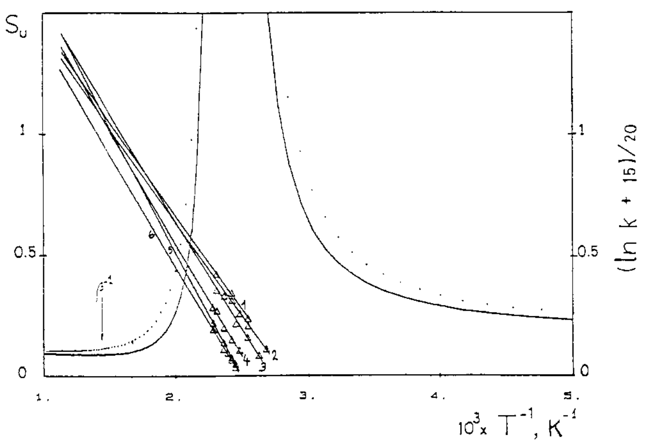

Figure 4. Dependence of the residual sum of squares S_u on the supposed isokinetic temperature T^{-1}. Broken line for all the diperoxides studied; full line for ACDP data excluded. Symbols for the Arrhenius plot are: **1**, PDP; **2**, BKDP; **3**, CHDP; **4**, BPDP; **5**, APDP; and **6**, ACDP.

°C, which is in reasonable agreement with the above β value.

Conclusions

1. The analysis of the reaction products of the thermolyses of some substituted tetraoxanes in benzene solution and the corresponding activation parameters for these unimolecular reactions support a general homolytic stepwise mechanism, rather than a concerted process.

2. A genuine "isokinetic relationship" is observed for the unimolecular homolyses of the acetophenone, benzyl ketone, benzophenone, cyclohexanone and pinacolone diperoxides, which is consistent with similar steric effects in the corresponding transition states of their reactions. The acetone diperoxide reaction deviates from this correlation.

Experimental Section

Materials. The BPDP, CHDP, and PDP diperoxides were prepared by methods described elsewhere,[17] and their purity was checked by GC and IR analysis (KBr, Nujol). Other organic compounds and the benzene solvent were commercial analytical reagents purified by standard techniques.

Kinetic Methods and Product Analyses. Pyrex glass ampoules (7 cm long × 0.8 cm o.d.) half-filled with the appropriate diperoxide solutions thoroughly degassed under vacuum were immersed in a thermostatic silicone oil bath (±0.1 °C) and withdrawn after predetermined times, stopping the reaction by cooling at 0 °C. The diperoxides (except BPDP) remaining in the reaction solutions and their decomposition products were identified by qualitative and quantitative GC analysis (internal standard method, *n*-octane) using a methylsilicone capillary column HP-SP-2100 (12 m × 0.2 mm i.d.) installed in a 5840 A Model Hewlett-Packard instrument (FID), with nitrogen as the carrier gas. Due to the nonvolatile character of the BPDP diperoxide, its quantitative determination in the benzene solutions was performed by a specially designed IR analytical method monitoring the 990 cm^{-1} absorption band. The first-order rate constant values were calculated by a least mean square treatment of the reactions data, and the activation parameters were determined from the corresponding Arrhenius equations.

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Registry No. BPDP, 16204-36-7; CHDP, 183-84-6; PDP, 124244-55-9.

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Photoinduced Electron Transfer from Dialkyl Nitroxides to Halogenated Solvents[1]

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Laser flash photolysis (LFP) at wavelengths within the charge-transfer absorption present in CCl_4 solutions of 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) yields the oxoammonium chloride of TEMPO, 1 (λ_{max} = 460 nm), and the trichloromethyl radical in an essentially instantaneous (≤18 ps) process. The primary photochemical event is an electron transfer from TEMPO to CCl_4, and this is followed by immediate decomposition of the $CCl_4^{\bullet -}$ radical anion to Cl^- and $Cl_3C^\bullet$. An independent synthesis of 1 confirmed that the absorption attributed to this species had been correctly assigned. The formation of $Cl_3C^\bullet$ was inferred by its trapping by molecular oxygen. LFP of TEMPO in other halogenated solvents and of other nitroxides in halogenated solvents has confirmed the generality of these photoreactions.

The photochemistry of *transient* free radicals is a new and rapidly developing subject.[3] It has been found[3] that the high energy content of photoexcited radicals generally does not lead to large increases in the rates of hydrogen atom abstraction,[4] but that these species do have greatly enhanced electron-transfer capabilities. We reasoned that the time-resolved photochemistry of a *persistent* radical should be much easier to study than that of a transient radical. However, a search of the literature revealed that although photolysis of the largest class of persistent rad-

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[1] Issued as NRCC No. 30777.

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[4] Excited nitroxides appear to be an exception to this rule.[3,5-8]

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Table I. Optical Densities of 5 × 10^{-2} M TEMPO in Various Solvents[a]

solvent	OD at 308 nm	OD at λ_{max}[b]	λ_{max},[b] nm
isooctane	1.3	0.53	476
CH_3CN	1.7	0.54	464
C_6H_6	1.9	0.61	474
$CF_2ClCFCl_2$	1.8	0.58	474
CH_2Cl_2	1.9	0.61	464
$CHCl_3$	2.7	0.62	460
CCl_4	3.1	0.61	472
CH_2Br_2	3.3	0.67	462

[a] Measured in a 1 cm cell at 20 °C. [b] Visible absorption band.

icals, the di-*tert*-alkyl nitroxides, has been fairly thoroughly investigated[5-12] and various processes have been identified,[13] there appeared to be only two papers describing the photolysis of a nitroxide which led to products suggestive of an initial electron transfer.[9] In those two papers, Koch and co-workers[9] reported that dilute solutions of di-*tert*-butyl nitroxide in CCl_4 had a charge-transfer absorption[14] in the region 310–370 nm and that irradiation at 313 or 366 nm resulted in an efficient destruction of the nitroxide ($\phi_{destruction} = 1.7$). The products of 366-nm photolysis of 0.1 M nitroxide were Me_3CNO ($\phi = 0.85$), $Me_2C{=}CH_2$ ($\phi = 0.55$), Me_3CCl ($\phi = 0.30$), $(Me_3C)_2NOCCl_3$ ($\phi = 0.56$), and $(Me_3C)_2N^+HOH/Cl^-$ ($\phi = 0.27$), and the primary photochemical event was presumed to be an electron transfer from the nitroxide to CCl_4 to form di-*tert*-butyloxoammonium chloride and the trichloromethyl radical, reaction 1. The $Cl_3C^\bullet$ radical was trapped by unreacted nitroxide, reaction 2. Di-*tert*-butyloxoammonium chloride was not detected, it was assumed to be very unstable and to decompose to the products mentioned above. There is, however, a possible alternative route to the oxoammonium chloride involving a chlorine atom abstraction by the excited nitroxide to form a hypochlorite and the trichloromethyl radical, reaction 3, with the hypochlorite subsequently undergoing an intramolecular redox reaction to form the oxoammonium chloride. Koch and co-workers[9] did not favor this as the primary photochemical event but were unable to rule it out unequivocally.

$$(Me_3C)_2NO^\bullet/CCl_4 \overset{h\nu}{\rightleftharpoons} [(Me_3C)_2N^+O/CCl_4^{\bullet -}]^* \rightarrow (Me_3C)_2N^+{=}O/Cl^- + Cl_3C^\bullet \quad (1)$$

$$Cl_3C^\bullet + (Me_3C)_2NO^\bullet \rightarrow (Me_3C)_2NOCCl_3 \quad (2)$$

$$(Me_3C)_2NO^\bullet \xrightarrow{h\nu} [(Me_3C)_2NO^\bullet]^* \xrightarrow{CCl_4} (Me_3C)_2NOCl + Cl_3C^\bullet \quad (3)$$

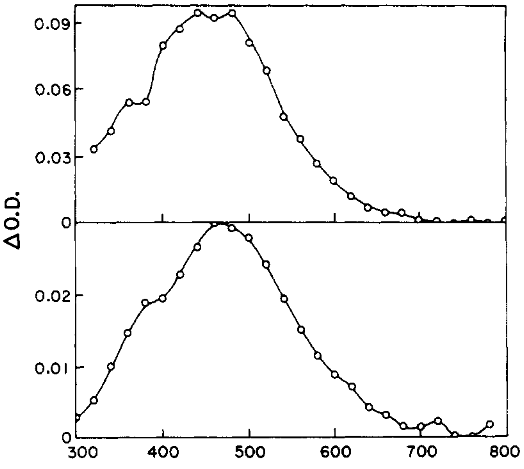
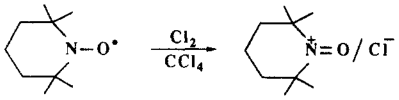


Figure 1. UV–visible spectra observed 2 μs after 308-nm LFP of 0.05 M TEMPO in CCl_4 (top) and 80 ns after 308-nm LFP of 0.001 M di-*tert*-butyl nitroxide in CCl_4 (bottom).

It is known[17] that the oxoammonium chloride, **1**, of the cyclic nitroxide, 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) can be prepared as a stable but moisture- and light-sensitive solid by reaction of TEMPO with chlorine gas in CCl_4 as solvent, reaction 4. We therefore decided to investigate the laser flash photolysis (LFP) of TEMPO in CCl_4 (rather than that of di-*tert*-butyl nitroxide) with the object of identifying the primary photochemical process unequivocally. If this process is indeed an electron transfer then **1** should be produced "instantaneously" upon LFP, whereas if the primary event were chlorine atom abstraction, then **1** could only "grow in" after the laser pulse. The knowledge that **1** was "pumpkin-colored"[17] assured us that its formation could be monitored by an absorption in the visible region of the spectrum.



(4)

TEMPO 1

Results

Absorption Spectrum of TEMPO. In isooctane TEMPO has an absorption in the UV ($\lambda_{max} = 246$ nm, $\epsilon = 1970$)[18] tailing to 330 nm and a broad, structureless absorption in the visible ($\lambda_{max} = 476$ nm, $\epsilon = 10.5$).[18] The short- and long-wavelength absorptions are due to π-π^* and n-π^* transitions, respectively.[9,19] In nonpolar solvents such as benzene and CCl_4 the visible band is almost identical with that seen in isooctane, but in polar solvents such as acetonitrile and $CHCl_3$ this band is blue-shifted (see Table I), an effect typical of an n-π^* transition.[20] In halogenated solvents additional charge transfer[14] absorp-

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(13) For example, hydrogen atom abstraction,[5-8] elimination of nitric oxide,[10] loss of a *tert*-alkyl radical.[11]

(14) The existence of a charge transfer absorption does not necessarily imply that charge transfer plays a significant role in the binding together of donor and acceptor.[15] Di-*tert*-butyl nitroxide and halogenated solvents, including CCl_4, have been shown to form complexes by ^{13}C NMR.[16] "Contact" has been used to describe both the charge-transfer absorption[9] and the ^{13}C chemical shifts,[16] but this word would appear to have no identifiable meaning for a solute in a neat solvent where an absence of "contact" is impossible.

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(18) For comparison,[9] di-*tert*-butyl nitroxide in pentane has $\lambda_{max} = 238$ nm ($\epsilon = 2580$) and $\lambda_{max} = 460$ nm ($\epsilon = 8.9$).

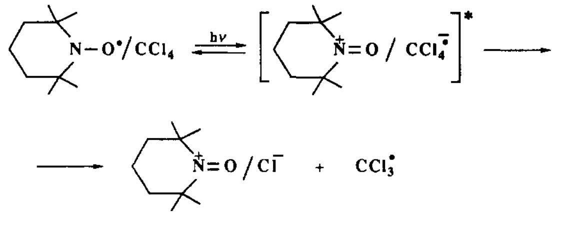
(19) Kikuchi, O. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 47–52. Salotto, A. W.; Burnelle, L. *J. Chem. Phys.* **1970**, *53*, 333–340.

(20) In benzene and in CH_3CN the UV π-π^* band is slightly red-shifted relative to isooctane.

tions are observed between 300 and 390 nm, with this absorption extending to longer wavelengths in the solvent order: $CF_2ClCFCl_2 \sim CH_2Cl_2 < CHCl_3 < CCl_4 < CH_2Br_2$. The 308-nm optical densities (OD) of 5×10^{-2} M TEMPO in these solvents increased in the same order (see Table I).

LFP of TEMPO in CCl_4. No transient signals (absorption or emission) were observed from 300 to 800 nm upon laser excitation (308 and 337 nm) of TEMPO in isooctane, acetonitrile, or benzene. By way of contrast, 308 and 337 nm LFP of TEMPO at concentrations ranging from 1×10^{-4} to 5×10^{-2} M in nitrogen-purged CCl_4 produced a strong, structureless absorption with $\lambda_{max} = 460$ nm (see Figure 1). This absorption was produced "instantaneously", i.e., within the width of the laser pulse,[21] and decays extremely slowly, viz., by only ca. 5% in 70 μs. Ignoring differences in intensity, the time profiles of this absorption are essentially identical at all wavelengths and at all TEMPO concentrations. Proof that this absorption is due to the oxoammonium chloride, 1, was obtained by comparison with the spectrum of authentic 1 (mp 113 °C) synthesized according to eq 4, as described.[17]

This "instantaneous"[21] formation of 1 upon LFP of the TEMPO/CCl_4 charge-transfer band virtually proves that the initial photochemical event is an electron transfer, reaction 5, but the identification of the $Cl_3C^\bullet$ radical would provide welcome additional evidence. Since this radical was not expected to have an observable adsorption in the spectral region available to us, we resorted to a trapping procedure. The choice of trap was critical. A trap of high reactivity toward $Cl_3C^\bullet$ was required since $Cl_3C^\bullet$ would be expected to react with TEMPO at a rate only slightly below the diffusion-controlled limit.[22,23] Furthermore, the trap should be unreactive toward 1. With these points in mind we investigated the effect of oxygen on the absorptions produced by LFP of TEMPO in CCl_4 since carbon-centered radicals are known to react with oxygen even more rapidly than they react with TEMPO.[24] In addition, the trichloromethylperoxyl radical should be easy to observe since it is known to have an absorption in the range 280–320 nm, with $\epsilon = 400$ at 310 nm.[25]

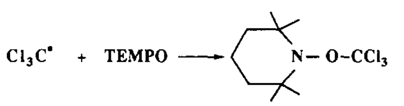


(5)

1

The intensity and decay of the absorption due to 1 following LFP of TEMPO in CCl_4 was unaffected by oxygen. Thus, identical traces were observed from the band maximum (460 nm) to all longer wavelengths in N_2-, air-, and O_2-saturated solutions. However, a new UV absorption was observed in the presence of oxygen.[26] This new absorption tails from ca. 330 to ca. 400 nm and overlaps with the absorption due to 1. It "grows-in" with pseudo-first-order kinetics and, as would be expected in view of the competitive trapping of $Cl_3C^\bullet$ by oxygen (reaction 6) and by TEMPO (reaction 7), the experimental rate constant, k_{exptl} (measured at 330 nm) was dependent on both the oxygen and TEMPO concentrations, i.e., $k_{exptl} = k_0 + k_6[O_2] + k_7[TEMPO]$.[27] Values of k_{exptl} were measured in O_2-saturated (760 Torr) CCl_4 at 20 °C over a range of TEMPO concentrations from 1×10^{-4} to 5×10^{-3} M. The plot of k_{exptl} vs [TEMPO] was linear (corr coef = 0.998) and had a slope which is, of course, equal to k_7 of $(9.1 \pm 0.5) \times 10^8$ M^{-1} s^{-1}. This value for k_7 is in the expected range,[22] e.g., the rate constant for trapping by TEMPO of the *tert*-butyl radical is $(7.6 \pm 1.6) \times 10^8$ M^{-1} s^{-1}.[22]

$$Cl_3C^\bullet + O_2 \longrightarrow Cl_3COO^\bullet \quad (6)$$



(7)

In order to confirm that the short-wavelength transient absorption could indeed be attributed to the $Cl_3COO^\bullet$ radical, we generated the $Cl_3C^\bullet$ radical by several independent routes in the absence and presence of oxygen. For example, 308 or 337 nm LFP of di-*tert*-butyl peroxide (10% and 50% v/v, respectively) in O_2-saturated (but not in N_2-saturated) chloroform (reactions 8 and 9) caused the grow-in of a transient absorption essentially identical with that observed in the TEMPO/CCl_4/O_2 system. Other methods for generating $Cl_3C^\bullet$ radicals[28] also gave essentially identical transient absorptions following LFP of oxygen-saturated solutions.

$$Me_3COOCMe_3 \xrightarrow{h\nu} 2Me_3CO^\bullet \quad (8)$$

$$Me_3CO^\bullet + CHCl_3 \rightarrow Me_3COH + Cl_3C^\bullet \quad (9)$$

LFP of TEMPO in Other Polychlorinated Solvents. The absorption attributable to 1 was also obtained by 308 or 337 nm LFP of TEMPO in N_2-purged $CHCl_3$, $CF_2ClCFCl_2$, and CH_2Cl_2. The relative efficiencies for the photoproduction of 1 in the different solvents were determined in matched experiments in which the OD's at the laser wavelength (308 nm) were made equal to 0.70 and the maxima in ΔOD at 460 nm were measured following the laser pulse. For CCl_4, $CHCl_3$, $CF_2ClCFCl_2$, and CH_2Cl_2 the relative efficiencies were 56:11:10:1, respectively. This solvent order may reflect the increasing importance of back electron transfer from the halocarbon radical anion to the oxoammonium cation so as to reform the nitroxide and the halocarbon. That is, the importance of back electron transfer may depend on the rate at which Cl^- is lost from the halocarbon radical anion.

LFP of Other Nitroxides in CCl_4. Absorptions we attribute to the corresponding oxoammonium chlorides were "instantaneously"[21] formed upon LFP of CCl_4 solutions of di-*tert*-butyl nitroxide ($\lambda_{max} = 460$ nm), 4-hydroxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl ($\lambda_{max} = 480$

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[21] Laser pulse widths were 4 ns at 308 nm, 8 ns at 337 nm, 6 ns at 355 nm (using nanosecond time resolution), and 18 ps at 355 nm (using picosecond time resolution). "Instantaneous" generation of oxoammonium halides on the very fast, picosecond time scale was proven with 0.1 M TEMPO and with 0.1 M di-*tert*-butyl nitroxide in CCl_4, in CH_2Br_2, and (probably) in CH_3I.

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[26] Removal of the O_2 by purging with N_2 eliminates this absorption which will, however, reappear following O_2 purging. This alteration between O_2 (signal) and N_2 (no signal) can be repeated many times.

[27] For details of the analysis in kinetically analogous systems, see: Paul, H.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520–4527.

[28] The following systems were employed: $Me_3COOCMe_3/Et_3SiH/CCl_4$; $MeCOOCMe_3/Me_2CHOH/CCl_4$; and $Me_2CO/Me_2CHOH/CCl_4$. The first of these relies on the $Et_3Si^\bullet$ radical and the other two on the Me_2COH radical to remove a chlorine atom from the CCl_4.

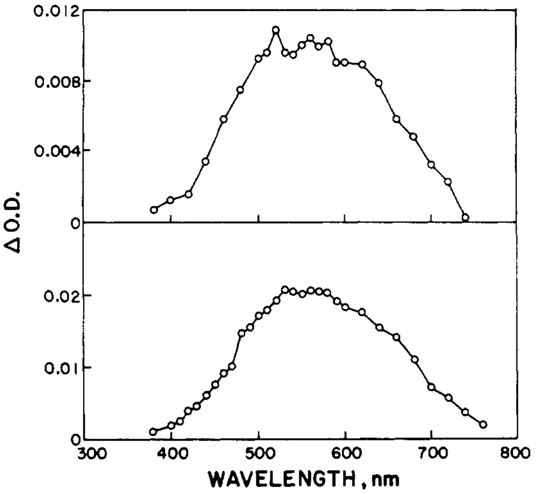


Figure 2. UV–visible spectra observed 230 ns after 355-nm LFP of 0.1 M TEMPO in CH_2Br_2 (top) and of 0.1 M di-*tert*-butyl nitroxide in CH_2Br_2 (bottom).

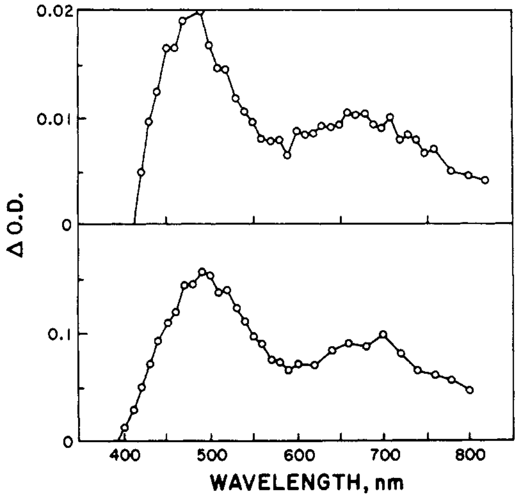


Figure 3. UV–visible spectra observed 235 ns after 355 nm LFP of 0.1 M TEMPO in CH_3I (top) and of 0.1 M di-*tert*-butyl nitroxide in CH_3I (bottom).

nm), and 1,1,3,3-tetramethylisoindolinyl-*N*-oxyl (λ_{max} = 465 nm).

LFP of Nitroxides in Brominated Solvents. Broad, structureless absorptions with maxima in the 500–600-nm range were formed "instantaneously"[21] upon 308 or 355 nm LFP of TEMPO or di-*tert*-butyl nitroxide in CH_2Br_2 (see Figure 2) and upon 308 or 337 nm LFP of TEMPO in $CHBr_3$, C_2H_5Br, and $C_6H_5CH_2Br/C_6H_6$ as solvents. We attribute these absorptions to oxoammonium bromides but were unable to obtain independent confirmation because, like others,[29] we were unable to synthesize these compounds in pure form.

LFP of Nitroxides in Iodinated Solvents. In contrast to the results obtained in chlorinated and brominated solvents, the LFP of TEMPO or di-*tert*-butyl nitroxide in alkyl iodides gave absorption in the visible region which underwent a very rapid evolution with time. Thus, with 0.1 M TEMPO or di-*tert*-butyl nitroxide in CH_3I, 355-nm LFP with nanosecond time resolution "instantaneously" (6 ns)[21] gave absorptions with maxima at ca. 500 and 700 nm (see Figure 3) which had lifetimes of a few microseconds. However, when the same solutions were subjected to 355-nm LFP with picosecond time resolution only the 500-nm band was produced "instantaneously" (18 ps),[21] while the 700-nm absorption "grew-in" ca. 1.0 to 1.5 ns after the laser pulse (see Figure 4).

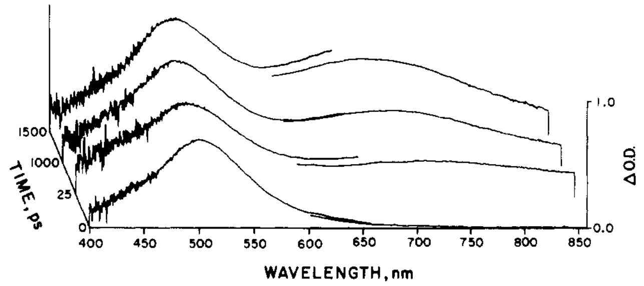
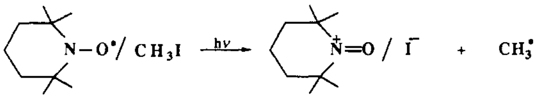


Figure 4. Time evolution of the visible spectra observed after 355-nm LFP of 0.1 M di-*tert*-butyl nitroxide in CH_3I. At each time point spectra were separately recorded in the range 400–650 and 600–850 nm.

It is logical to assign the 500-nm absorptions to the oxoammonium iodides since they are produced in less than 18 ps. Since the 500-nm absorptions do not decrease as the 700-nm band "grows-in" (see Figure 4), it is rather unlikely that the species responsible for the 700-nm absorptions could be derived from the oxoammonium iodide. Surprising as it may seem, this leaves responsibility for the long-wavelength absorption to the methyl radical or to the iodine atom. Therefore, we very tentatively suggest that the 700-nm absorption is due to a hypervalent iodine-centered radical, $CH_3\dot{I}CH_3$ and/or $CH_3\dot{I}I$. The reaction sequences would be:

 (10)

and $$CH_3I \xrightarrow{h\nu} CH_3^{\bullet} + I^{\bullet} \tag{11}$$

$$CH_3^{\bullet} + CH_3I \rightleftharpoons CH_3\dot{I}CH_3 \tag{12}$$

and/or $$I^{\bullet} + CH_3I \rightleftharpoons CH_3\dot{I}I \tag{13}$$

and we can calculate that k_{12} and/or k_{13} is about 10^8 M^{-1} s^{-1}.[30]

Following Martin's nomenclature for hypervalent nonmetallic species,[31] $CH_3\dot{I}CH_3$ and $CH_3\dot{I}I$ are 9I2 neutral radicals. We can find no report that such species have long-wavelength absorptions. However, reactions 12 and 13 are simply the combination of a species containing an unpaired electron with an iodine which has a complete valence shell of electrons. As such, it is formally equivalent to the combination of an iodine atom with the iodide anion to form $I_2^{\bullet-}$, reaction 14. The $I_2^{\bullet-}$ radical anion is known to have an absorption maximum at ca. 750 nm,[32] which

$$I^{\bullet} + I^{-} \rightleftharpoons I_2^{\bullet-} \tag{14}$$

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[29] Scott, A. C.; Tedder, J. M.; Walton, J. C.; Mhatre, S. *J. Chem. Soc., Perkin Trans. 2* **1980**, 260–266. Zhdanov, R. I.; Golubev, V. A.; Rozantsev, E. G. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1970**, 186–187. Golubev, V. A.; Voronina, G. N.; Rozantsev, E. G. *Ibid.* **1970**, 2605–2608.

[30] Iodine atom exchange between carbon-centered radicals and iodides is known to be an extremely rapid process with an overall rate constant $k > 5 \times 10^4$ M^{-1} s^{-1}, see, e.g.: (a) Lawler, R. G.; Ward, H. R.; Allen, R. B.; Ellenbogen, P. E. *J. Am. Chem. Soc.* **1971**, *93*, 789–791. (b) Ingold, K. U. In *Free Radicals*; Kochi, J. K., ed.; Wiley: New York, 1973; Vol. 1, Chapter 2. (c) Gilbert, B. C.; Norman, R. O. C.; Sealy, R. C. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1435–1441. (d) Castelhano, A. L.; Griller, D. *J. Am. Chem. Soc.* **1982**, *104*, 3655–3659. (e) Lehr, G. F.; Lawler, R. G. *Ibid.* **1984**, *106*, 4048–4049. (f) Newcomb, M.; Sanchez, R. M.; Kaplan, J. *Ibid.* **1987**, *109*, 1195–1199. (g) Newcomb, M.; Kaplan, J. *Tetrahedron Lett.* **1988**, *29*, 3449–3450.

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lends some support to either of our tentative assignment of the 700-nm band. It should be noted that CIDNP studies of iodine atom exchange between carbon-centered radicals would require $CH_3\dot{I}CH_3$ to have a lifetime no longer than a few microseconds.[30a,e] This is not inconsistent with our observations.

Discussion

Charge-transfer absorptions are observed whenever nitroxides are dissolved in polyhalogenated solvents. Laser irradiation at wavelengths within these bands "instantaneously" yields the corresponding oxoammonium halide and a carbon-centered radical via a photoinduced electron transfer followed by loss of halide ion, just as was first proposed by Koch and co-workers[9] for the specific case of di-*tert*-butyl nitroxide in CCl_4. This phenomenon indicates that care must be exercised in the choice of solvent during photochemical studies which directly involve nitroxides (e.g., the quenching of other molecules in photoexcited singlet and triplet states) or which involve them indirectly (e.g., the spin-trapping of photo-generated radicals by nitrones and nitroso compounds).

The "instantaneous" production of oxoammonium halides will make time-resolved kinetic studies on these species relatively simple. Similarly, a straightforward method for the "instantaneous" production of haloalkyl radicals may prove valuable in other kinetic studies.

Experimental Section

TEMPO (Aldrich) was purified by multiple sublimations. Di-*tert*-butyl nitroxide was used as received. All solvents were Aldrich gold-label grade. CCl_4 was distilled from K_2CO_3. The bromides and methyl iodide were passed through alumina (Aldrich, Brockman I, neutral, activated aluminum oxide) prior to use.

The 337- and 308-nm[33] and the 355-nm LFP equipment with nanosecond[34] and picosecond[35] time resolution have been described previously.

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Registry No. 1, 26864-01-7; TEMPO, 2564-83-2; CCl_4, 56-23-5; $Cl_3C^{\bullet}$, 3170-80-7; $Cl_3COO^{\bullet}$, 69884-58-8; $CHCl_3$, 67-66-3; $CF_2ClCFCl_2$, 76-14-2; CH_2Cl_2, 75-09-2; CH_2Br_2, 74-95-3; $CHBr_3$, 75-25-2; C_2H_5Br, 74-96-4; $C_6H_5CH_2Br$, 100-39-0; CH_3I, 74-88-4; di-*tert*-butyl nitroxide, 2406-25-9; 4-hydroxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl, 2226-96-2; 1,1,3,3-tetramethylisoindolyl-*N*-oxyl, 80037-90-7; 1-oxo-2,2,6,6-tetramethylpiperidinium, 124340-45-0.

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Electrochemical Reduction of 4-Iodo- and 4-Bromoanisole at Mercury and Carbon Cathodes in Dimethylformamide

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In dimethylformamide containing tetramethylammonium perchlorate, cyclic voltammograms for reduction of 4-iodo- and 4-bromoanisole at mercury and carbon electrodes exhibit single irreversible waves corresponding formally to two-electron cleavage of the carbon–halogen bond. In preparative-scale controlled-potential electrolyses of 4-iodoanisole at mercury pool cathodes, a two-to-one mixture of anisole and bis(*p*-anisyl)mercury is obtained at potentials close to the peak potential, whereas anisole is the only species formed at more negative potentials. Reduction of 4-iodoanisole at mercury appears to proceed via *p*-anisyl radicals that (i) yield adsorbed *p*-anisylmercury radicals which disproportionate to give bis(*p*-anisyl)mercury or (ii) undergo further reduction, followed by protonation, to afford anisole. Electrolyses of 4-iodoanisole at carbon electrodes, as well as reduction of 4-bromoanisole at both mercury and carbon, result solely in the production of anisole; presumably, even if *p*-anisyl radicals are generated transiently, they undergo facile reduction to *p*-anisyl carbanions, which are protonated immediately to yield anisole.

There have been numerous publications[1-15] dealing with the electrochemistry of unsubstituted and substituted monohalobenzenes. Whereas most of the papers are concerned either with the effect of various substituents on the polarographic characteristics of monohalobenzenes or with

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