shown by its quenching with methyl viologen.[1] Consequently, in analogy to our previous LJ studies[17] on the benzhydryl radical, for which chlorine abstraction was rationalized in terms of electron transfer between the excited benzhydryl radical and CCl_4,[18,19] we propose a similar pathway (Scheme 3) for the formation of 1-(chloromethyl)naphthalene (**3a**) in the LJ photolysis of ether **1** in CCl_4.

To explain the formation of the 1-naphthaldehyde (**5**), the major product both for the conventional and laser-jet photolyses in CCl_4 (Table 1, entries 1 and 3), we propose the electron-transfer mechanism in Scheme 4.

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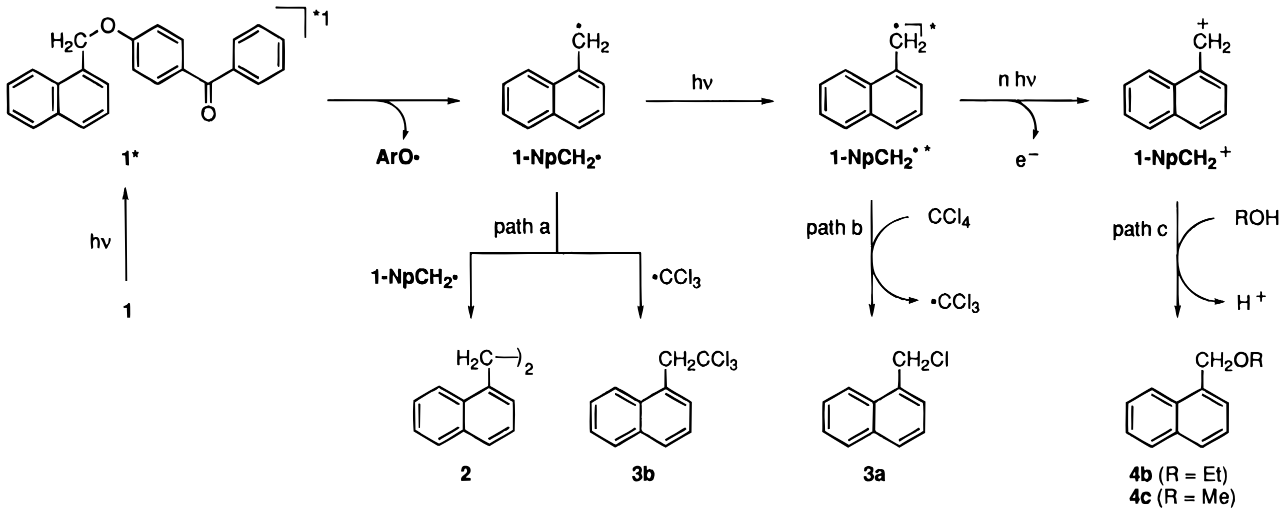
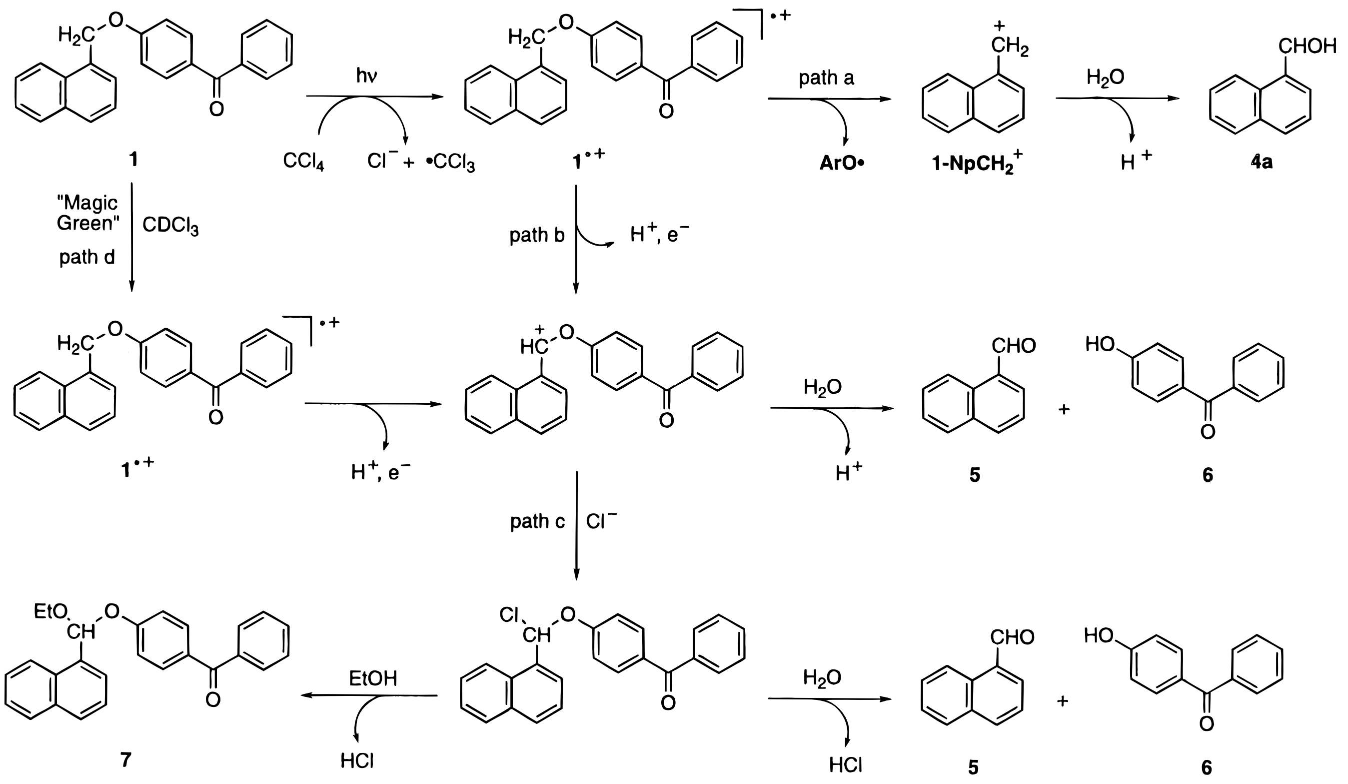
(19) However, as shown in ref 7, the free, fully solvated benzhydryl cation is not formed in the reaction of the excited benzhydryl radical with CCl_4.

Scheme 3. Product Formation in the Ground State and Multiple-Photon Chemistry of the 1-Naphthylmethyl Radical (1-NpCh₂⊙) in CCl₄ and Alcohols



Scheme 4. Mechanism for the Formation of 1-Naphthylmethyl Alcohol (4a) and 1-Naphthaldehyde (5) by Photoinduced and Chemical Electron-Transfer Oxidation of Ether 1



Thus, in competition with the C−O bond homolysis, the electronically excited ether **1*** is suggested to engage in electron transfer with CCl_4 to produce the radical cation $\mathbf{1}^{\bullet+}$ (ionization of the electron-rich naphthalene π system) and the $CCl_4^{\bullet-}$ radical anion, the latter readily dissociates into chloride ions and trichloromethyl radicals.[14] The radical cation $\mathbf{1}^{\bullet+}$ is the precursor to the alcohol **4a** (Scheme 4, path a) by loss of the aryloxy radical **ArO**$^{\bullet}$ to afford the **1-NpCH₂**$^{+}$ cation and trapping of the latter by adventitious water. Similar behavior was reported for radical cations derived from bibenzyl derivatives in solution.[15]

As the major pathway (Scheme 4, path b), however, the radical cation $\mathbf{1}^{\cdot+}$ deprotonates (Cl^- may act as proton acceptor), and further oxidation to its cation, followed by Cl^- trapping, leads to the chloro ether. Hydrolysis of the latter affords the 1-naphthaldehyde (**5**) and the phenol **6**. A similar reaction pathway is known for the C−C bond cleavage of bibenzyl and methoxymethyl phenyl radical cations in aqueous solution.[15,16] The adventitious water does not derive from the CCl_4 because control experiments with rigorously dried CCl_4 and this solvent saturated with water did not influence the product distribution. The hydrolysis of the chloro ether takes place presumably during the workup (less than 5×10^{-2} μL of water are necessary) and the NMR analysis of the crude reaction mixture.

In support of this mechanism is the fact that the photolysis of ether **1** in a 10:1 mixture of CCl_4 and ethanol (Table 1, entry 2) yields the labile acetal **7** instead of the aldehyde **5** from trapping of the chloro ether by ethanol (Scheme 4, path c). The fact that the chemical oxidation of the ether **1** by "Magic Green" affords appreciable amounts of aldehyde **5** and phenol **6** (Scheme 4, path d) suggests that the proposed photo-induced electron-transfer process is feasible. Moreover, electronically excited naphthalenes are known to undergo readily electron transfer with a variety of electron acceptors.[11]

Be this as it may, our control experiments (cf. Results section) establish unequivocally that the aldehyde **5** does not stem from further oxidation of the alcohol **4a** or from reaction of the **1-NpCH$_2^•$** radical with molecular oxygen, while the $Cl_3C^•$ radicals are not merely photolysis products of CCl_4 but derived from $CCl_4^{•-}$ through photochemical electron transfer. Besides chloride **3b**, the second coupling product of the $Cl_3C^•$ radicals is hexachloroethane, which was found, like aldehyde **5**, in the low- as well as high-intensity photolyses.

The 1-naphthaldehyde (**5**) is also a major product in the laser-jet photolysis (Table 1, entry 3); in fact, its relative amount is even greater than in the conventional photolysis (Table 1, entry 1). This is not surprising because in the laser-jet operation it is more difficult to exclude adventitious water in view of the free-falling liquid jet. (cf., Supporting Information).

In alcohol as solvent, a different product composition is obtained for both the conventional as well as the laser-jet photolyses (Table 1, entries 4 and 5). Mechanistically significant is the fact that in both these photolysis modes no 1-naphthaldehyde (**5**) is observed. This underscores the fact that CCl_4 is essential for the photoinduced electron transfer of ether **1** (Scheme 4), while alcohols do not serve as effective acceptors.

The fate of the **1-NpCH$_2^•$** radicals in the laser-jet photolysis in ethanol is such that besides the conventional dimer **2**, equal amounts of the ethyl ether **4b** (Table 1, entry 5) are produced (Scheme 3, path c). Since electron transfer from the excited radical **1-NpCH$_2^{•*}$** to the alcohol, as in the case of CCl_4, is hardly feasible, analogous to our previous study on the benzhydryl radical,[17] we postulate that photoionization competes with dimerization of the **1-NpCH$_2^•$** radical to generate the **1-NpCH$_2^+$** cation. Subsequently, the latter is nucleophilically trapped by the alcohol (Scheme 3, path c). Such photoionization has been documented for other aryl-substituted methyl radicals.[7,20]

The mechanistically relevant question arises of whether the photoionization of **1-NpCH$_2^•$**, like the benzhydryl radical,[7,17] requires several photons. Indeed, the results of the competition experiment in Table 2 support also for the **1-NpCH$_2^•$** radical the multiple-photon pathway (Scheme 3). Thus, in the LJ photolysis of the ether **1** in a mixture of CCl_4 and MeOH, the product ratio of 1-(chloromethyl)naphthalene (**3a**) and 1-naphthylmethyl methyl ether (**4c**) depends on the laser intensity in that **4c** increases at the higher laser power (Table 2). Consequently, the excited radical **1-NpCH$_2^{•*}$** competes between photons (ionization) and CCl_4 (Cl transfer) so that at the higher photon densities photoionization of **1-NpCH$_2^{•*}$** proportionally increases and the ether **4c** is favored as multiple-photon product. Thus, the formation of the ethers **4b,c** in the LJ photolysis is overall at least a three-photon process: one photon is required to generate the **1-NpCH$_2^•$** radical by cleavage of the substrate ether **1** and at least two photons are necessary for photoionization of the **1-NpCH$_2^•$** radical (Scheme 2).

Finally, our present results show impressively how well time-resolved spectroscopy and laser-jet photolysis complement each other for the mechanistic elucidation of multiphoton processes. The former method offers valuable absorption spectra and lifetime data on the transient radical intermediates such as the **1-NpCH$_2^•$** radical studied herein, while the laser-jet technique makes accessible sufficient quanitities of multiple-photon products for isolation and identification of the radical products. Thus, the combination of the laser-jet product studies and time-resolved laser-flash spectroscopy constitutes a valuable mechanistic tool to study the photochemistry of photolytically generated transients in solution.

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Supporting Information Available: A listing of the Experimental Section (5 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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