The Neophyl-like Rearrangement of Alkoxyl Radicals Revisited: Laser Flash and Laser Drop Photolysis Studies of 1,1-Diphenylethoxyl Radicals

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The radical 1,1-diphenylethoxyl (III) has been generated by laser photodecomposition of *tert*-butyl 1,1diphenylethyl peroxide (II). Radical III shows a visible absorption with λ_{max} 535 nm and decays by phenyl migration to yield the 1-phenoxy-1-phenylethyl radical (V). The conversion III \rightarrow V occurs with an activation energy of 5.9 \pm 0.4 kcal/mol and a preexponential factor (log A/s^{-1}) = 10.77 \pm 0.35, corresponding to a lifetime for III of ~400 ns in acetonitrile at room temperature. In the nanosecond time scale, the formation of V occurs concurrently with the decay of III. The results suggest that there is no need to invoke the intermediacy of the neophyl-like bridged intermediate IV. This intermediate is probably involved but if so is short-lived and not detectable with nanosecond laser photolysis techniques. The conclusion of earlier reports involving the characterization of IV needs to be revised. High-intensity laser excitation of II under *laser drop* conditions shows that III undergoes C-C photocleavage to yield acetophenone and benzophenone with virtually no selectivity.

The 1,2-migration of an aryl group in free radicals, known as the neophyl rearrangement¹ (Scheme 1), has been extensively studied. Although it is generally accepted to occur via a bridged-radical intermediate, direct evidence for this type of intermediate is scarce. ESR^{2-4} and CIDNP⁵ studies for the rearrangement of 2-arylpropyl-type radicals failed to detect signals for any bridged-radical intermediates.

The question as to whether the bridged intermediate in the neophyl rearrangement is a true intermediate or a transition state³ has been largely solved in at least one case by the spectroscopic detection of the bridged intermediate (spiro[2.5]octadienyl radical (I)) having the same structure that mediates the parent neophyl rearrangement.⁶ This intermediate, which was prepared



by hydrogen abstraction from the corresponding 1,4-cyclohexadiene, exhibited a weak absorption maximum at 560 nm. This radical (I) is believed to have the same structure as would be expected for the intermediate of a neophyl rearrangement.

I

The rearrangement of 1,1-diphenylethoxyl radicals generated from photodecomposition of *tert*-butyl 1,1-diphenylethyl peroxide (II) has been proposed⁷ to occur according to reactions 1-3 in Scheme 2.

The photochemistry of **II**, leading to the chemistry of Scheme 1, has been examined by laser flash photolysis by Schuster et al.,⁷ who report the detection of a reaction intermediate with a lifetime of 312 ns in acetonitrile at room temperature. This intermediate shows λ_{max} 535 nm and was assigned to the bridged intermediate **IV**. A key element in this assignment was that alkoxyl radicals were not known (or expected) to have absorption bands in the visible region of the spectrum.

Work published by Avila, Lusztyk, and Ingold shortly after Schuster's report demonstrated that aryl-substituted alkoxyl radicals have an absorption band in the visible region of the spectrum.⁸ Cumyloxyl shows λ_{max} 485 nm with $\epsilon = 1300 \text{ M}^{-1}$ cm⁻¹. This band is similar to that observed by Schuster⁷ and raises questions as to whether the 535 nm band may be due to **SCHEME 1**



SCHEME 2



III rather than IV. These observations suggest that the chemistry of radical III should be reexamined.

In recent work from this laboratory, we developed the *laser drop method* which allows for semipreparative multiphoton experiments.⁹ Under these conditions, extremely high light intensity can be achieved within small liquid drops. Among the systems examined, we observed the photoinduced fragmentation of cumyloxyl radicals (VI) according to reaction 4.



Our work with cumyloxyl⁹ suggested that radical **III** may undergo a similar type of photochemistry and provide some insight into the selectivity of free radical photofragmentations (vide infra). Thus, we decided to carry out laser drop experi-

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ments to explore the possible photofragmentations of either radical III or IV.

The spectroscopic and kinetic results included here agree with those reported by Schuster,⁷ but we find that the data need to be reinterpreted to reflect the new results reported here as well as the observation by Avila, Lusztyk, and Ingold⁸ of visible absorption bands by aryl-substituted alkoxyl radicals. Recent work by Ingold et al.¹⁰ also led to the same reassignment of the transient reported by Schuster.

Experimental Section

Materials. All solvents were spectral grade (BDH, Omnisolv) and were used as received. Compound II (1,1-diphenylethyl-tert-butyl peroxide) was synthesized according to Schuster.⁷ The sample was purified by passing it over a column of silica (70-230 mesh) with 10% ethyl acetate in hexanes as eluent; this treatment eliminated an impurity which absorbed at the laser wavelength (as shown by HPLC). The peroxide was then recrystallized twice from methanol. After purification, the peroxide was found to be pure by HPLC analysis. All experiments were carried out in acetonitrile unless another solvent is specified.

General Techniques. UV-visible spectra were recorded on a Hewlett-Packard model 8451 diode array spectrometer. Products from the photolysis of II 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 using acetonitrile-water as eluent, programmed between 50:50 and 100:0. Products were identified against authentic samples, and 1,4-di-*tert*-butylbenzene was used as an internal standard.

Semiempirical calculations were carried out using the AM1 SCF-MO method as implemented in the MOPAC program supplied with a Tektronix CAChe workstation with software version 3.5.

Low-Intensity Photolysis. Irradiations were carried out in 7 mm \times 7 mm 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 "home-designed" photochemical reactor equipped with nine Rayonet-300 lamps. The temperature of the irradiation chamber was not controlled but usually stabilized in the 30-35 °C range.

Laser Drop Irradiations. The beam from a Lumonics EX-530 excimer laser (Xe/HCl/Ne, 308 nm, ~6 ns, 80-130 mJ/ pulse) was focused 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 was irradiated by one laser pulse, which caused it to disintegrate into a mist of smaller droplets which was collected at the walls of the irradiation cell. Following 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. A full description of this technique is described in an earlier paper.⁹ The laser drop technique provides the capability for high-intensity irradiations comparable to those that can be achieved with the laser-jet technique.^{11,12} In the case of the laser jet, it has been proposed that laser irradiation leads to light amplification similar to that observed in lasing droplets.¹³ We note, however, that the drops used in our work (typically $1-10 \,\mu$ L) are considerably larger than those for which the amplification effects have been reported.13



Figure 1. Transient spectra recorded upon 248 nm laser photolysis of I in acetonitrile, 0.1 μ s (\bullet) and 1.0 μ s (\Box) after the laser pulse.

Laser Flash Photolysis. These experiments were carried out using a Lumonics EX-510 excimer laser operated with Kr/F₂/ He mixtures (248 nm, ~ 6 ns, ≤ 100 mJ/pulse). The samples were contained in guartz cells constructed of 7 mm \times 7 mm Suprasil tubing. Normally nitrogen, and occasionally oxygen, wass bubbled for at least 15 min before the laser experiments. Most experiments employed a flow system, with the exception of variable temperature work where the use of fresh static samples for each measurement ensured better temperature stability. Temperature control was achieved by a flow of nitrogen at the appropriate temperature through a quartz jacket that surrounded the sample and its holder. Transient signals were captured with a Tektronix-2440 digital scope which was interfaced to a Macintosh IIci computer which also controlled the laser flash photolysis instrument. The system was operated under LabVIEW 2.2 software from National Instruments. Other aspects of this instrument are similar to those described earlier.14,15

Thermal Decomposition of II. These experiments were carried out to establish if the laser drop results (vide supra) could involve contributions from thermal processes in the drop. Compound II (50 mg) was dissolved in 25 mL of *tert*-butylbenzene and refluxed under nitrogen (bp 169 °C) for 90 min. Chromatographic analysis showed that acetophenone and benzophenone were absent from the reaction mixture.

Results and Discussion

Pulsed laser excitation (248 nm) of deaerated solutions of peroxide II in acetonitrile leads to the transient spectrum of Figure 1. The visible band (monitored at 520 nm) decays with a lifetime of \sim 400 ns; concurrently with this decay, a band with $\lambda_{\rm max}$ 320 nm grows in, indicating that the intermediate absorbing at 535 nm is a precursor to that absorbing at 320 nm. We assign the 320 nm transient to the carbon-centered radical V; benzylic radicals frequently have strong absorptions in this region of the UV spectrum.¹⁶ Figure 2 shows 320 nm traces under nitrogen and under oxygen. Consistent with our assignment, the growth of the 320 nm band is absent in oxygen-saturated solutions, indicating that V reacts readily with oxygen, as expected;¹⁷ under these conditions, the traces at 320 nm reveal a decay with a lifetime similar to that observed at 535 nm, indicating that the intermediate absorbing at 535 nm also has some absorption in the ultraviolet region. We assign this intermediate to alkoxyl radical III; this assignment is consistent with all the available data (vide infra). Note that the 320 nm trace shows that part of the transient absorption is formed "instantaneously", in agreement with the results under oxygen which indicate some absorption by III.



Figure 2. Decay traces recorded under the conditions of Figure 1 at 320 and 520 nm under nitrogen (\triangle) and under oxygen (\bigcirc).

The traces at 535 nm show little sensitivity to oxygen, with a lifetime of ca. 320 ns under 1 atm of oxygen; this is consistent with the assignment of this intermediate as the alkoxyl radical III. In contrast, we would expect the carbon-centered radical IV to show a much higher reactivity toward oxygen with a lifetime at least 10 times shorter under oxygen.¹⁷ Further, it is noteworthy that the reactivity toward hydrogen donors for the 535 nm intermediate⁷ is in the range observed for other alkoxyl radicals, such as tert-butoxyl.^{18,19} For example, the intermediate assigned to III reacts with 1,3-dioxolane with a rate constant of $4.4 \times 10^{6} \text{ M}^{-1}\text{s}^{-1}$, compared with $7.7 \times 10^{6} \text{ M}^{-1} \text{ s}^{-1}$ for tert-butoxyl.¹⁹ Thus, we conclude that the signals in the 535 nm region are due to III and not IV. This assignment also avoids the need to invoke an equilibrium between III and IV as suggested by Schuster⁷ since hydrogen abstraction by III can compete with the intramolecular migration of the phenyl group. The fact that the ratio of intensities of the visible to UV bands in the spectrum assigned to III is temperature independent between 248 and 346 K suggests that the spectrum corresponds to a single intermediate, rather than to two species in equilibrium.²⁰

We have also examined the temperature dependence of the decay kinetics monitored at 535 nm. These experiments were carried out in acetonitrile in the -38 to 22 °C range. The data yield an excellent Arrhenius dependence (see Figure 3), corresponding to an activation energy of 5.9 ± 0.4 kcal/mol (errors as $\pm 2\sigma$) and a preexponential factor (log A/s^{-1}) = 10.77 ± 0.35 . The preexponential factor is quite informative; the fact that it is $\ll 10^{13} s^{-1}$ indicates a loss of entropy in the transition state. This is fully consistent with reaction 2 but would be inconsistent with reaction 3 where an entropy gain would be anticipated. These values can be compared with those reported for the



Figure 3. Arrhenius plot for the temperature dependence on the decay of IV monitored at 520 nm.

migration of phenyl from the 2-phenyl-2-methylpropyl radical,³ where the activation energy is 13.6 kcal/mol and the preexponential factor is 5.0×10^{11} s⁻¹. The activation energy for the rearrangement for III could be expected to be lower due to resonance stabilization of the benzylic radical product and the greater reactivity of an oxygen-centered radical. Maillard and Ingold's³ reported preexponential factor is also indicative of an entropy loss. The value of log A/s^{-1} of 11.7 ± 1.0 agrees well with our value for reaction 2.

The fact that the decay kinetics for III (at 535 nm) are consistent with the formation kinetics for V (at 320 nm) suggests that the lifetime of IV must be short in the time scale of these experiments ($k_3 > k_2$). A reasonable estimate based on our results indicates that IV must live less than 100 ns. Molecular calculations suggest that this is a conservative limit in view of the low activation energy estimated for reaction 3.

A series of AM1-UHF calculations²¹ were also carried out on the intermediates and transition states involved in reactions 1-3. The geometries were obtained using the eigenvector following the search algorithm as described by Baker.²² The transition state for the reaction III \rightarrow IV could not be fully optimized using the AM1-UHF method with appropriate search routines; however, no structure along the reaction surface could be found which corresponds to the "true" transition state.²³ The transition state for IV \rightarrow V was fully optimized, and only one imaginary vibrational mode was found when a force field calculation was done. The reaction coordinate as described by the AM1 calculations is shown in Figure 4. Thus, IV is expected to be a true intermediate, but reaction 3 is expected to be too fast for the experimental technique employed.

In view of the photolability of cumyloxyl and related radicals,^{9,24} a series of laser drop experiments was carried out in acetonitrile, employing the method described elsewhere.9 Laser excitation of small droplets (typically $\sim 5-10 \ \mu$ L) of solutions containing 0.1 M II with the focused 308 nm pulses from an excimer laser leads to the formation of acetophenone (VII) and benzophenone (VIII) in a 1-0.8 ratio (determined by HPLC). It should be noted that neither of these products is observed in low-intensity, low-conversion lamp irradiations, although small concentrations of acetophenone are formed under prolonged irradiation. Howard and Ingold reported that the photolysis of bis-(1,1-diphenylethyl) peroxide under an oxygen atmosphere produces acetophenone by a complex mechanism.²⁵ Benzophenone is not formed at all under lamp irradiation. Further, acetophenone and benzophenone are not produced when peroxide II is decomposed thermally at 169 °C. These results



Reaction coordinate

Figure 4. Reaction coordinate for the migration of phenyl from III to give V. Energies (kcal/mol) calculated by AM1-UHF.





suggest that reactions 5 and 6 take place under the high-intensity conditions of laser drop experiments. The lack of selectivity is not unprecedented in fragmentations of this type,²⁴ and it may suggest the involvement of a dissociative state in the reaction.

The methyl and phenyl radicals formed in the reactions of Scheme 3 are expected to decay by reaction with the acetonitrile used as a solvent. Thus, just as in the case of α , α -dialkoxy-benzyl radicals,²⁴ the photocleavage of **III** appears to show little, if any, selectivity. It is possible that a small amount of acetophenone could be produced by oxygen contamination during laser drop photolysis. Scheme 3 provides another example where high-intensity laser photochemistry¹² leads to new products, distinct from those obtained under conditions of lamp excitation.

Conclusion

The transient produced upon photolysis of **II** is formed from an alkoxyl radical precursor and has the following characteristics. (a) Its spectrum is consistent with that expected for an aryl-substituted alkoxyl radical.⁸ (b) It reacts with hydrogen donors with rate constants comparable with those for other alkoxyl radicals.^{18,19} (c) It undergoes photoinduced fragmentation to yield acetophenone and benzophenone as expected for alkoxyl radical **III**. (d) The temperature dependence of its decay leads to a low preexponential factor consistent with **III** but not **IV**. This evidence thus requires the reinterpretation of Schuster's conclusion that **IV** was the observable species. The results can be interpreted without the need to invoke the detection of bridged intermediate **IV**, which is probably too short-lived for detection with nanosecond techniques (i.e. $k_3 > k_2$). In this time scale, the formation of V occurs concurrently with the decay of **III**, with a lifetime of ~400 ns at room temperature. Laser drop experiments reveal the photofragmentation of **III** to yield methyl and phenyl radicals with virtually no selectivity.

The photochemistry of **II** leads to the rapid formation of alkoxyl radical **III** which decays by a competition between the rearrangement of reactions 2 and 3 and hydrogen abstraction when suitable donors⁷ are present. The absorption properties of **III** are similar to those of cumyloxyl radicals with λ_{max} 535 nm in the visible region. The oxygen-centered radical **III** has a lifetime of ca. 400 ns at room temperature and decays with an activation energy of 5.9 kcal/mol.

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References and Notes

- (1) Urry, W. H.; Kharasch, M. S. J. Am. Chem. Soc. 1944, 66, 1438.
- (2) Kochi, J. K.; Krusic, P. J. J. Am. Chem. Soc. 1969, 91, 3940.
- (3) Maillard, B.; Ingold, K. U. J. Am. Chem. Soc. 1976, 98, 1224.
- (4) Hamilton, E. J., Jr.; Fischer, H. Helv. Chim. Acta 1973, 56, 795.
- (5) Shevlin, P. B.; Hansen, H. J. J. Org. Chem. 1977, 42, 3011.
- (6) Effio, A.; Griller, D.; Ingold, K. U.; Scaiano, J. C.; Sheng, S. J. J. Am. Chem. Soc. **1980**, 102, 6063.
- (7) Falvey, D. E.; Khambatta, B. S.; Schuster, G. B. J. Phys. Chem. 1990, 94, 1056.
- (8) Avila, D. V.; Lusztyk, J.; Ingold, K. U. J. Am. Chem. Soc. 1992, 114, 6576.
- (9) Banks, J. T.; Scaiano, J. C. J. Am. Chem. Soc. 1993, 115, 6409.
 (10) Avila, D. V.; Ingold, K. U.; DiNardo, A. A.; Zerbetto, F.; Zgierski,
- M. Z.; Lusztyk, J. J. Am. Chem. Soc., submitted for publication, 1994. (11) Wilson, R. M.; Schnapp, K. A.; Hannemann, K.; Ho, D. M.;

Memarian, H. R.; Azadnia, A.; Pinhas, A. R.; Figureley, T. M. Spectrochim. Acta 1990, 46A, 551.

(12) Wilson, R. M.; Adam, W.; Schulte-Oestrich, R. *The Spectrum* **1991**, 4 (3), 8.

(13) Quian, S.-X.; Snow, J. B.; Tzeng, H.-M.; Chang, R. K. Science 1986, 231, 486.

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

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(15) Scaiano, J. C.; Tanner, M.; Weir, D. J. Am. Chem. Soc. 1985, 107, 439[°]6.

- (16) Chatgilialoglu, C. In Handbook of Organic Photochemistry; Scaiano, J. C., Ed.; CRC Press: Boca Raton, FL, 1989; Vol. II, p 3.
 (17) Maillard, B.; Ingold, K. U.; Scaiano, J. C. J. Am. Chem. Soc. 1983,
- 105, 5095.
- (18) Paul, H.; Small, R. D., Jr.; Scaiano, J. C. J. Am. Chem. Soc. 1978, 100. 4520.
- (19) Malatesta, V.; Scaiano, J. C. J. Org. Chem. 1982, 47, 1455. (20) D. V. Avila, unpublished results. If $\Delta H = 0$, the same condition can be met; however, this appears highly unlikely.

(21) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. J. Am. Chem. Soc. 1985, 107, 3902.

(22) Baker, J. J. Comput. Chem. 1986, 7, 385.

(23) The value in brackets in Figure 4 reflects the failure to define completely this transition state.

(24) Banks, J. T.; Scaiano, J. C.; Adam, W.; Oestrich, R. S. J. Am. Chem. Soc. 1993, 115, 2473.

(25) Howard, J. A.; Ingold, K. U. Can. J. Chem. 1969, 47, 3797.

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