Table VII

| diene | $T$, °C | irradiation time, min | % product 1 | 2 | 3 |
|---|---|---|---|---|---|
| 2 | -80 | 150 | 0 | 100 | 0 |
| | -40 | 30 | 2.2 | 96.8 | 1.0 |
| | -40 | 60 | 4.9 | 93.2 | 1.9 |
| 3 | -80 | 150 | 0 | 97.0 | 3.0 |
| | -40 | 30 | 2.1 | 88.2 | 9.7 |
| | -40 | 60 | 6.5 | 74.7 | 18.8 |

## Experimental Section

Preparative gas chromatographic separations were accomplished on a Gow-Mac gas chromatograph utilizing a 0.25 in. × 30 ft column packed with 20% Carbowax 20M on NAW 80/100 Chromosorb W. The retention times for the *E,E* isomer **1** was 141 min; the *E,Z* isomer **2**, 153 min; and the *Z,Z* isomer **3**, 159 min when the temperature of the column was set to 115 °C, the injector to 200 °C, the detector to 200 °C, and the He flow rate to 120 mL/min.

The UV spectra for dienes **1**–**3** were obtained in HPLC grade *n*-heptane on a Hitachi UV-visible spectrophotometer.

$^1$H and $^{13}$C NMR spectra were obtained on a JEOL FX270 spectrometer at 270 and 63.8 MHz, respectively, and all the chemical shifts were referenced to $Me_4Si$. Product ratios were determined by cutting and weighing peaks from expanded proton NMR spectra.

Acetone-$d_6$ and methylene chloride-$d_2$ (Aldrich) were filtered through basic alumina prior to use. Rose Bengal and *meso*-tetraphenylporphyrin (Aldrich) were used directly without any further purification.

The temperatures of the photooxidations were controlled by submersion in a methanol bath cooled with a FTS-systems Flexicool refrigerator.

**(*E*,*E*)-1,4-Dimethoxy-1,3-butadiene (1)** was synthesized according to the procedure of Hiranuma and Miller:[26] $^1$H NMR (acetone-$d_6$) $\delta$ 6.46 (dd, $J$ = 9.1, 2.7 Hz, 2 H), 5.44 (dd, $J$ = 9.1, 2.7 Hz, 2 H), 3.50 (s, 6 H); $^{13}$C NMR $\delta$ 147.8 (d, $J$ = 181 Hz), 102.5 (d, $J$ = 151 Hz), 56.3 (q, $J$ = 142 Hz).

**(*E*,*Z*)-1,4-Dimethoxy-1,3-butadiene (2)** was synthesized according to the procedure of Hiranuma and Miller:[26] $^1$H NMR (acetone-$d_6$) $\delta$ 6.55 (d, $J$ = 13.2 Hz, 1 H), 5.80 (d, $J$ = 5.9 Hz, 1 H), 5.69 (dd, $J$ = 13.2, 11.0 Hz, 1 H), 4.92 (dd, $J$ = 11.0, 5.9 Hz, 1 H), 3.59 (s, 3 H), 3.53 (s, 3 H); $^{13}$C NMR (acetone-$d_6$) $\delta$ 149.1 (d, $J$ = 181 Hz), 144.6 (d, $J$ = 179 Hz), 103.4 (d, $J$ = 157 Hz), 99.5 (d, $J$ = 153 Hz), 59.6 (q, $J$ = 144 Hz), 56.2 (q, $J$ = 144 Hz).

**(*Z*,*Z*)-1,4-Dimethoxy-1,3-butadiene (3)** was synthesized according to the procedure of Hiranuma and Miller:[26] $^1$H NMR (acetone-$d_6$) $\delta$ 5.85 (dd, $J$ = 3.7, 1.5 Hz, 2 H), 5.26 (dd, $J$ = 3.7, 1.5 Hz, 2 H), 3.59 (s, 6 H); $^{13}$C NMR (acetone-$d_6$) $\delta$ 145.7 (d, $J$ = 181 Hz), 108.4 (d, $J$ = 159 Hz), 59.8 (q, $J$ = 149 Hz).

**Methyl formate**: $^1$H NMR (acetone-$d_6$) $\delta$ 8.13 (q, $J$ = 0.7 Hz, 1 H), 3.69 (d, $J$ = 0.7 Hz, 3 H).

***trans*-2-Methoxyacrolein**: $^1$H NMR (acetone-$d_6$) $\delta$ 9.39 (d, $J$ = 7.7 Hz, 1 H), 7.64 (d, $J$ = 12.4 Hz, 1 H), 5.59 (dd, $J$ = 7.7, 12.4 Hz, 1 H), 3.83 (s, 3 H).

***cis*-2-Methoxyacrolein**: $^1$H NMR (acetone-$d_6$) $\delta$ 9.98 (d, $J$ = 8.4 Hz, 1 H), 7.19 (d, $J$ = 6.2 Hz, 1 H), 5.00 (dd, $J$ = 8.4, 6.2 Hz, 1 H), 3.93 (s, 3 H).

**3,6-Dihydro-3,6-dimethoxy-1,2-dioxine** (endoperoxide E, Figure 1): $^1$H NMR (acetone-$d_6$) $\delta$ 6.04 (dd, $J$ = 1.8, 0.7 Hz, 2 H), 4.97 (dd, $J$ = 1.8, 0.7 Hz, 2 H), 3.44 (s, 6 H).

**Photolysis Conditions.** A solution of 5–15 mg of the diene and 10 μL of a $10^{-3}$ M stock solution of Rose Bengal in acetone-$d_6$ was placed in a 5-mm NMR tube, and cooled to −80 °C. The sample was then saturated with oxygen by continuous bubbling for 25–30 min. The continually agitated solution was then irradiated with a WKO 120-V 750-W lamp through a 0.5% $K_2Cr_2O_7$ filter solution. The progress of the reactions was monitored by low-temperature NMR at −62 to −77 °C.

**Isomerization Studies.** Acetone-$d_6$ solutions (1 mL) containing 5–15 mg of the diene and 10 μL of a $10^{-3}$ M stock solution of Rose Bengal were saturated with argon for 25–30 min. These reaction mixtures were then irradiated with a Sylvania WKO 120-V 750-W lamp through a 0.5% $K_2Cr_2O_7$ filter solution to give the results in Table VII.

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# Relative Yields of Excited Ketones from Self-Reactions of Alkoxyl and Alkylperoxyl Radical Pairs

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**Abstract:** We have measured the ratios of excited ketones that arise from the self-reactions of alkoxyl ($2R_1R_2CHO^\bullet$) and peroxyl ($2R_1R_2CHO^\bullet$) radicals. This was accomplished by measuring the chemiluminescence emission from solutions of $R_1R_2CHO_2H$, or $R_1R_2CH_2$ and $O_2$, in the presence of a free-radical initiator *trans*-RON=NOR, in which R = *t*-Bu or $R_1R_2CH$ in paired experiments. The excited states were trapped with 2-*tert*-butyl-9,10-dibromoanthracene or another fluorescent derivative of anthracene. The peroxyls were less efficient sources by 17%, 48%, 36%, and 42% than the alkoxyls for the cases in which $R_1R_2C{=}O$ was acetophenone in ethylbenzene, cyclohexanone in cyclohexane, and 1-tetralone in *t*-BuPh and in *t*-BuOH, respectively. The activation energy for formation of excited 1-tetralone ($T_0$ and/or $S_1$) from two 1-tetralylperoxyl radicals was 6 ± 3 kcal/mol higher than for production of the excited state from the corresponding pair of alkoxyl radicals. The results are consistent with but do not demand the hypothesis that excited carbonyl states arise in peroxyl terminations by way of alkoxyl pairs.

Chemiluminescence (CL) produced from the termination of alkylperoxyl radicals is a nearly ubiquitious property of oxidizing organic materials. The characteristic has been exploited for measurement of oxidation rates,[1,2] antioxidant efficacy,[3] and other properties,[4] although some details of the excitation process are not well established.

In a previous publication[5] we suggested that excited-state production from caged $R_1R_2CHO^\bullet$ radicals might be a feature common to the decompositions of nontertiary alkyl hyponitrites,

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[1] Belyakov, V. A.; Vassil'ev, R. F. *Photochem. Photobiol.* **1970**, *11*, 179–192.

[2] George, G. A. *Polym. Degrad. Stab.* **1981**, *3*, 173–236.

[3] Ashby, G. E. *J. Polym. Sci.* **1961**, *50*, 99–106.

[4] Naito, K.; Kwei, T. K. *Polym. Eng. Sci.* **1979**, *19*, 841–844.

[5] Mendenhall, G. D.; Quinga, E. M. Y. *J. Am. Chem. Soc.* **1986**, *108*, 474–478 and previous papers in this series.

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**Table I.** Products from Induced Decomposition of TOOH (0.010 M)

| | M × $10^4$ | | | | |
|---|---|---|---|---|---|
| time, h | RONNOR | ΔTOOH | T=O | TOH | TOH/ $f$ΔBHN |
| | A. BHN (0.00563 M, BPh, 41.0 °C)[a] | | | | |
| 1.5 | 5.58 | 7.70 | 5.6 | 3.3 | 0.66 |
| 6.25 | 19.8 | 22.0 | 14.0 | 8.8 | 0.50 |
| 15.3 | 36.9 | 55.3 | 32.8 | 19.4 | 0.58 |
| | B. THN (0.00152 M, BPh, 41.0 °C)[a] | | | | |
| 1.0 | 8.97 | 14.8 | 9.84 | 15.6 | |
| 4.0 | 14.8 | 17.7 | 15.0 | 23.7 | |

[a] Product analysis on 25 × 0.25 cm normal-phase $SiO_2$, eluant 0.50% *t*-BuOMe–hexane, 1 mL/min, 220-nm detection.

$(R_1R_2CHON{=})_2$, and the corresponding tetraoxides $(R_1R_2CHOO)_2$, which are also intermediates in the termination of peroxyl radicals. We predicted that the latter might give a higher yield of triplet $R_1R_2C{=}O$ because the elimination of triplet molecular oxygen from a tetraoxide should, in the simplest analysis, leave a pair of reactive alkoxyls with a net triplet multiplicity but not when (singlet) nitrogen was lost to give the same pair from the hyponitrite.

In this paper we present the results of a study in which we used the previously studied, excited states generation from caged alkoxyls derived from hyponitrites (eq 1) to calibrate the excitated

$$(R_1R_2CHON)_2 \xrightarrow{1} 2R_1R_2CHO^{\bullet} + N_2 \xrightarrow{1} R_1R_2C{=}O\ (S_o, S_1, T_o) + R_1R_2CHOH \quad (1)$$

states arising from peroxyl self-reactions. In the first half of the experiment, the peroxyls are generated from *tert*-butyl hyponitrite (BHN) in the sequence:

$$\mathrm{BHN} \longrightarrow 2t\text{-}BuO^{\bullet} + N_2 \quad (2)$$

$$t\text{-}BuO^{\bullet} + (R_1R_2CH_2,\ O_2,\ \text{or}\ R_1R_2CHOOH) \rightarrow R_1R_2CHO_2^{\bullet} + t\text{-}BuOH \quad (3)$$

$$2R_1R_2CHO_2^{\bullet} \rightarrow R_1R_2C{=}O\ (S_o, S_1, T_o) + R_1R_2CHOH + O_2\ (T_o, S_1) \quad (4)$$

$$R_1R_2C{=}O\ (S_1, T_o) + \mathrm{tDBA} \rightarrow R_1R_2C{=}O + \mathrm{tDBA}\ (S_1) \quad (5)$$

$$\mathrm{tDBA}\ (S_1) \rightarrow \mathrm{tDBA}\ (S_o) + h\nu \quad (6)$$

$$\mathrm{tDBA}\ (S_1) \rightarrow \mathrm{tDBA}\ (S_o) \quad (7)$$

$$R_1R_2C{=}O\ (S_1, T_o) + O_2\ (T_o) \rightarrow R_1R_2CO\ (S_o) + O_2\ (T_o, S_1) \quad (8)$$

In this sequence the carbonyl excited states arise only from (4). When BHN is then replaced with $R_1R_2CHON{=}NOCHR_1R_2$, excited states arise from both (1) and (4). Their relative contributions can be determined from the chemiluminescence yields in the two experiments, if the cage effects in the initiation steps are known.

## Experimental Section

The apparatus and procedures for chemiluminescence measurements, product analysis by HPLC, and synthesis of alkyl hyponitrites and other reactants have been described previously.[5] The 1-tetralyl hyponitrite (THN) we synthesized in this study showed mp 80–81 °C dec, significantly higher than that reported.[6] Since a different stereoisomer may have been synthesized, the cage effect of the new THN sample in *t*-BuPh (BPh) at 41.0 °C was redetermined as 36.17 ± 0.14%.

2-*tert*-Butyl-9,10-dibromoanthracene (tDBA) was synthesized from 2-*tert*-butylanthracene[7] and stoichiometric $Br_2$ in $CCl_4$. After crystallization from ethanol, the yellow needles melted at 139–142 °C. The UV–visible spectral characteristics of tDBA and the parent DBA were very similar. Anal. Calcd for $C_{18}H_{16}Br_2$: C, 55.13; H, 4.11. Found: C, 54.97; H, 4.05.

9,10-Dibromoanthracene (DBA), 9,10-diphenylanthracene (DPA), 1-tetralol (TOH), and 1-tetralone (T=O) were purchased from Aldrich Chemical Co. 1-Tetralyl hydroperoxide[8] (TOOH) was crystallized from hexane: mp 53–54 °C (lit.[8] 54.0–54.5 °C). Solvents were of reagent grade or were redistilled before use. Combustion analyses were carried out at Spang Microanalytical Laboratories, Eagle Harbor, MI.

**Table II.** Yields of Hydrogen Peroxide from BHN/TOOH Mixtures after 0.5 h at 41.0 °C

| [BHN], M | [TOOH], M | OD[a] | OD (bkg)[b] | $10^4[H_2O_2]$, M | yield,[c] % |
|---|---|---|---|---|---|
| 0.103 | 0.01 | 0.123 | 0.036 | 1.94 | 6.4 |
| 0.101 | 0.102 | 0.105 | 0.045 | 1.34 | 4.7 |
| 0.66 | 0.010 | 0.058 | 0.022 | 0.80 | 5.4 |
| controls: | | | | | |
| 0 | 0 | 0.000 | | | |
| 0.10 | 0.01[d] | 0.045 | | | |

[a] At 410 nm. [b] Extract of unheated reaction mixture. [c] $[H_2O_2]/0.01(1 - f)\Delta$BHN. [d] Added after 0.5 h at 41.0 °C and cooling to 25 °C.

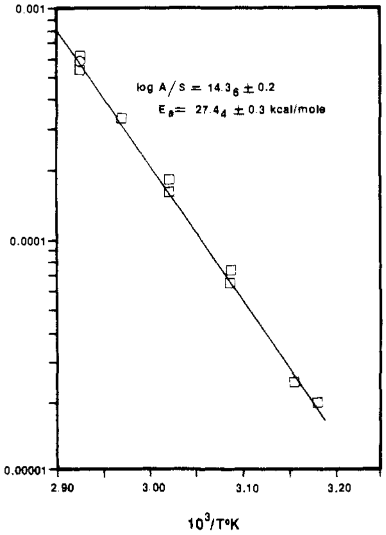

**Figure 1.** Arrhenius plot for decomposition of solutions of BHN in BPh containing TOOH, followed by decay of CL. The average of the rate constants derived from 1.27-μm emission (circle) was not included when the Arrhenius parameters were calculated.

Rate constants for *tert*-butyl hyponitrite (BHN) were determined from the first-order decay of CL emission in the presence of 0.0100 M TOOH and 2 × $10^{-3}$ M tDBA. The derived values were ($T$ °C, $10^5$ k/s) as follows. BPh: 41.0°, 1.93; 43.5°, 2.38; 50.0°, 6.67, 6.43; 57.8°, 16.5, 18.3; 62.9°, 32.1; 67.7°, 56.6, 59.3. PhEt: 41.0°, 2.42, 2.57. *t*-BuOH: 70.0°, 77.1, 78.2. c-$C_6H_{12}$: 41.0°, 1.53; 58.0°, 15.6; 62.2°, 32.0, 32.0, 32.0; 67.8°, 57.6, 55.6. Product analyses were carried out for the systems BHN/TOOH and THN/TOOH by HPLC and are presented in Table I. The oxidation products from the other hydrocarbons have been studied extensively.[9,10]

Hydrogen peroxide was determined with Ti(II) as described by Eisenberg.[11] Solutions of BHN and TOOH in 5 mL of BPh were allowed to decompose for short times, extracted with 0.50 mL of distilled water, and 0.2 mL of the extract was treated with 3.0 mL of the titanium reagent. The optical density of the solution was then measured at 410 nm with an HP Model 8451A spectrometer. The method was calibrated with solutions of hydrogen peroxide of eight known concentrations (0.9–22 mM), which led to the relation $[H_2O_2] = 0.022042[\mathrm{OD}] + 0.0001281$ ($r^2 = 0.9998$). The experimental data are shown in Table II.

IR emission measurements were carried out with a North Coast Optical Model 817-OL Ge detector at −196 °C, with signal chopping at about 100 Hz, phase-sensitive detection, and an interference filter (Janos Technology Co.) with $\lambda_{max}{}^{T}$ 1274 nm, Δnm at half-height = 21.7. When the filter was replaced by a similar one transmitting at 1150 nm, no signal was detected from the reaction mixtures.

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(6) Quinga, E. M. Y. Ph.D. Thesis, Michigan Technological University, 1985.

(7) Micione, E. *J. Org. Chem.* **1978**, *43*, 1829–1830.

(8) Knight, H. B.; Swern, D. *Organic Syntheses*; Wiley: New York, 1963, Collect. Vol. IV, pp 895–897.

(9) Emerson, W. S.; Heyd, J. W.; Lucas, V. E.; Cook, W. B.; Lyness, W. I.; Stevenson, J. K. *J. Am. Chem. Soc.* **1948**, *70*, 3764–3767.

(10) Druliner, J. D.; Krusic, P. J.; Lehr, G. F.; Tolman, C. A. *J. Org. Chem.* **1985**, *50*, 5838–5845.

(11) Eisenberg, G. M. *Ind. Eng. Chem. Anal. Ed.* **1943**, *15*, 327–328.

**Table III.** Cage Effects in Alkyl Hyponitrite Decomposition

| R in $R_2N_2O_2$ | $[R_2N_2O_2]_o$, M | solvent | *T*, °C | $[\text{product}]/R_2N_2O_2]_o$, % | cage effect[a] |
|---|---|---|---|---|---|
| $t$-Bu | 0.1076 | BPh | 41.0 | $t$-BuOH,[b] 178.4 ± 3.4 | 10.8 ± 3.4 |
| $t$-Bu | 0.1089 | PhEt | 41.0 | $t$-BuOH,[b] 181.2 ± 1.5 | 9.4 ± 1.5 |
| $t$-Bu | 0.136 | $t$-BuOH | 70.0 | $t$-$Bu_2O_2$,[b] 8.3 ± 0.9 | 8.3 ± 0.9 |
| 1-tetralyl | $4.03 \times 10^4$ | BPh | 43.7 | tetralone,[c,d] 36.2 ± 0.1 | 36.2 |
| 1-tetralyl | $1.74 \times 10^{-4}$ | $t$-BuOH | 70.0 | tetralone,[d] 66.2 ± 3 | 66.2 ± 3.2 |
| PhCHMe | $1.78 \times 10^{-3}$ | PhEt | 41.0 | PhCOMe,[d] 12.7 ± 0.3 | 12.7 ± 0.3 |
| $t$-Bu | 0.0938 | c-$C_6D_{12}$ | 62.2 | $t$-$Bu_2O_2$,[e] 10.4 | 10.4 |
| c-$C_6H_{11}$ | 0.098 | c-$C_6H_{12}$ | 80.0 | cyclohexanone,[f] 14.3 | 14.3 |

[a] Percent alkoxy radical pairs terminated in solvent cage. [b] Gas chromatography. [c] 31.6% from ref 6. [d] HPLC analysis. [e] $^1H$ NMR. [f] Reference 10.

**Table IV.** Excited-State Yields by Titration with tDBA at 41.0 °C

| | system | *y* int/slope | $(y\ \text{int})^{-1}$, Hz | $10^{-11} \times$ rel CL | CL(RO•)/(ROO•) |
|---|---|---|---|---|---|
| Ia. | BHN (0.0014 M), TOOH (0.100 M) in BPh | 839 | 90 | (7.2 ± 0.2)[a] | |
| Ib. | THN ($3.23 \times 10^{-4}$ M), TOOH (0.010 M) in BPh | 570 | 464 | (19.3 ± 0.4)[b] | 2.7 ± 0.1 |
| IIa. | BHN (0.0010 M) in PhEt | 858 | 71 | (6.0 ± 0.3)[a] | |
| | | 1008 | 69 | | |
| IIb. | 1-PhEtHN ($6.00 \times 10^{-4}$ M) in PhEt | 751 | 450 | (36.0 ± 0.4)[b] | 6.0 ± 0.1 |
| | | 755 | 445 | | |

[a] Defined as $1/0.005(1-f)[\text{HN}]_o k_d(y\ \text{int}) = x$. [b] Defined as $\{(y\ \text{int})^{-1} - 0.005(1-f)[\text{HN}]_o k_d x\}/0.005f[\text{HN}]_o k_d$.

**Table V.** Excited-State Yields by Integral Method[a]

| | system | *T*, °C | solvent | $10^{-12} \times$ rel CL | CL-(RO•)/(ROO•) |
|---|---|---|---|---|---|
| Ia. | BHN ($1.32 \times 10^{-5}$ M), TOOH (0.100 M), tDBA ($2.20 \times 10^{-3}$ M), | 70.0 | $t$-BuOH | 2.37, 2.46[b] | |
| Ib. | THN[(1.24–1.30) $\times 10^{-4}$ M], TOOH (0.0100 M), tDBA ($2.20 \times 10^{-3}$ M) | 70.0 | | 4.59, 5.65[c] | 2.4 ± 0.4[d] |
| IIa. | BHN (0.98–1.07) $\times 10^{-4}$ M), tDBA ($2.04 \times 10^{-3}$ M) | 62.2 | c-$C_6H_{12}$ | 6.17, 6.60 | |
| IIb. | CHN [(2.08–2.11) $\times 10^{-4}$ M], tDBA ($2.04 \times 10^{-3}$ M) | 62.2 | | 7.75, 7.91 | 1.7 ± 0.1[e] |
| IIIa. | BHN [(3.82 – 5.56) $\times 10^{-6}$ M], tDBA ($2.04 \times 10^{-3}$ M) | 62.2 | c-$C_6H_{12}$ | 8.50, 9.09[b] | |
| IIIb. | CHN [(5.21 – 5.22) $\times 10^{-6}$ M), tDBA ($2.04 \times 10^{-3}$ M) | 62.2 | | 12.19, 10.59[c] | 2.1 ± 0.2 |

[a] Total emission in presence of (2.04 – 2.20) $\times 10^{-3}$ M tDBA. [b] $[(\text{CL} - \text{bkg})]/0.005(1-f)[\text{HN}]_o$. [c] $[(\text{CL} - \text{bkg})]/0.005f[\text{HN}]_o$. [d] $\{[\text{CL}_{\text{THN}} - \text{CL}_{\text{BHN}}(1 - f_{\text{BHN}})]/f_{\text{BHN}}\}/\text{CL}_{\text{BHN}}$. [e] $\{[\text{CL}_{\text{CHN}} - \text{CL}_{\text{BHN}}(1-f)]/f_{\text{CHN}}\}/\text{CL}_{\text{BHN}}$.

## Results

The cage effects and rate constants for initiator decomposition are both necessary for the desired calculations. Cage effects not available from previous studies were measured by several techniques and are summarized in Table III. Rate constants from the nonluminescent decomposition of BHN could nonetheless be measured by following the light emission in the presence of TOOH, from which we derived Arrhenius parameters (Figure 1) in good agreement with those calculated from rate constants for decomposition in *n*-hexane.[12]

The relative yields of excited states were measured by both differential (e.g. Figure 2) and integral methods, and are given in Tables IV and V, respectively. In the former case, a plot of $CL^{-1}$ vs fluorescer$^{-1}$ was made. The ratio of *y* intercept/slope is $k_5\tau_k$, where $k_5$ is the rate of energy transfer from excited $R_2CO$ to tDBA, and $\tau_k$ is the lifetime of the excited ketone. The intercept/slope ratios in Table IV are all in the range of 500–1000, which is consistent with triplet ketones as predominent excited states and in agreement with previous conclusions from studies of the self-terminations of TOO•,[13] (1-phenylethyl)peroxyl,[1,14] and 2-propylperoxyl[15] radicals. The triplets may arise directly or from intersystem crossing from short-lived singlet states.

The integral method, in which the total relative CL is measured at higher temperatures as the radical initiator decomposes completely, was preferred in cases where reagent solubilities were limited (Table V). Duplicate determinations were reasonably close, although the method is potentially subject to errors due to side reactions between radicals and reaction products.

The ratio of excited state production from caged $R_1R_2CHO^\bullet$ pairs relative to $R_1R_2CHOO^\bullet$ recombinations varied from 1.7 for the cyclohexyl system in cyclohexane to 6.0 for the 1-phenylethyl system in ethylbenzene. The factors are substantial and could not be ascribed to any known systematic errors.

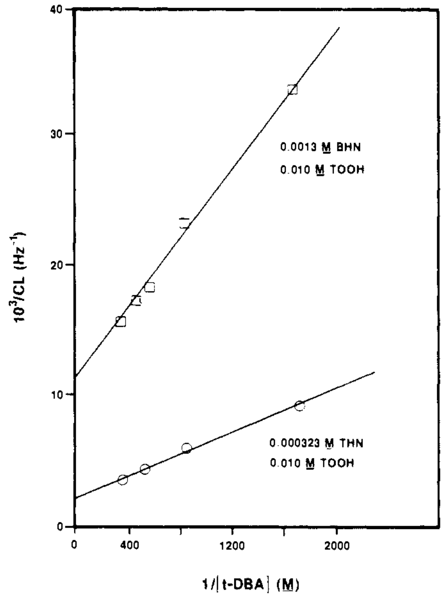

**Figure 2.** Determination of excited-state yields in BPh by the differential method.

The BHN-initiated decomposition of TOOH could also be followed by IR emission at 1.27 μ arising from transitions of singlet ($^1\Delta_g$) $O_2$.[16] First-order rate constants were derived from the decay

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(12) Kiefer, H.; Traylor, T. G. *Tetrahedron Lett.* **1966**, 6163–6168.

(13) Lundeen, G.; Livingstone, R. *Photochem. Photobiol.* **1965**, *4*, 1085–1096.

(14) Hofert, M. *Photochem. Photobiol.* **1969**, *9*, 427–432.

(15) Bogan, D. J.; Celii, F.; Sheinson, R. S.; Coveleskie, R. A. *J. Photochem.* **1984**, *25*, 409–417.

(16) (a) Kanofsky, J. R.; Axelrod, B. J. *Biol. Chem.* **1986**, *260*, 15 and references therein. (b) Howard, J. A.; Ingold, K. U. *J. Am. Chem. Soc.* **1968**, *90*, 1056–1058. (c) Gorman, A. A.; Rodgers, M. A. J. *Ibid.* **1986**, *108*, 5074–5078.

**Table VI.** Activation Energy for CL from Temperature-Jump Experiments

| concentration,[a] mM | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| init | TOOH | fluorescer | $T_1$, °C | CL, Hz | $T_2$, °C | CL, Hz | $T_3$, °C | CL, Hz | $R_{1,2}$[b] | $E_{2,3}$[b] | $E_{av}$[b] |
| BHN, 3.22 | 60 | tDBA, 3.06 | 41.0 | 1593 ± 6 | 60.0 | 23808 ± 800 | 24.5 | 40 ± 2 | 29.6 | 35.4 | 32.5 ± 2.9 |
| BHN, 2.99 | 70 | tDBA, 3.67 | 41.0 | 1832 ± 20 | 60.0 | 36956 ± 900 | 42.0 | 2374 ± 80 | 32.9 | 31.8 | 32.4 ± 2.2 |
| BHN, 1.61 | 7 | tDBA, 2.14 | 26.8 | 235 ± 3[c] | 44.6 | 4256 ± 20[c] | 27.5 | 242 ± 5[c] | 30.0 | 31.8 | 30.9 ± 1.0 |
| | | | | | | | | | av (6) | | 31.9 ± 2.1 |
| BHN, 4.00 | 1520 | DBA, 3.39 | 25.0 | 478 ± 9 | 45.0 | 13439 ± 100 | 25.0 | 348 ± 6 | 31.5 | 34.4 | 33.0 ± 1.3 |
| BHN, 2.99 | 70 | DPA, 2.97 | 40.0 | 39 ± 2 | 60.0 | 1275 ± 10 | 40.0 | 42 ± 2 | 36.1 | 35.3 | 35.7 ± 2.9 |
| THN, 0.99 | 0 | tDBA, 1.89 | 26.1 | 4987 ± 60[c] | 44.5 | 63693 ± 500[c] | 27.7 | 5867 ± 90[c] | 26.1 | 27.0 | 26.6 ± 0.7 |
| BHN,[d] 1.21 | 6 | DBA, 2.11 | 26.0 | 68 ± 1 | 45.0 | 1935 ± 6 | 26.0 | 66 ± 5 | 33.3 | 33.6 | 33.5 ± 2.7 |
| BHN,[e] 1.32 | 6 | DBA, 2.05 | 26.0 | 14 ± 1 | 43.3 | 237 ± 3 | 26.5 | 15 ± 2 | 30.7 | 31.0 | 30.9 ± 3.0 |

[a] Total volume = 5 mL in BPh. Sequence was $T_1 \rightarrow T_2 \rightarrow T_3$. [b] Kilocalories/mole. [c] CL corrected for changes in hyponitrite concentrations with time. [d] The solution was filtered through molecular sieves (4A) into the reaction flask under $N_2$ before decomposition. [e] Solution in 5 mL of PhCN passed through molecular sieves (4A) before decomposition.

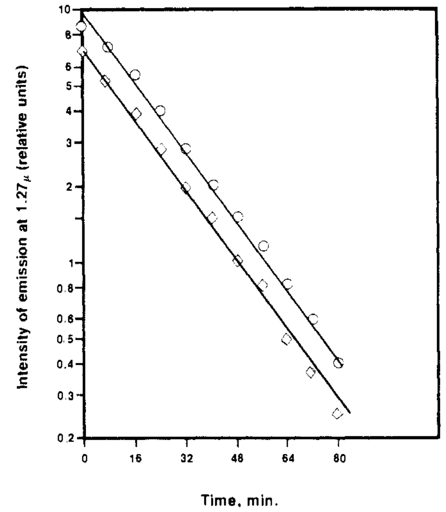

**Figure 3.** Decay of 1.27-μm emission from BPh solution at 67.6 °C with initial concentrations of BHN (0.016 and 0.03 M) and TOOH (0.083 and 0.30 M, respectively).

curves (Figure 3). These were in excellent agreement with those obtained from analysis of the CL emission in the visible region (Figure 1). Since we were unable to see 1270-nm emission from thermolysis of oxygen-purged solutions of tetramethyl-1,2-dioxetane under the reaction conditions, step 8 is probably not the source of this emission.[16c]

**Control Experiments.** In Figure 4 we demonstrate that all of the alkoxyls from BHN appear to be intercepted by TOOH above about 0.002 M TOOH. The H atoms in BPh and *tert*-butyl alcohol are relatively unreactive toward alkoxyl and alkylperoxyl radicals,[17] so that side reactions with solvent are not expected to compete significantly with the desired sequence. The linearity of CL with initiator concentration is predicted by a kinetic analysis of the sequence 2–8 and is demonstrated in Figure 5.

**Temperature-Jump Experiments.** The activation energy for chemiluminescence ($E_1$) was determined from measurements of the light emission from solutions of initiator and other components at two temperatures within a short time period (Table VI). Digital correction of the data to take into account the loss of initiator during the experiment led to negligible changes in the calculations when BHN was the initiator. A similar correction was applied to the data from the less stable THN and resulted in a significant increase in the derived values of $E_1$.

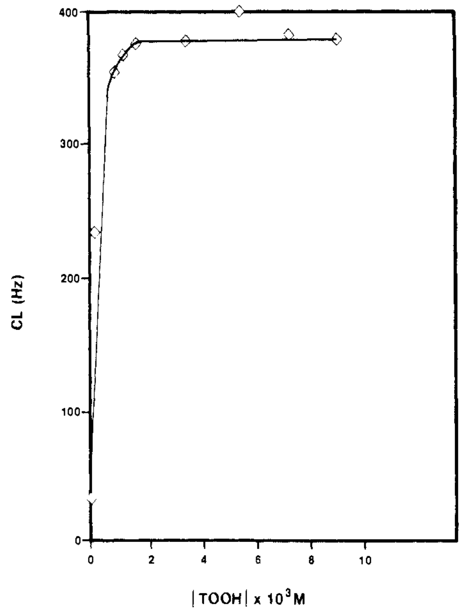

**Figure 4.** Effect of TOOH on CL from a solution of BHN (2.98 × $10^{-4}$ M) and tDBA (2.38 × $10^{-3}$ M) in BPh at 41.0 °C. The data are corrected for dilution of initiator.

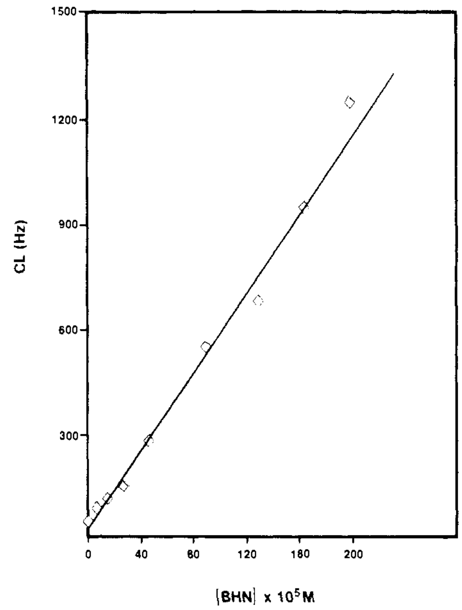

**Figure 5.** Chemiluminescence vs initiator concentration (BPh, 2.38 × $10^{-3}$ M tDBA, 0.010 M TOOH, 41.0 °C).

The activation energies derived from the experiments initiated by BHN were 30–35 kcal/mol with tDBA as the fluorescer (F), 32–34 kcal/mol with the parent DBA, and 35–36 kcal/mol with solutions containing DPA. The value of $E_1$ with DBA was not changed significantly if the reaction mixture was dried with 4A molecular sieves and filtered into the reaction cell under nitrogen, or if benzonitrile replaced BPh as the solvent.

If tDBA has $d[k_6/(k_6 + k_7)]/dT = E_{F,app} \simeq -4$ kcal/mol as does DBA,[18] then all of the values of $E_1$ are consistent with an

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(17) Hendry, D. G.; Mill, T.; Piszkiewicz, L.; Howard, J. A.; Eigenmann, H. K. *J. Phys. Chem. Ref. Data* **1974**, *3*, 937–978.

inherent activation energy of about 36 ± 2 kcal/mol in the systems initiated by BHN. This is significantly higher than the value of $E_2$ = 27.4 kcal/mol derived from curves of CL decay (Figure 1).

Analysis of the reaction sequence shown above, with suitable approximations, leads to the expression below, in which $k_4$ and $k_{4T}$ are the rate constants for formation of ground-state and triplet ketone, respectively:

$$I_{\mathrm{BHN/TOOH}} \equiv \mathrm{d}h\nu/\mathrm{d}t = \frac{k_{4\mathrm{T}}k_5k_6[\mathrm{F}]}{(k_6 + k_7)(k_5[\mathrm{F}] + k_8[\mathrm{O_2}])}\left[\frac{k_2(1 - f)[\mathrm{BHN}]}{k_4}\right]$$

Since the fractional cage effect $f$ in this expression and the rate constants for energy transfer both have little dependence on temperature in the experimental range, we can approximate

$$E_1^{\mathrm{BHN}} = E_{\mathrm{F,app}} + E_2 + E_{4\mathrm{T}} - E_4$$

Substituting the known values into this equation, we then estimated $E_{4\mathrm{T}} - E_4 \simeq 9 \pm 2$ kcal/mol. Livingstone and Lundeen[13] derived quantities analogous to $E_{4\mathrm{T}} - E_4$ by analysis of chemiluminescence from the spontaneous and benzoyl peroxide induced oxidation of tetralin. They obtained values of 8.9 ± 2.5 and 3.2 ± 1.8 kcal/mol from the two methods. The higher value is in agreement with ours, although only the lower one was obtained at experimental temperatures close to those of this study.

For the temperature-jump experiment with solutions of THN and a fluorescer, a similar analysis gives

$$I_{\mathrm{THN}} = \frac{k'_{1\mathrm{T}}k_5k_6[\mathrm{F}]}{(k_6 + k_7)(k_5[\mathrm{F}] + k_8[\mathrm{O_2}])}\left[\frac{fk_1[\mathrm{THN}]}{k'_1}\right]$$

$$E_1^{\mathrm{THN}} = E_{\mathrm{F,app}} + E'_{1\mathrm{T}} + E_1 - E'_1$$

Here $k'_{1\mathrm{T}}$ and $k'_1$ are the rate constants for production of triplet and ground-state ketones, respectively, from the caged RO$^•$ pairs.

The activation energy of chemiluminescence from THN, obtained by the temperature-jump method in the presence of tDBA, was 26.6 kcal/mol. A value of $E_1$ = 27.2 kcal/mol was obtained earlier from decay curves of CL from THN at several temperatures.[6] These values are consistent with a small activation energy for the excitation process, $E'_{1\mathrm{T}} - E'_1$, of 26.6 − (−4) −27.2 = 3 ± 2 kcal/mol. We concluded in the earlier study that the corresponding $E'_{1\mathrm{T}}$ and $E'_1$ showed no difference within error for three other nontertiary alkyl hyponitrites.[5]

**Product Study.** The product analysis (Table I) for induced decomposition of TOOH showed an excess of T=O over TOH, in agreement with similar studies with chlorobenzene as solvent.[19] This excess can be ascribed to induced decomposition of TOOH[19,20] or to oxidation of the alcohol to the ketone by TOO$^•$ or other radicals. The latter process can be represented by eq 9 and 10.

$$\mathrm{RO_2^•} + \mathrm{R_1R_2CHOH} \rightarrow \mathrm{RO_2H} + \mathrm{R_1R_2{}^•COH} \quad (9)$$

$$\mathrm{R_1R_2{}^•COH} + \mathrm{X^•} \rightarrow \mathrm{R_1R_2C{=}O} + \mathrm{XH}\ (\mathrm{X^•} = \mathrm{RO_2^•}, \mathrm{O_2}, \mathrm{HO_2^•}, \text{etc.}) \quad (10)$$

In Figure 6 we show that this reaction can compete significantly with the production of excited states in reaction 4, although at concentrations higher than those present in the experiments from which we determined yields of light by the differential method. By contrast, the production of light from THN is reduced only by a small amount because TOH does not intercept the caged alkoxyls that are the precursors to the excited states (Figure 6, upper points).

Hydrogen peroxide is another recognized[19] product from the side reactions 9 and 10 and could be detected in small quantities from the initiated decomposition of TOOH. Its depressing effect on CL emission was demonstrated by addition a 30% aqueous solution to an initiated reaction in *tert*-butyl alcohol (Figure 7). A control experiment with water showed a modest increase in CL at relatively high concentrations. Neither substance appeared to have an effect at the concentrations of $H_2O_2$ ($10^{-4}$ M) found in our reaction mixtures (Table II), although the solvents were admittedly different.

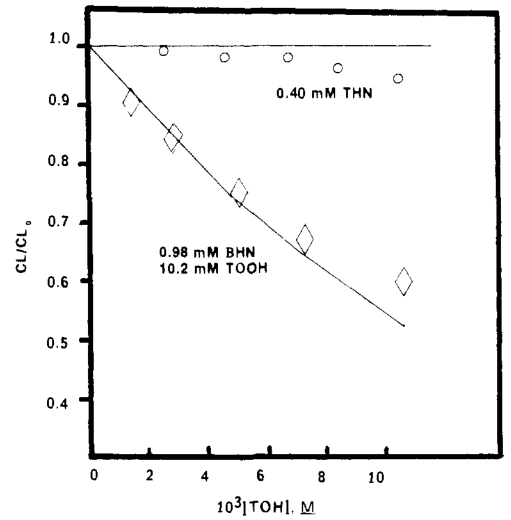

Figure 6. Effect of TOH on CL from excited 1-tetralone arising from different sources in the presence of tDBA (2.09 × $10^{-3}$ M). The lower curve was calculated from the equations $\mathrm{CL/CL_o} = [\mathrm{TO_2^•}]^2_{\mathrm{ss}}/[\mathrm{TO_2^•}]_o^2$, and $[\mathrm{TOO^•}]_{\mathrm{ss}} = [-k_9[\mathrm{TOH}] + (k_9[\mathrm{TOH}]^2 + 4k_4k_2f[\mathrm{BHN}])^{0.5}]/2k_4$. The latter equation was derived from the sequence of eq 2–9 under the assumptions that X = $\mathrm{TO_2^•}$ only in eq 9. We used values of $2k_4 = 7.2 \times 10^6\ \mathrm{M^{-1}\ s^{-1}}$ (Howard, J. A.; Ingold, K. U. *Can. J. Chem.* **1968**, *46*, 2661–2666) and $k_8 = 9\ M^{-1}\ \mathrm{s^{-1}}$.

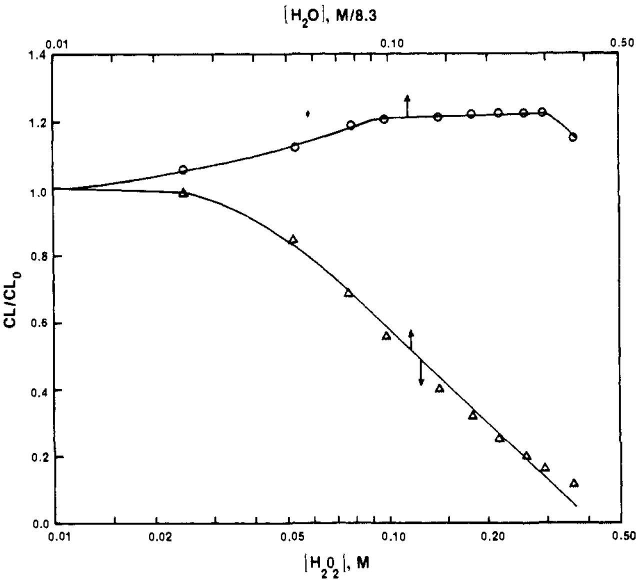

Figure 7. Effects of 30% $H_2O_2$ (lower curve) and water (upper curve) on CL from a solution of BHN (1.10 × $10^{-3}$ M), TOOH (0.010 M), and tDBA (2.05 × $10^{-3}$ M) in *t*-BuOH at 41.0 °C.

## Discussion

We could support our conclusions on the relative yields of excited states with results published recently by Druliner et al.[10] These workers were able to separate reactions 1 and 4 by carrying out decompositions of cyclohexyl hyponitrite (CHN) in cyclohexane in the presence and absence of dissolved oxygen.

Their experiment demonstrated that cyclohexylperoxyl radicals were responsible for most of the emitted light, when cyclohexyl hyponitrite initiated the oxidation of cyclohexane. The relative CL that they obtained from experiments conducted under $N_2$, 14 ± 2, when divided by the fraction of cyclohexyloxyl pairs that underwent cage disproportionation (0.143) in reaction (1), gives

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[18] Wilson, T.; Golan, D. E.; Harris, M. S.; Baumstark, A. L. *J. Am. Chem. Soc.* **1976**, *98*, 1086–1091.

[19] Baignee, A.; Chenier, H. B.; Howard, J. A. *Can. J. Chem.* **1983**, *61*, 2037–3043.

[20] Hiatt, R.; Mill, T.; Irwin, K. C.; Castleman, J. K. *J. Org. Chem.* **1968**, *33*, 1428–1435.

a normalized value of 98 ± 14. The relative CL from corresponding experiments in air, 42 ± 5, similarly leads to the normalized contribution from cyclohexylperoxyl radicals = (42 − 14)/0.796 = 35 ± 6.[22] The ratio 98/35 = 2.8 ± 0.6 is somewhat higher than our ratios of 1.7 ± 0.1 and 2.1 ± 0.2 (Table V), but the calculation fails to take into account the quenching of excited cyclohexanone by dissolved oxygen (reaction 8), which was probably comparable in magnitude to triplet energy transfer to 9,10-dibromoanthracene in their system. This correction of $k_5[F]/(k_5[F] + k_8[O_2])$ can change the ratio by as much as a factor of two,[21] which would bring it into good agreement with the two values of our study.

All of our results can be described by the conventional "Russell" or concerted termination scheme for peroxyls,[23] with an activation energy about 9 kcal/mol higher for production of a ketone in the triplet than in the ground state. It is tempting, however, to ascribe this $\Delta E_a$ to the difference between a stepwise termination of $R_2O_4$ via $2RO^\bullet$, which gives excited ketones, and a concerted process that does not. The yield of triplet tetralone from THN, measured in an earlier[5] study relative to tetramethyl-1,2-dioxetane with $\Phi$(triplet acetone) = 0.3, was $(2.2 \pm 0.3) \times 10^{-3}$. From the ratio of excited state yields in Table IV, we calculate $\Phi = 8.0 \times 10^{-4}$ for triplet production from $2TOO^\bullet$. Approximating this triplet yield as $k_{4T}/k_4$ and expanding the terms with the Arrhenius equation, we have $8.0 \times 10^{-4} = k_{4T}/k_4 = (A_{4T}/A_4)\exp(E_4 - E_{4T})/RT$. For a temperature of 41 °C and with our experimental value of $E_4 - E_{4T}$, we calculate $A_{4T}/A_4 = 1500$. This ratio is consistent with our alternate hypothesis, since the concerted transition states proposed for peroxyl termination are cyclic and should have lower $A$ factors because of the loss of rotational modes in the transition state.[24,25]

When the stepwise process of $R_2O_4$ is considered in detail, one may write an extended sequence

$$[R_2CHO^\bullet\ {}^\bullet OOOCHR_2] \rightarrow [R_2CO\ HOOOCHR_2] \rightarrow [HOO^\bullet\ {}^\bullet OCHR_2] \rightarrow H_2O_2 + R_2CO \quad (11)$$

in competition with cage escape of the species in brackets. The scission-dismutation reactions of $R_2O_4$ and $RO_3H$ in this sequence can alternatively be described as concerted, four-center elimination processes. The thermolysis of hydrotrioxides is known to produce alcohols, oxygen, and singlet oxygen.[26] We were unable, however, to see an OH signal in the $^1$H NMR spectrum at low field[26a] from TOOOH in oxidized mixtures of TOOH and ceric ammonium nitrate in acetone-$d_6$ at −75 °C, although the spectrum was not well resolved. On the basis of economy of assumptions (Occam's razor), the original Russell scheme[23] remains a preferred explanation for generation of both ground- and excited-state species.

It is unfortunate that spin-orbit coupling in the alkoxyl radicals makes it impossible to analyze the system by conventional EPR methods.[27] More definitive evidence on the viability of the alternate schemes involving $R_2O_4$ may come from molecular orbital calculations and measurement of yields of singlet oxygen now in progress.

**Acknowledgment.** We thank the 3M Co. for a fellowship to S.-H. Lee and Himont USA for partial support, Dr. G. A. Russell for his continued interest, and a referee for contributing additional references.

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(21) Kellogg, R. E. *J. Am. Chem. Soc.* **1969**, *91*, 5433-5436.

(22) The fraction of alkoxyls undergoing cage disproportionation (0.143) and escape (0.796) are based on their analytical data.[10] They do not add up to unity because of the formation of cyclohexyl peroxide.

(23) Russell, G. A. *Chem. Ind.* (*London*) **1956**, 1483.

(24) Howard, J. A. *Organic Free Radicals*; Pryor, W. A., Ed.; ACS Symposium Series **1978**, *69*, 413-432.

(25) Bennett, J. E.; Brunton, G.; Smith, J. R. L.; Salmon, T. M. F.; Waddington, D. J. *J. Chem. Soc., Faraday Trans. 1*, **1987**, *83*, 2433-2447.

(26) (a) Pryor, W. A.; Ohto, N.; Church, D. F. *J. Am. Chem. Soc.* **1983**, *105*, 3614-3622 and references therein. (b) Kovac, F.; Plesnicar, B. *J. Chem. Soc., Chem. Commun.* **1978**, 122-124.

(27) Yakimchenko, O. E.; Lebedev, Y. S. *Russ. Chem. Rev.* (*Engl. Transl.*) **1978**, *47*, 531-548.

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# Association, Photodimerization, and Induced-Fit Types of Host-Guest Complexation of Anthracene-Appended γ-Cyclodextrin Derivatives

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**Abstract:** γ-Cyclodextrin derivatives bearing one and two anthracene moieties (**1** and **2**, respectively) were prepared, and their host-host and/or host-guest association behaviors were studied by spectroscopy in solution. The host **1** was found to exist as an equilibrium between a monomer and an association dimer with $1.1 \times 10^5$ M$^{-1}$ as its association constant. The 1:1 host-guest association constant of **1**, which was obtained by digital simulation analysis of the absorption data, was compared with those of **2** and a β-cyclodextrin derivative bearing an anthracene moiety (**3**). Arguments are presented suggesting that host-guest complexation of these hosts is associated with locational changes of their anthracene moieties. The circular dichroism spectrum of **1** exhibits an exciton coupling band of $R$ helicity in the $^1B_b$ transition region of anthracene due to the interaction of the two anthracene moieties in the cavity of the association dimer. The host **2** also exhibits a similar exciton coupling pattern, but this arises from intramolecular interaction of its two anthracene moieties. Fluorescence spectra of **1** and **2** exhibit broad peaks above 470 nm, which are also seen in the spectra of **3** and anthracene-modified methyl α-D-glucoside **4** and are consequently assigned to monomer fluorescence. The photodimerization of anthracene proceeds in the association dimer of **1** as well as in **2** at rates that are suppressed upon addition of *l*-borneol.

Cyclodextrins (CDs) are a series of cyclic oligomers consisting of six or more α-1,4-linked D-glucopyranose units and designated by α, β, and γ for the hexamer, heptamer, and octamer, respectively. The smaller α- and β-CDs usually form 1:1 complexes,[1] but γ-CD has been shown to accommodate two guest molecules in its large cavity (1:2 host-guest complexation).[2-5] This property

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† Tohoku University.

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(1) Bender, M. L.; Komiyama, M. *Cyclodextrin Chemistry*; Springer-Verlag: New York, 1977.

0002-7863/88/1510-4323$01.50/0