remained which was purified by preparative GC on a 20 ft × 0.25 in. 15% carbowax 20M on Chromosorb p column at 140 °C to give 0.273 g (27%) of the diene: NMR ($CDCl_3$, 360 MHz) δ 1.067 (d, J = 6.5 Hz, 6 H), 2.020–2.180 (m, 4 H), 2.257–2.365 (m, 2 H), 4.72 (d, J = 1.81 Hz, 2 H), 4.687 (d, J = 1.8 Hz, 2 H); MS, m/e 136.1249 (calcd for $C_{10}H_{16}$ 136.1253).

***trans*-2,3-Dimethyl-*cis*-1,4-bis(dideuteriohydroxylmethyl)cyclohexane (25).** The deuterated diol was prepared from 2.91 g (12.7 mmol) of ester **21** with 0.638 g (16.3 mmol) of lithium aluminum deuteride by employing the same method as used for conversion of **21** to protio diol **22**. A total of 2.20 g (98%) of deuterio diol **25** was obtained: mp 89–90 °C; NMR ($CDCl_3$, 90 MHz) δ 0.9–1.0 (d, J = 6 Hz, 6 H), 1.1–2.0 (br m, 8 H).

***trans*-2,3-Dimethyl-1,4-bis(dideuteriomethylene)cyclohexane (TXD) (26).** The deuterated diene was prepared from 1.28 g (7.3 mmol) of deuterio diol **25**, 3.93 g (17 mmol) of *o*-nitrophenyl selenocyanate, and 3.68 g (17 mmol) of tri-*n*-butylphosphine in the same way as diene **24** was prepared from diol **22** to give 0.223 g (22%) of material. NMR ($CDCl_3$, 360 MHz) δ 1.069 (d, J = 6.9 Hz, 6 H), 2.020–2.179 (m, 4 H), 2.257–2.345 (m, 2 H); MS, m/e 140.1515 (calcd for $C_{10}H_{12}D_4$ 140.1504).

Pyrolysis of *trans*-2,3-Dimethyl-1,4-dimethylenecyclohexane to *anti*-1,4-Diethylidenecyclohexane (A). Samples of 3 μL of T were pyrolyzed at 305 °C for 12 h. The combined, recovered pyrolysates were analyzed by NMR with the spectrum of starting T subtracted by computer. The resulting spectrum in $CDCl_3$ at 360 MHz is δ 5.209 (q, J = 6.86, 2 H), 2.188 (t, J = 5.42 Hz, 4 H), 2.115 (t, J = 5.42 Hz, 4 H), 1.59 (d, J = 6.14 Hz, 6 H).

Pyrolysis of *cis*-2,3-Dimethyl-1,4-dimethylenecyclohexane to *syn*-1,4-Diethylidenecyclohexane (S). Samples of 3 μL of C were pyrolyzed at 305 °C for 12 h. The combined, recovered pyrolysates were analyzed by NMR with the spectrum of starting C subtracted by computer. The resulting spectrum in $CDCl_3$ at 360 MHz is δ 5.201 (q, J = 6.50 Hz, 2 H), 2.17 (s, 4 H), 2.118 (s, 4 H), 1.605 (d, J = 6.5 Hz, 6 H).

Gas-Phase Pyrolyses. The reaction vessel consisted of a 2-L Pyrex round-bottomed flask which was treated with dimethylchlorosilane and then with dimethylamine. This flask was connected to a vacuum line fitted with a spiral trap and the usual arrangement to allow the introduction of the sample into the system. The flask was immersed in a molten potassium nitrate–sodium nitrate (10:7) bath heated by a 500-W Vycor immersion heater. The fine adjustment of the temperature was accomplished with a Bayley controller Model 76-8 connected to a 125-W Vycor immersion heater. The temperature was measured with an Omega platinum resistance thermometer probe and the readout was performed with an Omega temperature indicator, Model 410A-PT3-C. The temperature reported was measured at the middle point of the reactor. Temperature variation across the vessel was less than 0.5 °C, and it was constant to 0.1 °C.

Acknowledgment. We thank the National Science Foundation for generous financial support as well as the Venezuelan Government for a Fellowship to J.L.J.

Appendix

SMPXKS is a Fortran 77 program written for the IBMPC by K. E. Gilbert with modifications of I/O by J. J. Gajewski. It utilizes the Gear algorithm for numerical integration of first-order differential rate equations and varies specified rate constants to obtain the best fit to experimental mole fractions by the Simplex algorithm. The response function to be minimized is the sum of the squares of the residuals of each concentration. Any number of ks can be fixed and all (or some) K_{eq}s can be entered so that the $k_{j,i}$s can be determined by the set of $k_{i,j}$s and $K_{i,j}$s. The residuals can be weighted according to the extent of reaction by a factor that is user selectable. The program will accept data sets starting with one or all isomers, does the integration, and calculates the sum of the squares of the residuals to be minimized from all data sets. The data output and plots reported for the interconversions of T with A and TXD with TND and AD are provided by the program. This and other kinetics programs are available from SERENA SOFTWARE.

Chemiluminescence from Free-Radical Sources. Excited States from Thermolysis of Hyponitrite Esters

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Abstract: Chemiluminescence was observed from the thermolysis of 11 symmetrical *trans*-alkyl hyponitrites (RON=NOR), in which the alkyl groups contained α-hydrogen atoms, in solutions containing aromatic fluorescers. The excited-state production occurs by disproportionation of alkoxyl radicals within the solvent cage, possibly by a mechanism involving spin inversion in the caged radical pair followed by reaction on a triplet surface. The reactions are characterized by large T_1/S_1 ratios in the carbonyl products and exited-state yields that were more sensitive to changes in the alkyl structure than to changes in the solvent. The approximate total quantum yields in *tert*-butylbenzene varied from 3.3×10^{-3} (R = PhCHMe) to 5×10^{-6} (R = Me) einsteins/mol of hyponitrite.

Studies of chemiluminescence have traditionally focused on reactions which produce high quantum yields. For many of the visible examples of these reactions, an electron-transfer, charge-recombination and high yields of singlet excited states are a common feature.[1] The rate constants for excited state production in some bimolecular chemiluminescent reactions can be related directly to the redox potentials of one reactant.[2] 1,2-Dioxetanes, on the other hand, generally show high specifically for the generation of excited triplet states, and the quantum yields are a sensitive function of substituents.[3]

The chemiluminescent thermolysis of hyponitrites in solution gives excited states via cage dismutation of alkoxyl radicals. We have studied this reaction because (1) the transition state for alkoxyl self-reaction exhibits a formal similarity to the 1,4-bis(alkoxyl) biradical postulated as an intermediate from 1,2-diox-

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[1] (a) Lytle, F. E.; Hercules, D. M. *Photochem. Photobiol.* **1971**, *13*, 123–133. (b) Faulkner, L. R. *Int. Rev. Sci.: Phys. Chem., Ser. 2*, **1976**, *9*, 213–263. (c) Schuster, G. B.; Schmidt, S. P. *Adv. Phys, Org. Chem.* **1984**, *18*, 187–234. (d) Chandross, E. A.; Sonntag, F. I. *J. Am. Chem. Soc.* **1964**, *86*, 3179–3180. (e) McCapra, F. *Q. Rev. Chem. Soc. (London)* **1966**, *20*, 485–510.

[2] Dixon, B. G.; Schuster, G. B. *J. Am. Chem. Soc.* **1979**, *101*, 3116–3118.

[3] Review of dioxetanes: Adam, W.; Yang, F. In "The Chemistry of Heterocyclic Compounds"; Hassner, A., Ed.; Wiley: New York, 1985; Vol. 42, Part 3, pp 351–430.

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Table I. Quantum and Product Yields from *trans*-Hyponitrite Esters in *tert*-Butylbenzene

	y-intercept/slope						
R in RON=NOR	DBA	DPA	$10^6\Phi_T$[a]	$10^6\Phi_S$[b]	Φ_T/Φ_S	% ket[c]	$10^2\Phi_T$/ket
$C_6H_5CHCH_3$	2632	2976	3250 ± 300[d]	3.7 ± 0.1[e,f]	869	30.3	1.07
$C_6H_5CDCH_3$	1852		1420 ± 500			22.2	0.64
c-C_6H_{11}	1850	3025	280 ± 50[d]	≤0.46 ± 0.02	≥607	30.0	0.093
$C_6H_5CH_2$	562	4808	27 ± 4[d]	≤0.04 ± 0.00	≥675	34.8	0.0078
CH_3	4024		5 ± 0			37.6[g]	0.0013
CH_3CH_2	1422		707 ± 80			40.2	0.18
$(CH_3)_2CH$	921		2240 ± 200			12.1	1.8
$(CH_3)_2CHCH_2$	764		6 ± 0			23.0	0.0026
n-C_4H_9	1650		16 ± 3			24.0	0.0066
1-tetralyl	3431		2150 ± 300			31.6	0.68
$(C_6H_5)_2CH$	720		370 ± 50			24.3	0.15

[a] Total quantum yield ≅ Φ (triplet) from intercept with DBA, uncorrected for DBA excitation efficiency. [b] Singlet quantum yield from intercept with DPA. Reference TMD, assuming Φ (singlet) = 0.0050. [c] Percent carbonyl product, based on starting hyponitrite, from BHT-inhibited solution at 45 °C. [d] Calculations relative to tetramethyl-1,2-dioxetane (TMD) assuming Φ_T (TMD) = 0.030; otherwise relative to 1-phenylethyl hyponitrite assuming Φ_T = 0.003 25. [e] Corrected for triplet contribution (cf. Figure 1). [f] At 48.6 °C, we determined $\Phi_T/\Phi_S \geq 1500$ (ref 5a). [g] Yield of methanol. The yield of formaldehyde was assumed also to be 37.6%.

etanes, (2) the reaction was expected to be a prototype "weak" source of excited states derived from free-radical sources, and (3) the reaction might be of relevance to the luminescence that accompanies autoxidation. Some of this "oxyluminescence"[4] we reasoned could arise from caged alkoxyl pairs derived from alkyl peroxides or from other sources. An improved understanding of the processes involved in the phenomenon would be useful to its application.

Experimental Section

The synthesis of hyponitrites and measurement of rates of decomposition by monitoring the exponential decay of the sensitized chemiluminescence have been described in recent papers.[5]

Most of the excited-state yields were determined by addition of successive amounts of 0.020 M 9,10-dibromoanthracene (DBA) or 9,10-diphenylanthracene (DPA) to magnetically stirred solutions (5 mL) of the hyponitrite (0.50–0.55 mM) until the total volume was 6 mL (S–V method).[6] The emission rates, determined by photon counting after each addition of fluorescer, were measured as the average of five to ten 40-s counting periods, expressed in hertz and corrected for background readings with solvent alone. Appropriate care was taken with the tetramethyl-1,2-dioxetane (TMD) to prevent induced decomposition.

Solutions of benzyl hyponitrite in *tert*-butylbenzene containing DBA gave irregular first-order plots of the chemiluminescence emission. Good first-order plots were obtained from similar solutions that were 1.2 mM in 2,6-di-*tert*-butyl-4-methylphenol (BHT) and flushed with N_2 for 3 min after each addition of fluorescer. For the other hyponitrites, these measures were unnecessary. In each case, however, the standard (1-phenylethyl hyponitrite or TMD) solution used for comparison contained the same concentrations of solutes as were in the hyponitrite solutions. In most cases, with *tert*-butylbenzene solvent, nitrogen flushing was omitted, since it can actually promote induced decomposition of dioxetanes.[7] Control experiments with *tert*-butyl hyponitrites showed negligable chemiluminescence in air-saturated solutions, which demonstrated the absence of interfering excited states formed outside of the solvent cage. The temperature (43.7 ± 0.1 °C) for the experiments was low enough that errors from decomposition of the hyponitrite or dioxetane were small and not detrimental to the outcome of the S–V experiment.

Product analyses were done by gas chromatography (Model HP5830A with a 60/80 Carbopack glass column, 8 ft 2 mm i.d. or Model HP5880A with a Supelco Wax capillary column) or by liquid chromatography (Model HP1084B with IBM C-18 column, 4.6 × 250 mm, detection at 254 nm).

The syntheses of the compounds used in this study have been described previously.[5] 1-Phenylethanol-*1-d* was prepared from $NaBD_4$ (Alfa) and acetophenone followed by the usual sequence to give the corresponding hyponitrite. The ^1H NMR spectrum of the product showed the complete absence of methine protons.

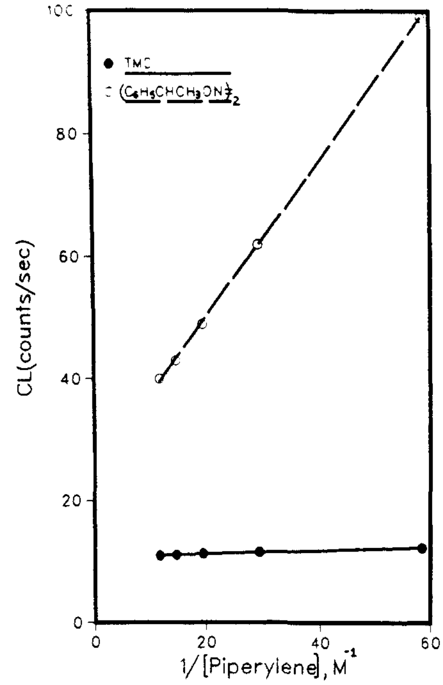

Figure 1. Quenching of triplet-derived DPA fluorescence from 1-phenylethyl hyponitrite with piperylene. The DPA fluorescence from tetramethyl-1,2-dioxetane is unaffected.

Results

Excited-State Yields. The conventional methods we used for estimation of quantum yields gave linear plots of 1/(light intensity) vs. 1/[fluorescer]. The intercept/slope ratios, which equal, in a simple analysis,[8] the rate constant for energy transfer to fluorescer times the excited-state lifetime, appear in Table I.

The similar ratios for both DPA and DBA sensitization led[5a] to an additional experiment which demonstrated (Figure 1) that the triplet state was responsible for exciting both fluorescers. A very small singlet yield could be estimated by extrapolation of the line in Figure 1 to infinite piperylene concentration. The "singlet" yields calculated from two other hyponitrites from experiments with DPA were small to begin with and are likewise assumed to be derived from triplet carbonyls because of the high slope/intercept ratios.

Cage Effect. Table I also contains the yields of carbonyl products from the hyponitrites. A number of control experiments

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(6) Wilson, T., Golan, D. E., Harris, M. S.; Baumstark, A. L. *J. Am. Chem. Soc.* **1976**, *98*, 1086–1091 and references therein.

(7) Wilson, T.; Schaap, A. P. *J. Am. Chem. Soc.* **1971**, *93*, 4126–4136.

(8) This treatment is on approximation which is valid here because the singlets, which can contribute to the excitation of DBA, are formed in such small yields.

Table II. Calculated Exothermicities of the Disproportionation Reactions and the α-Hydrogen Bond Strengths

hyponitrite	D$H°$, kcal/mol (α-H)	disproportionation prod	$-\Delta H°_f(g)^a$, kcal/mol	$-\Delta H°_r$, kcal/mol	E_T, kcal/mol
$(CH_3ON{=})_2$	19.98	CH_2O	28.69	83.82	72.5
		CH_3OH	48.07		
$(CH_3CH_2ON{=})_2$	17.11	CH_3CHO	39.73	86.69	
		CH_3CH_2OH	56.24		
$((CH_3)_2CHON{=}_2$	13.80 ± 0.21	$(CH_3)_2CO$	51.92 ± 0.16	90.00 ± 0.2	80
		$(CH_3)_2CHOH$	65.12 ± 0.13		
$(n\text{-}C_4H_9ON{=})_2$	17.00 ± 0.17	C_3H_7CHO	48.96 ± 0.03	86.80 ± 0.2	
		C_4H_9OH	65.36 ± 0.17		
$((CH_3)_2CHCH_2ON{=}_2$	19.19 ± 0.26	$(CH_3)_2CHCHO$	49.06 ± 0.20	84.51 ± 0.3	
		$(CH_3)_2CHCH_2OH$	67.75 ± 0.16		
$(c\text{-}C_6H_{11}ON{=})_2$	14.77 ± 0.75	$c\text{-}C_6H_{10}O$	54.04 ± 0.52	89.05 ± 0.75	
		$c\text{-}C_6H_{11}OH$	68.21 ± 0.54		
$(C_6H_5CH_2ON{=})_2$	15.80 ± 2.02	C_6H_5CHO	8.9 ± 1.0[b]	88.0 ± 1.1	72
		$C_6H_5CH_2OH$	24.00 ± 0.33		
$(C_6H_5CHCH_3ON{=})_2$	13.00 ± 0.40	$C_6H_5COCH_3$	20.71 ± 0.40	90.8 ± 0.4	74
		$C_6H_5CH_3CHOH$	33.11		

[a] Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970. [b] Solly, R. K.; Benson, S. W. J. Chem. Thermodyn. **1971**, 3, 203–209.

were caried out to demonstrate that the aldehydes or ketones arose entirely from cage reactions. The yield of cyclohexanone from 6.19 × 10^{-4} M cyclohexyl hyponitrite was not increased by prior addition of 0.96 M cyclohexanol to the solution. The yields of acetophenone from 7.0 × 10^{-4} M 1-phenylethyl hyponitrite were 30.7, 29.0, and 30.4% when the solution contained 0.091, 0.0213, and 0.0045 M BHT, respectively. The yield of acetophenone from 10^{-4} M hyponitrite at 45 °C did increase to 34.5 ± 1.3% in *n*-hexadecane and to 86.7 ± 1.3% in mineral oil, which is entirely parallel to the increased yields of *tert*-butyl peroxide from *tert*-butyl hyponitrite with increases in solvent viscosity.[9] It is entirely possible for cage-escaped alkoxyls to produce luminescence by generating solvent-derived peroxyl radicals, but this does not appear to be a significant process in the solvents we (carefully) chose for the quantum yield measurements.

Methyl hyponitrite posed a special problem because of the high volatility of the reagent and its decomposition products and the high reactivity of formaldehyde. Although its decomposition kinetics were well-behaved and comparable to those of other hyponitrite esters, analysis of decomposed solutions for methanol gave a yield which was below that expected for complete cage reaction. Similar results were found earlier[10] with ^1H NMR analysis of solutions in benzene-d_6. We arbitrarily assumed that the formaldehyde yield was equal to the methanol yield in this case. Since methyl hyponitrite is dangerous when isolated[10] and since it gave the lowest triplet yield in the entire series, we were not inclined to examine the compound further.

Relation of Triplet Yield to Thermodynamics. A linear relation between the excited-state yield and the exothermicity of the disproportionation was suggested by early results.[5a] The updated plot shown in Figure 2 reveals, at most, a rough trend. For ground and excited states that are produced after a common rate-determining step (cf. Figure 3),

$$HN \rightarrow X \xrightarrow{k_S} R_1R^2CO\ (S_0) + R_1R_2CHOH \qquad (1)$$

$$HN \rightarrow X \xrightarrow{k_T} R_1R_2CO\ (T_1) + R_1R_2CHOH \qquad (2)$$

If both reactions designated by k_S and k_T follow Evans–Polanyi[11] relationships, then $E_{a,T} = \alpha_T \Delta H_T + \beta_T$ and $E_{a,S} = \alpha_S \Delta H_S + \beta_S$. The quantum yield may then be written in terms of the respective Arrhenius equations for (1) and (2),

$$\Phi_T = \frac{k_T}{k_S + k_T} \cong k_T/k_S = (A_T/A_S)\exp((E_S - E_T)/RT) \qquad (3)$$

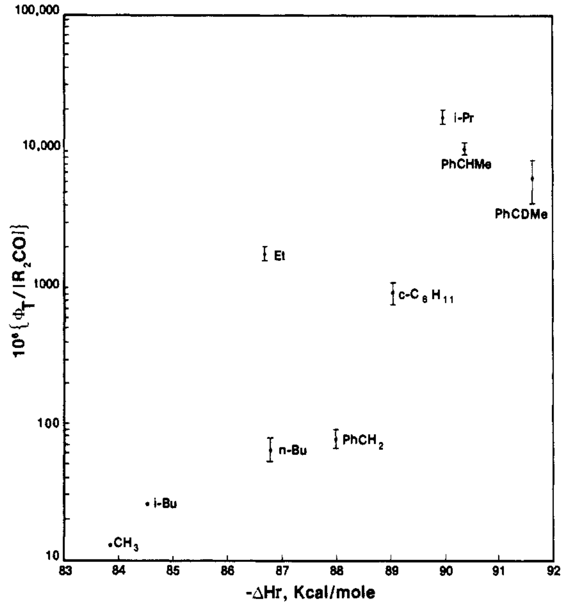

Figure 2. Intrinsic yield of triplets (Table I, last column) vs. gas-phase enthalpy of dismutation of alkoxyl radicals (Table II, column 4).

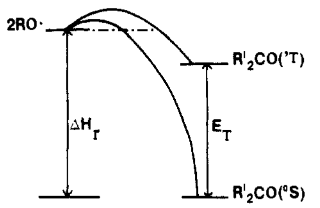

Figure 3. Generation of triplet and ground states from the same precursors.

Noting that $\Delta H_S = \Delta H_T + E_T$, where E_T is the triplet energy of the carbonyl product, we obtain by substitution

$$\Phi_T = \frac{A_T \exp[-\alpha_T \Delta H_T - \beta_T]/RT}{A_S \exp[-\alpha_S \Delta H_S - \beta_S]/RT} \qquad (4)$$

or

$$\ln \Phi_T = \ln (A_T/A_S) + [(\beta_S - \beta_T) + (\alpha_S - \alpha_T)\Delta H_S - \alpha_T E_T]/RT \qquad (5)$$

Equation 5 suggests that the logarithm of the quantum yield should indeed be a function of ΔH_S but also of E_T and the temperature. Experiments with step increases in the temperature of hyponitrite solutions (Table III) led us to conclude that there was no appreciable temperature dependence of the quantum yield[5a,12]

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(9) Neumann, R. C., Jr.; Bussey, R. J. *J. Am. Chem. Soc.* **1970**, *92*, 2440–2445.

(10) Mendenhall, G. D.; Cary, L. W. *J. Org. Chem.* **1975**, *40*, 1646–1647.

(11) (a) Evans, M. G.; Polanyi, M. *Trans. Faraday Soc.* **1936**, *32*, 1333–1360; **1938**, *34*, 11–24. (b) Polanyi, M. *Nature (London)* **1937**, *139*, 57–56.

Scheme I. Cage Reactions of Products from Non-*tert*-Hyponitrite Esters. The Caged Species Are Overlined

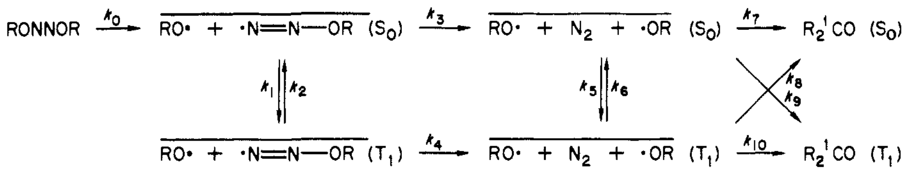

Table III. Activation Parameters of Hyponitrites and Tetramethyl-1,2-dioxetane in *tert*-Butylbenzene

		activation energy, E_a, kcal/mol		
compound	sensitizer	decay expt	temp jump expt[a]	log A, s^{-1}
TMD	DPA	25.9 ± 0.0	26.2 ± 0.5	13.0 ± 0.0
$(C_6H_5CHCH_3ON=)_2$	DBA	25.2 ± 0.2	21.5 ± 0.6	13.5 ± 0.1
	DPA		25.2 ± 0.5	
$(C_6H_5CDCH_3ON=)_2$	DBA	25.7 ± 0.2		13.8 ± 0.2
$(c\text{-}C_6H_{11}ON=)_2$	DBA	27.3 ± 0.3	23.3 ± 0.0	14.4 ± 0.2
	DPA		26.8 ± 0.3	
$(C_6H_5CH_2ON=)_2$	DBA	26.1 ± 0.4	20.4 ± 1.1	14.4 ± 0.2
	DPA		27.4 ± 0.9	

[a] Uncorrected for fluorescence activation energy (−4 kcal/mol with DBA).

Table IV. Differences in Zero Point Energies for C–H, O–H, and C–D, O–D in the Disproportionation Reactions of 1-Phenylethoxyl, and Deuterated 1-Phenylethoxyl Radicals

bond	ν_0, cm^{-1}	ΔE, kcal/mol
C–H	2990	0.873
O–H	3601	
C–D	2175	0.464
O–D	2500	

and that a correlation of quantum yield with E_T alone was unlikely. Examination of Tables I and II, however, shows that further analysis of the data in terms of (5) would not be fruitful. The aldehydes derived from *n*-butyl and ethyl hyponitrites, for instance, are expected to have identical values of E_T and ΔH_S but differ by nearly 2 orders of magnitude in Φ_T.

Finally, we noted that the relationship sought in Figure 2 might be obscured to some degree by differing efficiencies for transferring the energy from triplet ketone to DBA or by differential solvation or exciplex formation[13] of reactive intermediates. For this reason, we synthesized 1-phenylethyl-*1*-*d* hyponitrite and compared its triplet yield with that of the unlabeled compound. Acetophenone is the cage product from both precursors, so

$$2\text{PhCH(CH}_3\text{)O}\cdot \xrightarrow{\Delta H_g \simeq 90.8\ \text{kcal/mol}} \text{PhCOCH}_3 \xleftarrow{\Delta H_g \gtrsim 91.2\ \text{kcal/mol}} 2\text{PhCD(CH}_3\text{)O}\cdot \quad (6)$$

that the detailed fate and energetics of the excited states should be identical. If the CH/CD and OH/OD vibrational frequencies in the corresponding alcohol are compared (Table IV), we calculate from zero-point energies that deuterium substitution should *increase* the exothermicity of alkoxyl self-reaction by about 400 cal/mol. This calculation is a lower limit because other vibrational modes also contribute to the zero-point energy difference, and because the CH/CD frequencies in the 1-phenylethoxyl radicals may be proportionately lower than in the alcohols. The triplet yield however was distinctly lower from the deuterated hyponitrite, even after correction for a lower degree of cage reaction in the latter (Table II and Figure 3).

Solvent Effects. The influence of solvent was studied briefly by comparing tetramethyl-1,2-dioxetane (TMD) with isopropyl hyponitrite, both of which lead to excited acetone. When normalized for ketone yield, the results (Table V) show that benzonitrile increases the relative yield from the hyponitrite by about a factor of 5, while *tert*-butanol lowers the yield by a factor of 2. The measurement in *tert*-butylbenzene gave slightly different results depending on the method, and the triplet yield from isopropyl hyponitrite in benzonitrile, in contrast to results in *tert*-butylbenzene, appeared to decrease between 43.7 and 68 °C. We have made some studies of triplet yields from hyponitrite esters in viscous media, but the results are irregular and we defer a discussion of them to a later publication.

Discussion

Mechanism of Excitation. The production of excited states from the hyponitrite esters in this study is assumed to proceed in a solvent cage through a number of discrete steps among those shown in Scheme I.

The first-order decomposition of hyponitrites with E_a of 22–28 kcal/mol is believed to correspond to rate constant k_0, which of course is rate-determining. The steps represented by k_3 and k_4 are exothermic by about 30 kcal/mol,[14,15] and from the magnitude of the activation volume for *tert*-butyl hyponitrite[9] homolysis, we infer that the loss of nitrogen (k_3 and k_4) is rapid and irreversible. There are two possibilities for the mode of $R_2{}^1CO$ (T_1) formation: First, the singlet and triplet alkoxyl pairs undergo a branching process during the approach to the transition state for the dismutation to give predominantly singlet and some triplets ($k_7 > k_9$ and/or $k_8 > k_{10}$). Second, we may postulate that there is leakage of some singlet pairs to triplets during the lifetime of the cage via k_1 and k_5, followed by reaction on the triplet surface to give excited carbonyl product (k_{10}) and predominant ground-state products from singlet pairs via k_7.

The second of the two explanations is attractive because the rate constants for triplet to singlet spin inversion ($k_T \rightarrow k_S$) in both radical pairs in micelles[16] and in a cyclic biradical[17] have been calculated to lie between 10^6 and 10^7 s^{-1}. Since the rate of decay of the caged pair in homogeneous solution is probably 10^9 to 10^{10} s^{-1}, where this figures includes both radical dismutation and escape,[18] the yield of triplet product should be roughly 10^{-4} to 10^{-2}, which indeed encompasses most of the range of our examples (Table I). The examples outside this range are at the low end and can be explained in terms of a lower rate of intersystem crossing to the triplet radical pair. Slightly larger rates might have been expected if $k_{T\rightarrow S} = 3k_{S\rightarrow T}$ as predicted on statistical grounds, since it is the latter process which can give rise to triplet products in the case under discussion.

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(12) Hence from eq 3, we obtain $\Phi_T \simeq A_T/A_S$ directly.

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Table V. Solvent Effect on Φ_T of Isopropyl Hyponitrite with DBA

solvent	T, °C	$10^3\Phi_T$[a]	$10^3\Phi_T/R_2CO$[b]	expt	% acetone
$C_6H_5C(CH_3)_3$	43.7	2.24 ± 0.2	18.5	S–V	12.1 ± 1.7
C_6H_5CN	43.7	22.2 ± 3.8	96.1	S–V	23.1 ± 0.5
	43.7	15.5 ± 0.4	67.1	I[d]	
	68.9	10.5 ± 1.2		I	
$HOC(CH_3)_3$	68.9	1.06 ± 0.3	4.8	I	22.1 ± 1.3
	68.9	1.58 ± 0.6		I	

[a] Calculations relative to tetramethyl-1,2-dioxetane. [b] Preceding column divided by fractional yield of acetone. [c] S–V, Stern–Volmer experiment. [d] I, calculated from the area under the chemiluminescence curve during complete thermolysis.

The lack of a temperature dependence of triplet yield is an important point, since this rules out any *simple* explanations of the range of triplet yields in terms of a higher activation energy for k_9 or k_{10} than for k_7 or k_8, or in terms of a rapid equilibrium between singlet and triplet radical pairs which gives widely varying amounts of the latter. Either of these cases would predict increasing triplet yields with higher temperatures, as long as the fraction of pairs escaping the cage does not change appreciably with temperature, which is true for two examples.[19]

If the rate of spin inversion is controlling the production of triplet carbonyl products, then it is entirely reasonable that exothermicity relationships such as attempted in Figure 1 would fail to predict the triplet yields. In addition to the temperature independence of excitation and the deuterium isotope experiment, we note that benzhydryl hyponitrite gives a low yield of triplet benzophenone, even though the methine hydrogen in the precursor is weakened by benzylic stabilization from at least one aromatic ring.

In 1-tetralyl hyponitrite, the CH is fixed in a favorable position to overlap with the aromatic π-orbitals, but this feature is also not significant because the triplet yield was actually lower than from the comparable 1-phenylethyl ester.

There is, however, an obvious trend in Table I toward the higher triplet yield with α-methyl substitution. Thus, with the hyponitrite series which give formaldehyde, acetaldehyde, and acetone, the yields of the excited states increase by factors of 225 and 10, respectively; benzaldehyde and acetophenone yields differ by 140 from their respective precursors.

Relation to 1,2-Dioxetanes. Recently Adam and co-workers reported a synthetic feat in the preparation and characterization of 1,2-dioxetane itself.[20] The compound shows $\Phi_{(\mathrm{triplet})} = 0.0024 \pm 0.006$ on decomposition, although induced processes and volatility made the determination of rate constants difficult. The quantum yields from 1,2-dioxetane increase in homologues with progressive methylation at the 3 and 4 positions.[20] What is perhaps more interesting is that the range of quantum yields in their series extends over about 2 orders of magnitude, so that the highest intrinsic triplet yields from hyponitrites are larger than those of dioxetane itself. If the triplet yield from TMD in benzonitrile is the same as in benzene, then the intrinsic quantum yield of excited acetone from isopropyl hyponitrite in the former solvent may be as high as 20% (Table II).

It is thus apparent that the presence of a four-membered ring is not sufficient for high efficiency of product excitation. The similar effect of α-methyl substitution in the 1,2-dioxetane and hyponitrite series suggests a hyperfine interaction with that group which enhances the relative rate of spin inversion.

Light Standard. Dioxetanes have frquently been used as primary emission standards but suffer from several kinds of induced decomposition.[21] The hyponitrite esters are well-behaved kinetically in dilute solutions,[5] are not subject to catalysis by transition metals, and appear from this study to be essentially pure triplet sources. Most of our quantum yields were determined with 1-phenylethyl hyponitrite as a secondary standard, since this crystalline ester was nonvolatile and relatively easy to prepare and purify. In addition, the kinetics of the triplet acetophenone–DBA system have been extensively characterized by Wilson and Halpern.[13a]

Relevance to Autoxidation. The analogy between cleavage of *tert*-butyl hyponitrite and *tert*-butylperoxyl dimer to give caged alkoxyl radical pairs in each case was originally pointed out by Kiefer and Traylor.[22]

$$RON{=}NOR \rightarrow \overline{RO\cdot + N_2/O_2 + \cdot OR} \leftarrow ROOOOR \quad (7)$$

These workers noted that the amount of cage escape, although calculated in different ways, was similar in the two cases. We have elsewhere[19] suggested that the decreased yield of cage products from α-deuterated hyponitrites can explain the retardation in the apparent rate of self-reaction of α-deuterated alkylperoxyl radicals, since only the alkoxyl pairs which react in the cage will actually be terminating. The step shown in eq 7 may thus be common to primary and secondary as well as tertiary alkylperoxyls.

Since chemiluminescence from autoxidation processes has been shown to be proportional in many model systems[23–26] to the rate of alkylperoxyl termination, we suggest that cage alkoxyl dismutation may be generally responsible for this nearly ubiquitous chemiluminescence emission. Studies are under way to compare the quantum yields of excited states from autoxidation in which the terminating radicals will be the same as from the hyponitrites reported here. One might anticipate a higher triplet yield from the tetroxide than from the hyponitrite in eq 7, since the preferred elimination of the ground state of the diatomic molecule will generate the alkoxyl pairs in different initial spin states from the two sources.[27]

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Registry No. BHT, 128-37-0; TMD, 35856-82-7; $C_6H_5CH(CH_3)ON{=}NOCH(CH_3)C_6H_5$, 82522-46-1; $C_6H_5CD(CH_3)ON{=}NOCD(CH_3)C_6H_5$, 97012-03-8; c-$C_6H_{11}ON{=}NOC_6H_{11}$-*c*, 82522-48-3; $C_6H_5CH_2ON{=}NOCH_2C_6H_5$, 19657-56-8; $CH_3ON{=}NOCH_3$, 29128-41-4; $CH_3CH_2ON{=}NOCH_2CH_3$, 4549-46-6; $(CH_3)_2CHON{=}NOCH(CH_3)_2$, 82522-47-2; $(CH_3)_2CHCH_2ON{=}NOCH_2CH(CH_3)_2$, 99643-10-4; *n*-$C_4H_9ON{=}NOC_4H_9$-*n*, 29128-39-0; (1-tetralyl)ON=NO(1-tetralyl), 97012-09-4; $(C_6H_5)_2CHON{=}NOCH(C_6H_5)_2$, 99643-11-5; c-$C_6H_{10}O$, 108-94-1; C_6H_5CHO, 100-52-7; CH_3OH, 67-56-1; HCHO, 50-00-0; $(CH_3)_2CO$, 67-64-1; $(CH_3)_2CHCHO$, 78-84-2; $CH_3CH_2CH_2CHO$, 123-72-8; $(C_6H_5)_2CO$, 119-61-9; $C_6H_5CH(OH)CH_3$, 98-85-1; c-$C_6H_{11}OH$, 108-93-0; $C_6H_5CH_2OH$, 100-51-6; CH_3CH_2OH, 64-17-5; $(CH_3)_2CHOH$, 67-63-0; $(CH_3)_2CHCH_2OH$, 78-83-1; $CH_3CH_2CH_2CH_2OH$, 71-36-3; $(C_6H_5)_2CHOH$, 91-01-0; CH_3CHO, 75-07-0; $PhCD(CH_3)O\cdot$, 99643-12-6; $PhCH(CH_3)O\cdot$, 76377-89-4; 9,10-dibromoanthracene, 523-27-3; 9,10-diphenylanthracene, 1499-10-1; 1-phenylethanol-*1-d*, 3101-96-0; acetophenone, 98-86-2; 1-tetralone, 529-34-0; 1,2,3,4-tetrahydro-1-naphthalenol, 529-33-9.

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