

# Photochemical Reactivity of the Di-*tert*-butyl Nitroxide $\pi, \pi^*$ State and Di-*tert*-butyl Nitroxide Halocarbon Charge-Transfer Excited States

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**Abstract:** The photochemical reactivity of the di-*tert*-butyl nitroxide (DTBN)  $\pi, \pi^*$  state and DTBN-chlorocarbon charge-transfer excited states is described. Irradiation of DTBN in pentane solvent at 254 nm produces the locally excited,  $\pi, \pi^*$  state which yields 2-methyl-2-nitrosopropane (**1**,  $\phi = 0.094$ ) and di-*tert*-butyl-*tert*-butoxyamine (**2**,  $\phi = 0.087$ ). DTBN interacts with carbon tetrachloride and chloroform by contact charge transfer as indicated by the UV-visible spectrum. Irradiation in the DTBN- $\text{CCl}_4$  charge-transfer absorption region yields 2-methyl-2-nitrosopropane (**1**,  $\phi = 0.85$ ), di-*tert*-butylhydroxylammonium chloride (**3**,  $\phi = 0.27$ ), *tert*-butyl chloride (**4**,  $\phi = 0.30$ ), isobutylene (**5**,  $\phi = 0.55$ ), and di-*tert*-butyl(trichloromethoxy)amine (**6**,  $\phi = 0.56$ ). Irradiation in the DTBN- $\text{CHCl}_3$  charge-transfer region yields **1** ( $\phi = 1.01$ ), **3** ( $\phi = 0.60$ ), **4** ( $\phi = 0.06$ ), **5** ( $\phi = 0.99$ ), and di-*tert*-butyl(dichloromethoxy)amine (**7**,  $\phi = 0.56$ ). Irradiation of DTBN at 300 nm in methylene chloride solvent gives products characteristic of the locally excited,  $\pi, \pi^*$  state, **1** and **2** ( $\phi = 0.014$ ), and the DTBN- $\text{CH}_2\text{Cl}_2$  charge-transfer state, **1** ( $\phi = 0.11$ ), **3** ( $\phi = 0.047$ ), **4** ( $\phi = 0.004$ ), **5** ( $\phi = 0.093$ ), and di-*tert*-butyl(chloromethoxy)amine (**8**,  $\phi = 0.050$ ). In all reactions the concentration of DTBN was 0.01 M and quantum yields were measured at approximately 10% reaction. Varying degrees of self-quenching occur. Plots of reciprocal of quantum yield of formation of **1** vs. DTBN concentration are linear with the following slopes and intercepts: pentane solvent,  $1.5 \pm 0.1 \text{ M}^{-1}$ ,  $10.5 \pm 0.1$ ; methylene chloride solvent,  $29 \pm 2 \text{ M}^{-1}$ ,  $7.3 \pm 0.8$ ; chloroform solvent,  $3.5 \pm 0.1 \text{ M}^{-1}$ ,  $0.69 \pm 0.02$ ; carbon tetrachloride solvent,  $0.24 \pm 0.03 \text{ M}^{-1}$ ,  $1.15 \pm 0.02$ , respectively. The reaction in pentane solvent and 35% of the reaction in methylene chloride solvent are proposed to occur via  $\alpha$ -cleavage, and the reactions in chloroform and carbon tetrachloride solvents and 65% of the reaction in methylene chloride solvent are proposed to occur by electron transfer to the chlorocarbon with initial formation of di-*tert*-butyloxoammonium chloride **9** and  $\text{Cl}_n\text{CH}_{3-n}$  radical. Mechanisms are proposed for formation of products from the reactive intermediates.

Although nitroxides, especially di-*tert*-butyl nitroxide (DTBN), have been extensively investigated as quenchers of electronically excited species, little is known about their photochemical reactivity and about the photochemistry of free radicals in general. Two modes of reactivity of some excited, cyclic nitroxides, hydrogen atom abstraction and fragmentation, have been reported. Keana and co-workers have noted the photoreduction of 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxy in toluene solvent with irradiation from black lamps with principal emission at 350 nm.<sup>1</sup> The products are 1,4-dihydroxy-2,2,6,6-tetramethylpiperidine and 1-(benzyloxy)-4-hydroxy-2,2,6,6-tetramethylpiperidine. Spencer and co-workers have described an analogous intramolecular hydrogen atom abstraction from the irradiation of a steroidal doxyl.<sup>2</sup> Intramolecular hydrogen atom abstraction also occurs upon excitation of a *tert*-butyl-substituted cyclic nitronyl nitroxide in protic solvent as reported by Ullman and co-workers.<sup>3</sup> In aprotic solvent a photorearrangement reaction of the nitronyl nitroxide takes place.<sup>4</sup> Keana and Baitis have observed photoelimination of nitric oxide from 3-carbamoyl-2,2,5,5-tetramethylpyrrolinyl-1-oxy and have noted the need for excitation of a higher energy band of the nitroxide to affect reaction.<sup>5</sup> Other photoreactions of free radicals include the photoconversion of triphenylmethyl to bis(biphenylene)diphenylethane and triphenylmethane<sup>6</sup> and the photoreduction of diphenylpicrylhydrazyl to diphenylpicrylhydrazine in solvents possessing benzylic hydrogens.<sup>7</sup>

We report here in detail on the photochemical reactivity of di-*tert*-butyl nitroxide (DTBN) in pentane, carbon tetrachloride, chloroform, and methylene chloride solvents. We have previously communicated (1) that efficient bond homolysis occurs upon

excitation of the  $\pi, \pi^*$  doublet state of DTBN in pentane solvent,<sup>8</sup> (2) that DTBN weakly interacts by contact charge transfer with carbon tetrachloride,<sup>9</sup> and (3) that irradiation in the DTBN- $\text{CCl}_4$  charge-transfer absorption region results in very efficient one-electron transfer to carbon tetrachloride.<sup>9</sup>

## Results and Discussion

**UV-Visible Absorption Spectra.** The UV-visible spectrum of DTBN in pentane solvent shows an  $n-\pi^*$  band at 460 nm ( $\epsilon$  8.9) and a  $\pi-\pi^*$  band at 238 nm ( $\epsilon$  2580).<sup>10</sup> A 0.050 M solution of DTBN in pentane solvent is almost transparent in the region between 310 and 370 nm. A 0.050 M solution of DTBN in carbon tetrachloride solvent, however, shows appreciable absorption in the 310-370-nm region in addition to the  $n-\pi^*$  band at 460 nm (see Figure 1). In methylene chloride solvent there is no additional absorption in the 310-370-nm region relative to absorption in pentane solvent, and in chloroform solvent there is an intermediate level of absorption in this region. More dilute solutions of DTBN in carbon tetrachloride solvent and DTBN-carbon tetrachloride solutions diluted with pentane do not reveal the presence of an additional absorption band maximum.

Absorption in the 310-370-nm region by DTBN in chloroform and carbon tetrachloride solvents can be explained in terms of contact charge transfer.<sup>11</sup> In contact charge transfer the interaction between the donor and the acceptor in the ground state is weak and results simply from contact of the donor and acceptor, possibly even outside the van der Waals contact distance. There is no apparent band maximum because the charge-transfer ground state is at most only a weakly bound state. Contact charge-transfer

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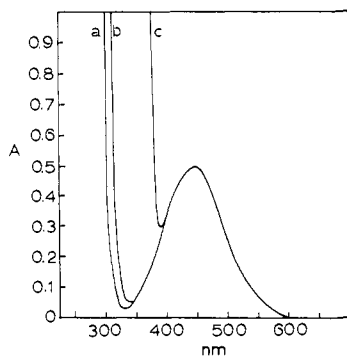


Figure 1. UV-visible absorption spectra of 0.05 M di-*tert*-butyl nitroxide in (a) pentane or methylene chloride, (b) chloroform, and (c) carbon tetrachloride solvents.

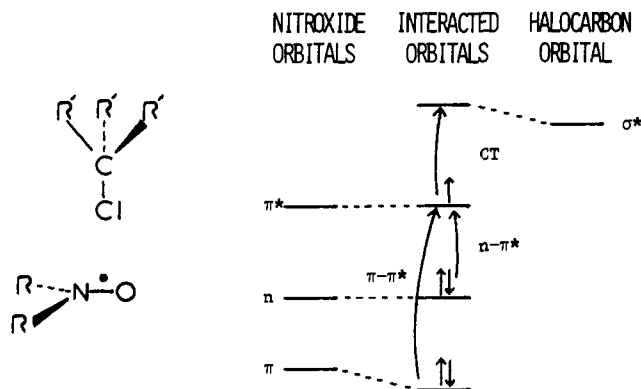


Figure 2. Orbital energy level diagram showing the interaction between halocarbon and nitroxide orbitals for the molecular orientation shown.

absorption has been observed from oxygen,<sup>12</sup> iodine, bromine, and tetranitromethane<sup>13</sup> dissolved in hydrocarbon solvents and from amines dissolved in chloroform solvent.<sup>14</sup>

Evidence for charge-transfer interaction between nitroxides and halocarbons has also been obtained by <sup>13</sup>C NMR spectroscopy.<sup>15</sup> In this study unrestricted Hartree-Fock SCF-MO calculations of various orientations of DTBN and halocarbon were performed. The calculations suggested more interaction of the nitroxide  $\pi$  orbitals than the nitroxide  $n$  orbital with a halocarbon antibonding orbital.

The various UV-visible absorptions of DTBN in halocarbon solvents can be rationalized, although in oversimplified terms, by using the orbital energy level diagram shown in Figure 2. For the charge-transfer interaction the halocarbon is oriented to allow interaction of a halocarbon  $\sigma^*$  orbital with the nitroxide  $\pi$  orbital. The halocarbon  $\sigma^*$  orbital has the proper symmetry for interaction with the nitroxide  $\pi$  orbital but not the nitroxide  $\pi^*$  orbital. The large energy separation between the nitroxide  $\pi$  orbital and the halocarbon  $\sigma^*$  orbital accounts for the weakness of the interaction in the ground state.

**Photochemical Reactivity of DTBN in Various Solvents.** Irradiation of the  $n-\pi^*$  band of DTBN in pentane solvent results in no destruction; however, irradiation of the  $\pi-\pi^*$  band at 254 nm results in efficient formation of 2-methyl-2-nitrosopropane (**1**,  $\phi = 0.094$ ) and di-*tert*-butyl-*tert*-butoxyamine (**2**,  $\phi = 0.087$ ). The quantum yields of destruction of DTBN and formation of **1** were measured by using visible spectrophotometric analysis, and the quantum yield of formation of **2** was measured by using GLC analysis. The quantum yield of formation of **1** is slightly dependent

Table I. Quantum Yields of Product Formation and DTBN Destruction in Various Solvents<sup>a</sup>

substance	quantum yields as a function of solvent and wavelength			
	CCl <sub>4</sub> (366 ± 10 nm)	CHCl <sub>3</sub> (310 ± 10 nm)	CH <sub>2</sub> Cl <sub>2</sub> (300 ± 10 nm)	pentane (254 ± 33 nm)
DTBN	1.7	2.0	0.21	0.21
(CH <sub>3</sub> ) <sub>3</sub> CNO ( <b>1</b> )	0.85	1.01	0.11	0.094
((CH <sub>3</sub> ) <sub>3</sub> C) <sub>2</sub> -N <sup>+</sup> HOHCl <sup>-</sup> ( <b>3</b> )	0.27	0.60	0.047 <sup>b</sup>	
(CH <sub>3</sub> ) <sub>3</sub> CCl ( <b>4</b> )	0.30	0.06	0.004 <sup>b</sup>	
(CH <sub>3</sub> ) <sub>2</sub> C=CH <sub>2</sub> ( <b>5</b> )	0.55	0.99	0.093 <sup>b</sup>	
((CH <sub>3</sub> ) <sub>3</sub> C) <sub>2</sub> -NOCCl <sub>n</sub> H <sub>3-n</sub> ( <b>6-8</b> )	0.56	0.56	0.050 <sup>b</sup>	
((CH <sub>3</sub> ) <sub>3</sub> C) <sub>2</sub> -NOC(CH <sub>3</sub> ) <sub>3</sub> ( <b>2</b> )			0.014	0.087

<sup>a</sup> Samples were 0.10 M in DTBN. <sup>b</sup> These values were calculated by assuming the proposed mechanism (vide infra).

Table II. Quantum Yields of Formation of 2-Methyl-2-nitrosopropane as a Function of DTBN Concentration and Solvent<sup>a</sup>

[DTBN], M	$\phi$ in pentane	$\phi$ in CCl <sub>4</sub>	$\phi$ in CHCl <sub>3</sub>	$\phi$ in CH <sub>2</sub> Cl <sub>2</sub>
0.10	0.094	0.87	1.01	0.105
0.16				0.079
0.20	0.092	0.83	0.83	
0.39				0.052
0.40	0.090	0.78	0.49	
0.60	0.088	0.79	0.37	0.041
0.72			0.32	
0.80	0.085	0.76		0.033
1.00		0.72		

<sup>a</sup> Samples in pentane, carbon tetrachloride, chloroform, and methylene chloride were irradiated to low conversion ( $\leq 10\%$ ) at 254 ± 33, 366 ± 10, 310 ± 10, and 300 ± 10 nm, respectively.

on the concentration of DTBN with an inverse relationship. The various quantum yields are summarized in Tables I and II.

Irradiation of the  $n-\pi^*$  band of DTBN in carbon tetrachloride solvent again results in no reaction. Irradiation in the charge-transfer absorption region at 313 or 366 nm, however, results in very efficient destruction ( $\phi = 1.7$ ). The products are 2-methyl-2-nitrosopropane (**1**), di-*tert*-butylhydroxylammonium chloride (**3**), *tert*-butyl chloride (**4**), isobutylene (**5**), and di-*tert*-butyl(trichloromethoxy)amine (**6**). Hexachloroethane is not formed, and the solution is not significantly paramagnetic when the reaction is carried to completion. The quantum yields of destruction of DTBN and formation of **1** were again determined by using spectrophotometric analysis. The quantum yield of formation of **4** was measured by using GLC analysis. The quantum yields of formation of **4** and the other products were calculated from product ratios at completion and the quantum yield of formation of **1**. Product ratios were obtained by <sup>1</sup>H NMR spectroscopy and by a gravimetric determination in the case of **3**. The quantum yield of formation of 2-methyl-2-nitrosopropane is again inversely related to the concentration of DTBN, and the quantum yields are summarized in Tables I and II.

The photoreaction of DTBN in chloroform solvent is analogous to that of DTBN in carbon tetrachloride solvent. The  $n, \pi^*$  state is photoinert. Irradiation at 313 nm very efficiently destroys DTBN ( $\phi = 2.0$ ) producing **1**, **3**, **4**, **5**, and di-*tert*-butyl(dichloromethoxy)amine (**7**). The quantum yields, determined in the same manner as determined for the irradiation of DTBN in carbon tetrachloride solvent, are reported in Tables I and II. The dependence of the quantum yield of formation of **1** on DTBN concentration is more dramatic than observed in pentane or carbon tetrachloride solvents.

The  $n, \pi^*$  state of DTBN in methylene chloride solvent is also photoinert. Irradiation of DTBN at 300 nm in methylene chloride solvent destroys DTBN although with significantly lower efficiency

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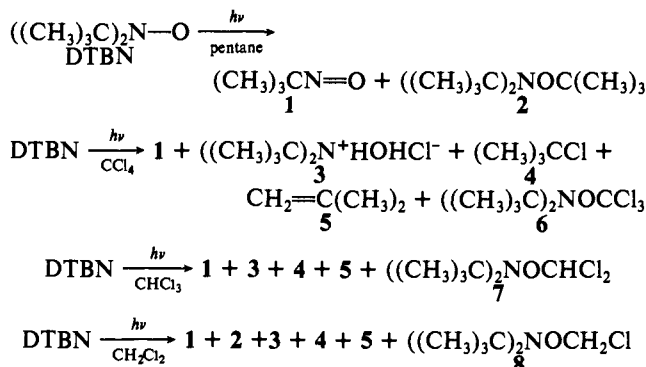
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Morhisima, I.; Inubushi, T.; Endo, K.; Yonezawa, T.; Goto, K. *J. Am. Chem. Soc.* **1972**, *94*, 4812.

Morhisima, I.; Inubushi, T.; Yonezawa, T. *Ibid.* **1976**, *98*, 3808.

than similar irradiation of DTBN in chloroform or carbon tetrachloride solvent ( $\phi = 0.21$ ). The products are **1**, **2**, **3**, **4**, **5**, and di-*tert*-butyl(chloromethoxy)amine (**8**). The products formed from irradiation of DTBN in methylene chloride solvent and the other solvents are summarized in Scheme I. The quantum yields of

#### Scheme I



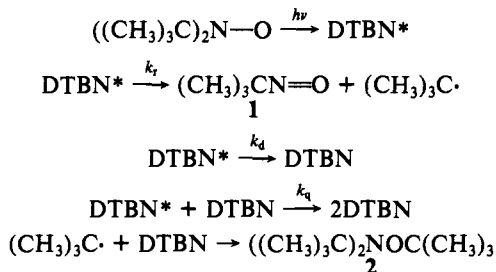
destruction of DTBN and formation of **1** and **2** were determined by using the analytical techniques described above. The ratio of **3** to **8** at completion was determined by <sup>1</sup>H NMR spectroscopy. The quantum yields of formation of **3**, **4**, **5**, and **8** were calculated from the data assuming a mechanism for reaction analogous to that which satisfies the quantum yield data for reaction in the other solvents (*vide infra*). The calculated and measured quantum yields are reported in Tables I and II. The dependence of the quantum yield of formation of **1** on DTBN concentration is similar to that observed in chloroform solvent.

The (mono-, di-, and trichloromethoxy)amine products (**6**, **7**, and **8**) are unstable. Isolation proved to be difficult and/or impossible. When **6** was isolated and subsequently dissolved in polar solvents, it rapidly and sometimes violently decomposed with the noticeable odor of phosgene. In the injection port of a gas chromatograph **6** is also unstable, decomposing to phosgene as the only volatile product which was identified by GC-mass spectrometry. Structures were assigned to **6**, **7**, and **8** from the spectroscopic data reported in the Experimental Section.

The structural assignment for di-*tert*-butylhydroxylammonium chloride (**3**) was made from a comparison of its spectral properties and chemical properties with those of the known compound.<sup>16</sup> In particular, treatment of **3** with a sodium hydroxide solution followed by air oxidation yielded DTBN.

**Proposed Mechanisms for the Photochemical Reactions.** Formation of 2-methyl-2-nitrosopropane (**1**) and di-*tert*-butyl-*tert*-butoxyamine (**2**) from irradiation of DTBN at 254 nm is satisfactorily explained in terms of homolytic cleavage  $\alpha$  to the nitrogen to give **1** and *tert*-butyl radical (Scheme II). Subsequent combination of

#### Scheme II

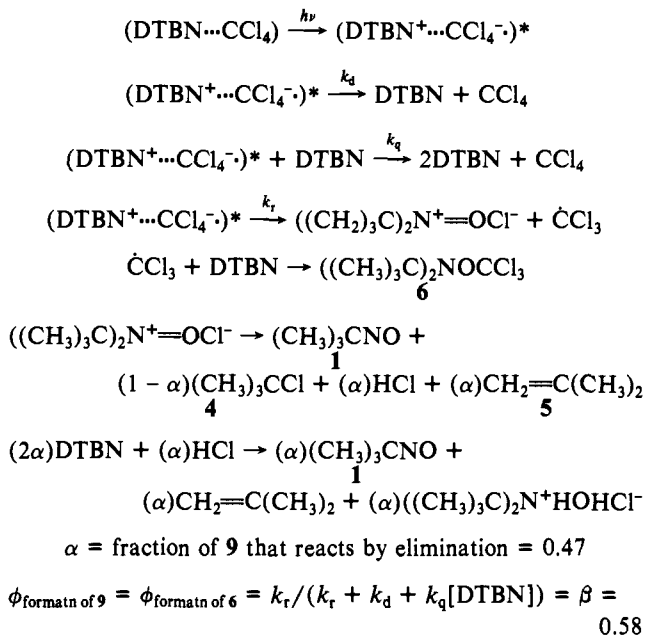


*tert*-butyl radical and DTBN yields **2**. The reaction, however, is more characteristic of an  $n, \pi^*$  state than a  $\pi, \pi^*$  state. Because of the low energy of the  $n, \pi^*$  state,  $\alpha$ -cleavage in this state may be slow even though the C-N bond is weak.<sup>17</sup> Cleavage in the  $\pi, \pi^*$  state appears to be symmetry forbidden.<sup>18</sup> The apparent

forbiddenness may be circumvented by nonplanarity of the nitroxide functional group in the excited state. The ground state of the nitroxide functional group is predicted to deviate from planarity by unrestricted Hartree-Fock SCF-MO calculations.<sup>10c</sup> A reviewer has suggested that  $\alpha$ -cleavage might logically arise from a  $n, \sigma^*$  state and that the  $n, \sigma^*$  transition might be obscured by the more intense  $\pi, \pi^*$  transition. This is also a reasonable possibility. MO calculations assuming a planer geometry for the ground and excited states predict that the  $n, \sigma^*$  transition should be 1.5-eV higher energy than the  $\pi, \pi^*$  transition of dimethyl nitroxide; however, the author concludes that this energy difference may be within the error in the calculations introduced by the approximations.<sup>10b</sup> The  $\alpha$ -cleavage reaction of DTBN and its wavelength dependence are analogous to the photoelimination of nitric oxide from 3-carbamoyl-2,2,5,5-tetramethylpyrrolinyl-1-oxy.<sup>5</sup>

The products and stoichiometry of the irradiation of DTBN in carbon tetrachloride solvent can be explained as shown in Scheme III. The primary photochemical event in the contact

#### Scheme III



$$\phi_{\text{DTBN destructn}} = \beta(2 + 2\alpha) = 1.7$$

charge-transfer excited state is electron transfer from DTBN to  $\text{CCl}_4$  with formation of di-*tert*-butyloxoammonium chloride (**9**) and trichloromethyl radical. Di-*tert*-butyloxoammonium chloride is unstable and decomposes to 2-methyl-2-nitrosopropane, isobutylene, *tert*-butyl chloride, and hydrogen chloride by elimination and nucleophilic substitution. Cyclic oxoammonium halides have been reported as unstable products from oxidation of cyclic nitroxides by chlorine,<sup>19</sup> bromine,<sup>20</sup> nitrogen dioxide,<sup>21</sup> and peroxides.<sup>22</sup> The fraction of oxoammonium chloride that decomposes to isobutylene and hydrogen chloride is designated by the symbol  $\alpha$ . Reaction of DTBN with hydrogen chloride gives 2-methyl-2-nitrosopropane (**1**), isobutylene (**5**), and di-*tert*-butylhydroxylammonium chloride (**3**). Reaction of nitroxides with hydrogen chloride has been noted previously.<sup>16,23</sup> We have shown

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Table III. Observed and Calculated Quantum Yields<sup>a</sup>

product	quantum yield expressn <sup>b</sup>	obsd	calcd	obsd	calcd
		$\phi$ in CCl <sub>4</sub>	$\phi$ in CCl <sub>4</sub>	$\phi$ in CHCl <sub>3</sub>	$\phi$ in CHCl <sub>3</sub>
(CH <sub>3</sub> ) <sub>3</sub> CCl	$\beta(1 - \alpha)$	0.30 <sup>c</sup>		0.06	0.04
(CH <sub>3</sub> ) <sub>3</sub> CNO	$\beta(1 + \alpha)$	0.85	0.85	1.01	1.02
6 or 7	$\beta$	0.56	0.58	0.56	0.54
3	$\alpha\beta$	0.27	0.27	0.60	0.52
CH <sub>2</sub> =C(CH <sub>3</sub> ) <sub>2</sub>	$2\alpha\beta$	0.55	0.54	0.88 <sup>c</sup>	

<sup>a</sup> Quantum yields were measured at 366 nm in carbon tetrachloride solvent and at 313 nm in chloroform solvent with 0.10 M argon-degassed solutions of DTBN. <sup>b</sup> The symbol  $\alpha = 0.47$  (CCl<sub>4</sub>) and 0.92 (CHCl<sub>3</sub>) represents the fraction of di-*tert*-butyloxammonium chloride (9) which decomposes to isobutylene and hydrogen chloride. The symbol  $\beta = 0.58$  (CCl<sub>4</sub>) and 0.54 (CHCl<sub>3</sub>) represents the quantum yield of reaction of the charge-transfer excited state (see Scheme I). <sup>c</sup> This quantum yield together with the quantum yield of destruction of DTBN was used to calculate  $\alpha$  and  $\beta$ .

Table IV. Quantum Yield Expressions for the Photoreaction of DTBN in Methylene Chloride Solvent<sup>a</sup>

compd	quantum yield expressn	compd	quantum yield expressn
DTBN	$2\beta(1 + \alpha) + 2\gamma$	CH <sub>2</sub> =C(CH <sub>3</sub> ) <sub>2</sub>	$2\alpha\beta$
(CH <sub>3</sub> ) <sub>3</sub> CNO	$\beta(1 + \alpha) + \gamma$	8	$\beta$
3	$\alpha\beta$	2	$\gamma$
(CH <sub>3</sub> ) <sub>3</sub> CCl	$\beta(1 - \alpha)$		

<sup>a</sup> The symbol  $\alpha$  represents the fraction at di-*tert*-butyloxammonium chloride (9) which decomposes to isobutylene and hydrogen chloride.

by <sup>1</sup>H NMR spectroscopy that DTBN reacts with hydrogen chloride in carbon tetrachloride solvent to give **1**, **3**, and **5** in an equimolar ratio as proposed in Scheme III. The trichloromethyl radical is efficiently scavenged by a second equivalent of DTBN to give the alkoxyamine **6**.

The quantum yields for the reaction in carbon tetrachloride are completely consistent with the mechanism in Scheme III as shown in Table III. The mechanism predicts as observed that the quantum yield of formation of 2-methyl-2-nitrosopropane is exactly half of the quantum yield of destruction of DTBN. The quantum yield of reaction of the charge-transfer excited state ( $\beta$ ) and the fraction of the oxoammonium chloride decomposing by elimination ( $\alpha$ ) can be calculated from the quantum yields of destruction of DTBN and formation of *tert*-butyl chloride by using the quantum yield expressions in Table III and are 0.58 and 0.47, respectively. Similarly, the quantum yields of formation of **3**, **5**, and **6** can be calculated. The observed and calculated quantum yields agree well within the experimental error of the measurements and are compared in Table III.

The photochemistry of DTBN in chloroform solvent can also be explained by using the mechanism in Scheme III. The DTBN chloroform charge-transfer excited state now yields di-*tert*-butyloxammonium chloride and dichloromethyl radical. Trapping of dichloromethyl with DTBN gives **7**. Due to the low quantum yield of *tert*-butyl chloride formation, the quantum yield of isobutylene formation was used along with the quantum yield of DTBN destruction to calculate the values of  $\alpha$  and  $\beta$  which are 0.92 and 0.54, respectively. Again the calculated quantum yields show good agreement with the observed ones as shown in Table III. The large value of  $\alpha$  indicates that chloride ion is a better base in chloroform solvent than in carbon tetrachloride solvent.

A mechanism for product formation from irradiation of DTBN in methylene chloride solvent is a little more complicated. Products formed (Scheme I) are characteristic of both the locally excited  $\pi, \pi^*$  doublet state and the DTBN solvent charge-transfer state. The simplest mechanism then is approximately a combination of the mechanisms for photoreaction in pentane and carbon tetrachloride solvents utilizing a single excited state, the  $\pi, \pi^*$  doublet state. Reactivity of the excited state via electron transfer to methylene chloride yields **9** and chloromethyl radical which is

Table V. Calculated Rates of Reaction and Decay of Excited DTBN and Excited-State Lifetimes of DTBN in Various Solvents Based on Plots of Reciprocal of Quantum Yield of 2-Methyl-2-nitrosopropane Formation vs. DTBN Concentration<sup>a</sup>

solvent	slope, M <sup>-1</sup>	intercept	10 <sup>-10</sup> .			$\tau$ , ns
			$k_{diff}^b$ , M <sup>-1</sup> s <sup>-1</sup>	10 <sup>-10</sup> .	10 <sup>-10</sup> .	
pentane	1.5 ± 0.1	10.5 ± 0.1	4	3	30	0.003
CH <sub>2</sub> Cl <sub>2</sub>	29 ± 2	7.3 ± 0.8	0.8	0.01 <sup>c</sup>	0.2	0.5
CHCl <sub>3</sub>	3.5 ± 0.1	0.69 ± 0.05	2	0.3	0.03	0.3
CCl <sub>4</sub>	0.24 ± 0.03	1.15 ± 0.02	1	3	2	0.02

<sup>a</sup> Rate constants were calculated from the quantum yield expressions for the proposed mechanisms, the slopes and intercepts of the quenching plots, and the assumption that DTBN quenches at diffusion controlled rates. <sup>b</sup> Rates of diffusion were taken from ref 26. <sup>c</sup> This rate constant is the sum of the rate constants for  $\alpha$ -cleavage and electron transfer to methylene chloride.

trapped with DTBN to give **8**. Reactivity via  $\alpha$ -cleavage gives **1** and **2**. Quantum yields expressions for this combined mechanism are shown in Table IV. The quantum yield of formation of di-*tert*-butyl-*tert*-butoxyamine (**2**) and di-*tert*-butyl(chloromethoxy)amine (**8**) are assigned the symbols  $\gamma$  and  $\beta$ , respectively, and the symbol  $\alpha$  has the same meaning as before. The values 0.94 and 0.050 for  $\alpha$  and  $\beta$  were calculated from the quantum yield of formation of 2-methyl-2-nitrosopropane and the ratio of **8** to **3**, equal to 0.97. The quantum yields of formation of **3**, **4**, **5**, and **8** reported in Table I were calculated from  $\alpha$  and  $\beta$  by using the quantum yield expressions in Table IV.

A mechanism more complex than indicated above cannot be eliminated for the reaction in methylene chloride solvent. Reaction may occur from two distinct excited states, the locally excited  $\pi, \pi^*$  state and the solvent charge-transfer state. The two states may also be in equilibrium. Alternatively, the solvent charge-transfer state may actually be an exciplex formed from the locally excited,  $\pi, \pi^*$  state.

Di-*tert*-butyl nitroxide is an efficient quencher of electronically excited species at or near diffusion-controlled rates. The mechanism of quenching is generally thought to be either an electron-exchange relaxation process or vibrational quenching where a complex deactivates directly to ground state.<sup>24</sup> The  $\pi, \pi^*$  state or solvent charge-transfer states of DTBN in principle can be quenched by DTBN via the electron-exchange mechanism, by vibrational quenching with the intermediacy of a complex, by collisional energy transfer with formation of the lower energy, unreactive  $n, \pi^*$  state, or by a long-range Förster-type mechanism. Kinka and Faulkner have proposed a Förster-type mechanism for the quenching of fluorescence from anthracene, perylene, and fluoranthene by Wurster's Blue cation radical (the cation radical of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine).<sup>25</sup> We have observed that the quantum yields of formation of 2-methyl-2-nitrosopropane (**1**) in pentane, carbon tetrachloride, chloroform, and methylene chloride solvents are inversely related to the concentration of DTBN (Table II) and propose that DTBN is operating as a quencher of the reactive excited state. Plots of reciprocal of quantum yield of formation of **1** vs. DTBN concentration are linear and are reported in Table V. From the quantum yield expressions, the slope and intercepts of the quenching plots, and the assumption that DTBN quenches at diffusion-controlled rates,<sup>26</sup> the rates of reaction of the excited states and of internal conversion can be calculated and are summarized in Table V. The actual rate of quenching may deviate from the rate of diffusion depending upon the mechanism. The rate constants in Table V, however, can still be compared unless the deviation from the rate of diffusion is solvent dependent. The

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rates of internal conversion are consistent with the anticipated short lifetimes for the proposed reactive upper excited states.<sup>27</sup> The rate constants for reaction of the charge-transfer excited states parallel the stability of the chloromethyl radicals produced and the reduction potentials of the halocarbon solvents.<sup>28</sup>

A possible alternate route to the oxoammonium chloride **9** is chlorine atom abstraction by excited DTBN to form a hypochlorite and the trichloromethyl radical. The hypochlorite might then react via an intramolecular redox process to give di-*tert*-butyloxammonium chloride. We do not favor this process for the primary photochemical event for the following reasons. (1) The reaction does not occur from the  $n,\pi^*$  state, the state associated with atom abstraction. (2) There is a definite charge-transfer interaction between DTBN and the halocarbon solvents observed in the UV spectrum, and the degree of charge-transfer interaction parallels the half-wave electrode reduction potentials of the solvents.<sup>28</sup> (3) Ground-state DTBN is known to react as a one-electron reducing agent with easily reduced compounds such as peroxides.<sup>20</sup> (4) The photochemical reactivity described here is preceded in the photochemical reactions of amines with halogenated solvents which most likely occur by one-electron transfer.<sup>14</sup>

In summary we have reported that di-*tert*-butyl nitroxide (DTBN) is labile when in the  $\pi,\pi^*$  state and when a partner with some halocarbons in charge-transfer excited states. In the  $\pi,\pi^*$  state reactivity is via  $\alpha$ -cleavage and in the charge-transfer excited states, via electron transfer. We note that the efficiency of reaction in the charge-transfer excited states can be high and caution the use of nitroxides as quenchers in solvents of moderate to low reduction potential.

### Experimental Section

Infrared spectra were recorded by using a Perkin-Elmer Model 337 infrared spectrophotometer. NMR spectra were obtained by using Varian EM-390 and JOEL PFT-100 spectrometers, and chemical shifts are reported in parts per million on the  $\delta$  scale from internal tetramethylsilane. Mass spectra were obtained at 70 eV by using a Varian MAT CH-5 mass spectrometer. GLC analyses were performed with a Varian Aerograph Model 1700 gas chromatograph equipped with a thermal conductivity detector, and peak areas were measured by Disc integration. UV-visible absorption data were obtained with a Beckman DU spectrometer modified with Gilford electronics and with a Varian Techtron Model 635 spectrometer.

**Quantum Yield Measurements.** Quantum yield measurements were performed with a linear-type quantum yield apparatus consisting of a Bausch and Lomb 250-mm monochromator equipped with a UV-visible grating blazed at 300 nm, a 200-W Bausch and Lomb super-pressure mercury light source, and a thermostated cell compartment maintained at  $20 \pm 0.5$  °C. The monochromator was adjusted for irradiation with a 22nm band-pass at all wavelengths described except at 254 nm where the band-pass was 66 nm. A circular rotating shutter with a 72.5° or 46° sector removed was attached between the monochromator and the sample compartment to attenuate the light intensity for actinometry measurements.

Potassium ferrioxalate actinometry was used to measure light intensity.<sup>29</sup> Solutions (3.0 mL) of  $1.3 \times 10^{-2}$  M ferrioxalate were irradiated for 300 s with the rotating sector. The light intensity without the rotating sector was in the range of  $10^{16}$ – $10^{17}$  quanta/s.

Samples (2.8 mL) of the appropriate concentration of di-*tert*-butyl nitroxide (DTBN) were prepared in spectrograde solvents in quartz cuvettes with tight-fitting, Teflon stoppers. The samples were oxygen degassed by bubbling a slow stream of argon through the solutions for 1 min prior to irradiation.

Quantitative measurements of product formation and DTBN destruction were made by using absorption spectroscopy, GLC with internal standards, <sup>1</sup>H NMR spectroscopy, and in one case a gravimetric determination. The concentrations of DTBN and 2-methyl-2-nitrosopropane (**1**) were determined at low conversion ( $\leq 10\%$ ) spectrophotometrically at 460 and 680 nm, respectively. Both DTBN and 2-methyl-2-nitrosopropane concentrations were obtained from Beer's law plots at the re-

spective wavelengths in the various solvents. Di-*tert*-butyl-*tert*-butoxyamine (**2**) concentration was measured at low conversion ( $\leq 10\%$ ) by GLC with a 1.2 m  $\times$  0.64 cm column of 5% silicone vacuum grease on 60/80 mesh Chromosorb W at 60 °C (He, 60 mL/min) with ethylbenzene as an internal standard, correcting for differences in thermal conductivity. *tert*-Butyl chloride (**4**) concentration was measured by GLC at low conversion ( $\leq 10\%$ ) with the same column at ambient temperature (He, 60 mL/min) with hexane as an internal standard, again correcting for differences in thermal conductivity. The extent of formation of di-*tert*-butylhydroxylammonium chloride (**3**) was measured gravimetrically at high conversion. Product ratios were determined by <sup>1</sup>H NMR spectroscopy at high conversion. The quantum yields of formation were then calculated from the quantum yields of 2-methyl-2-nitrosopropane formation at low conversion determined spectrophotometrically and the product ratios.

**Isolation of Di-*tert*-butylhydroxylammonium Chloride (**3**) from Irradiation of DTBN in Carbon Tetrachloride.** A 100-mL sample of 0.10 M DTBN in spectral grade carbon tetrachloride was placed in a water-cooled, Pyrex, irradiation vessel, degassed with a stream of nitrogen, and irradiated in a Rayonet Reactor with 3500-Å lamps for 15 min. Spectroscopic analysis at 460 nm indicated greater than 95% destruction of DTBN. A solid product which precipitated as colorless needles was isolated by suction filtration. The product (0.22 g, 14% relative to DTBN destroyed) melted with decomposition at 175–185 °C and was identified as di-*tert*-butylhydroxylammonium chloride (**3**) by comparison of its spectral and chemical properties with those of the known compound. The spectral properties are as follows: IR (KBr) 3.36, 3.67, 3.95, 6.78, 7.17, 7.25  $\mu\text{m}$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.62 (s, 18 H), 10.6 (d, 1 H,  $J = 6$  Hz), 11.33 (d, 1 H,  $J = 6$  Hz). The product was dissolved in 10 mL of 10% aqueous sodium hydroxide and extracted with three 10-mL portions of ether. The ether extracts were combined and dried with sodium hydroxide. Rotary evaporation of the ether yielded 0.13 g (75%) of a white solid, di-*tert*-butylhydroxylamine, which gave the following infrared absorptions: IR (KBr) 2.90, 3.38, 6.75, 7.21, 7.35  $\mu\text{m}$ . The di-*tert*-butylhydroxylamine readily air oxidized to di-*tert*-butyl nitroxide.

**Determination of Quantum Yields of Product Formation from Irradiation of DTBN in Carbon Tetrachloride.** The quantum yield of formation of 2-methyl-2-nitrosopropane from irradiation of 0.10 M DTBN in carbon tetrachloride at  $366 \pm 10$  nm was determined spectrophotometrically at low conversion as described above. The quantum yields of formation of the other products were determined as follows. A 2.8-mL sample of 0.10 M DTBN in carbon tetrachloride was irradiated to completion at  $366 \pm 10$  nm as indicated by the appearance of a sky blue color and the generation of a flocculent white precipitate. After the solution was cooled in a refrigerator, the white precipitate was isolated by suction filtration, dried, and weighed. The precipitate was di-*tert*-butylhydroxylammonium chloride (**3**). The blue filtrate was analyzed by <sup>1</sup>H NMR spectroscopy. Integration of the hydrogen absorbances or expansion of appropriate NMR signals and area determination by triangulation gave the relative abundance of the other products. The quantum yields of formation were determined from the product ratios relative to 2-methyl-2-nitrosopropane (**1**) and the quantum yield of formation of 2-methyl-2-nitrosopropane. <sup>1</sup>H NMR analysis gave a quantum yield of *tert*-butyl chloride (**4**) formation of 0.27 and GLC analysis as described above in a separate experiment at low conversion gave a quantum yield of *tert*-butyl chloride formation of 0.33. An average quantum yield of 0.30 for formation of *tert*-butyl chloride is reported in Table I. Calculated and observed quantum yields for all products are also reported in Table I.

Di-*tert*-butyl(trichloromethoxy)amine (**6**) was isolated by vacuum evaporation of all volatile components after removal of di-*tert*-butylhydroxylammonium chloride by filtration. The waxy off-white solid (mp 40–45 °C) obtained, slowly decomposed during isolation. When dissolved in more polar solvents, it rapidly and sometimes violently decomposed with the noticeable odor of phosgene. The product was characterized as di-*tert*-butyltrichloromethoxyamine (**6**) from the following spectral properties: IR (CCl<sub>4</sub>) no N–H, OH, or multiple-bond stretching bands; <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta$  1.39 (s); <sup>13</sup>C NMR (CCl<sub>4</sub> + DCCl<sub>3</sub>)  $\delta$  30.3 (strong), 64.1 (weak), 119.8 (weak); mass spectrum,  $m/e$  196, 194, 192, 190 (M – CH<sub>3</sub> – C<sub>4</sub>H<sub>9</sub>), 144 (M – CCl<sub>3</sub>), 128 (M – OCCl<sub>3</sub>), 98, 88, 72, 71, 65, 63, 58, 57, 56. The <sup>13</sup>C NMR spectrum was obtained with a sample which was not vacuum evaporated to dryness.

**Determination of Quantum Yields of Product Formation from Irradiation of DTBN in Chloroform.** The quantum yield of formation of 2-methyl-2-nitrosopropane (**1**) from irradiation of 0.10 M DTBN in chloroform at  $310 \pm 10$  nm was determined spectrophotometrically at low conversion (vide supra). The quantum yields of formation of all the other products from irradiation of DTBN under the same conditions were determined by using the method described above for irradiation in carbon tetrachloride except the quantum yield of formation of *tert*-butyl chloride

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was not determined separately by GLC at low conversion. Calculated and observed quantum yields are reported in Table I. Di-*tert*-butyl(dichloromethoxy)amine (7) was not sufficiently stable for isolation. It was characterized from the  $^1\text{H}$  NMR spectrum ( $\text{DCCl}_3$ ) which showed singlets at  $\delta$  1.28 (18 H) and 7.80 (1 H).

**Determination of Quantum Yields of Product Formation from Irradiation of DTBN in Methylene Chloride.** The quantum yield of formation of 2-methyl-2-nitrosopropane (1) from irradiation of 0.10 M DTBN in methylene chloride at  $300 \pm 10$  nm was determined spectrophotometrically at low conversion (*vide supra*). The quantum yield of formation of di-*tert*-butyl-*tert*-butoxyamine (2) was determined in the same experiment by GLC (*vide supra*). The ratio of the quantum yields of formation of di-*tert*-butylhydroxylammonium chloride (3) and di-*tert*-butyl(chloromethoxy)amine (8) was determined as follows. A 2.8-mL sample of 0.10 M DTBN in methylene chloride was irradiated for 3 h at  $300 \pm 10$  nm at which time the solution was a blue green color. Vacuum distillation of all volatile materials was followed by  $^1\text{H}$  NMR analysis. Integration of the NMR spectrum showed the ratio of 3 to 8 to be 0.97. Di-*tert*-butyl(chloromethoxy)amine (8) was not sufficiently

stable for isolation. It was characterized from the  $^1\text{H}$  NMR spectrum ( $\text{CH}_2\text{Cl}_2$ ) which showed singlets at  $\delta$  1.41 (18 H) and 5.53 (2 H). Because 2-methyl-2-nitrosopropane is photolabile and absorbs light at wavelengths less than 300 nm, determination of the relative quantum yields of formation of the volatile products by  $^1\text{H}$  NMR spectroscopy after irradiation to completion was impossible. The calculated and observed quantum yields are reported in Table I.

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## Reactivity Control in Micelles and Surfactant Vesicles. Kinetics and Mechanism of Base-Catalyzed Hydrolysis of 5,5'-Dithiobis(2-nitrobenzoic acid) in Water, Hexadecyltrimethylammonium Bromide Micelles, and Dioctadecyldimethylammonium Chloride Surfactant Vesicles

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**Abstract:** Rate constants have been determined for the hydrolysis of 5,5'-dithiobis(2-nitrobenzoic acid) (DTNB) as functions of hydroxide ion concentrations in water, micellar hexadecyltrimethylammonium bromide (CTAB), and dioctadecyldimethylammonium chloride (DODAC) surfactant vesicles. The observed second-order rate constants at 26.4 °C in micellar CTAB ( $8.4 \text{ M}^{-1} \text{ s}^{-1}$ ) and in DODAC surfactant vesicles ( $840 \text{ M}^{-1} \text{ s}^{-1}$ ) are approximately 15- and 1500-fold larger than that in water ( $0.54 \text{ M}^{-1} \text{ s}^{-1}$ ). The rate-concentration profiles in both surfactant systems fit the pseudophase-type models of micellar catalysis. The "true" second-order rate constants in the pseudophases of micelles and surfactant vesicles are 0.1-1.1 and 0.75-7.7  $\text{M}^{-1} \text{ s}^{-1}$ , respectively. Rate enhancements are the consequences of highly increased DTNB and hydroxide ion concentrations in the micelles and surfactant vesicles. Binding constants for the association of DTNB with micellar CTAB and DODAC vesicles, determined spectrophotometrically as well as derived from the kinetic treatments, are approximately  $(1-3) \times 10^4$  and  $(1-4) \times 10^4 \text{ M}^{-1}$ . Binding constants for the hydroxide ion association with CTAB micelles and DODAC vesicles, determined from the kinetic data, are  $(1-2) \times 10^2$  and  $(3-8) \times 10^2 \text{ M}^{-1}$ , respectively. Kinetic treatments derived from micellar catalysis are also applicable to surfactant vesicles.

### Introduction

The influence of environmental factors on chemical reactions in various organized systems is of considerable current interest. Incorporation of reactants in micellar aggregates dramatically affects their apparent reactivity compared to that observed in water.<sup>3</sup> Enhanced rate effects have been rationalized in terms of favorable reagent distribution and/or changes in the apparent dissociation constants of ionizable functional groups.<sup>4-6</sup> Several quantitative kinetic treatments have been developed to assess the

intrinsic reactivity in micelles.<sup>4-12</sup>

Completely synthetic surfactant vesicles have also been utilized as models for interfacial effects on chemical reactivity and for membrane-mediated processes.<sup>13</sup> Vesicles readily form upon

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