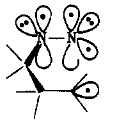
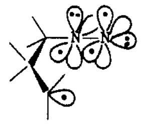
co-workers[3d,9,16] have postulated, based on theoretical work of others,[17] that thermolyses of azo compounds should give ground state σ diazenyl radicals (crudely represented by **12**), whereas photochemical cleavage should initially produce excited-state π-type (e.g., **13**). This proposition follows from Salem diagram symmetry analysis. They argue[9] that direct loss of nitrogen from **12** would produce ground-state nitrogen, but cleavage of excited **13** would give n,π^* N_2. It was suggested that **13** should thus be longer lived than the thermally generated radical, leading to the question why turnaround is not more often observed in photochemical denitrogenations, even in systems giving thermal turnaround (e.g., **5**).

We wish to point out a possible resolution of this dilemma, consistent with larger extents of thermal than photochemical turnaround.[18] This analysis parallels the well-understood behavior of the isoelectronic formyl radical,[19] and similar reasoning has been used to analyze the photochemical α cleavage of cyclic ketones.[20] It should first be noted that significant barriers are predicted for the loss of N_2 from the thermally produced ground-state radical **12**, due to mixing of the σ and π states.[6a,b,21]



12



13

As pointed out by several authors,[17,21] the equilibrium geometry of the excited-state n,π^* diazenyl radical **13** is expected to be linear, as is the isoelectronic excited $HCO^{\bullet}$ radical.[19] The photochemically formed **13** is, to first order, degenerate with the ground-state σ radical inversional transition state. This surface touching offers an efficient radiationless decay path to the ground-state radical.[19,21] There is hence no reason to expect a photochemically generated diazenyl radical to have a longer lifetime than one formed thermally. In fact, crossing from the excited to the ground electronic surface should produce vibrationally excited diazenyl radical, denitrogenating more readily than the thermally produced intermediate and giving less turnaround. This process is analogous to the known electronic predissociation of excited formyl.[19] Hot diazenyl radicals might also explain the photochemical formation of biradicals from azo compounds at low temperatures, under conditions where diazenyl radicals are expected to be stable.[22]

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Supplementary Material Available: Spectral data and select synthetic details for new compounds **6–9** and the precursor urazoles (3 pages). Ordering information is given on any current masthead page.

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Singlet Oxygen Production from the Reaction of Superoxide Ion with Halocarbons in Acetonitrile

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There is controversy about the mechanism of singlet oxygen ($^1O_2$) formation from systems that contain superoxide ion ($O_2^{\bullet -}$), halocarbons, and H_2O.[1-4] Khan[1] and Corey et al.[2] have proposed that the $^1O_2$ results from the water-induced disproportionation of $O_2^{\bullet -}$, while Arudi et al.[3] and Kanofsky[4] have proposed that the $^1O_2$ is a product of the reaction of $O_2^{\bullet -}$ with halocarbons, where X is Br or Cl. Several prior studies support the latter hypothesis.[5]

$$2O_2^{\bullet -} + H_2O \rightarrow O_2(^1\Delta_g) + HO_2^- + OH^- \qquad (1)$$

$$O_2^{\bullet -} + RX \rightarrow RO_2^{\bullet} + X^- \qquad (2)$$

$$2RO_2^{\bullet} \rightarrow [ROOOOR] \rightarrow O_2(^1\Delta_g) + \text{products} \qquad (3)$$

The interpretation of past experimental results is difficult, however, because all prior chemiluminescence studies that demonstrate $^1O_2$ production have used either a two-phase system (halocarbon–^2H_2O/solid KO_2)[4] or a three-phase system (halocarbon/H_2O/solid KO_2).[1,2] Via the use of a homogeneous system with acetonitrile as the solvent, we now report that (1) $O_2^{\bullet -}$ reacts with a number of halocarbons to produce $^1O_2$, (2) the addition of ^2H_2O to $O_2^{\bullet -}$ in acetonitrile does not produce $^1O_2$, and (3) the addition of ^2H_2O to halocarbon plus $O_2^{\bullet -}$ reactions does not increase the yield of $^1O_2$.[6]

Figure 1 illustrates the time course of the 1268-nm emission from the reactions of $O_2^{\bullet -}$ with CCl_4, with CBr_4, with α,α,α-trichlorotoluene, and with 1-bromobutane. Spectral analysis of the infrared chemiluminescence in Table I demonstrates an emission peak near 1268-nm for all the systems studied.[7] As shown in Table II, the addition of ^2H_2O to $O_2^{\bullet -}$ in acetonitrile does not produce 1268-nm emission, and the addition of ^2H_2O to the $O_2^{\bullet -}$/CCl_4 reaction does not increase the yield of singlet oxygen.

The failure of ^2H_2O to produce $^1O_2$ from $O_2^{\bullet -}$ or to increase the yield of $^1O_2$ from $O_2^{\bullet -}$/halocarbon reactions is consistent with prior work[4] but in conflict with the conclusions drawn by Corey

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(7) Quantitative estimates of the $^1O_2$ yield from these reactions could not be made because the concentration of $O_2^{\bullet -}$, a potent $^1O_2$ quencher (Guiraud, H. J.; Foote, C. S. *J. Am. Chem. Soc.* **1976**, *98*, 1984–1986), varied during the course of the reaction.

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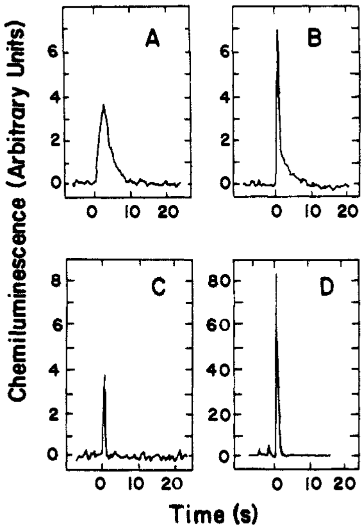

Figure 1. Time course for the 1268-nm emission from the reactions of $O_2^{\bullet -}$ with halocarbons in acetonitrile: (A) 0.4 mM $O_2^{\bullet -}$, 1.3 mM CCl_4; (B) 0.4 mM $O_2^{\bullet -}$, 35 mM α,α,α-trichlorotoluene; (C) 1 mM $O_2^{\bullet -}$, 350 mM 1-bromobutane; (D) 3 mM $O_2^{\bullet -}$, 3.8 mM CBr_4.

Table I. Spectral Analysis of Near-Infrared Emission from the Reactions of $O_2^{\bullet -}$ with Halocarbons in Acetonitrile

	relative emission[a]			
Filter (nm)	O_2^- + CBr_4[b]	O_2^- + CCl_4[c]	O_2^- + $C_6H_5CCl_3$[d]	O_2^- + C_4H_9Br[e]
1070	0.003 ± 0.002	0.03 ± 0.03	−0.04 ± 0.10	0.03 ± 0.02
1170	−0.002 ± 0.001	0.09 ± 0.03	0.10 ± 0.14	0.01 ± 0.03
1268	1.00 ± 0.06	1.00 ± 0.04	1.00 ± 0.03	1.00 ± 0.16
1377	0.61 ± 0.06	0.45 ± 0.03	0.40 ± 0.03	0.39 ± 0.05
1475	0.06 ± 0.01	0.12 ± 0.11	0.21 ± 0.11	0.05 ± 0.03

[a] The emission in each system was normalized so that the value for the 1268-nm filter was 1.0. Emission intensities were corrected for filter transmissions and detector responses. [b] CBr_4 (3.8 mM), 3 mM $O_2^{\bullet -}$. [c] CCl_4 (1.3 mM), 5 mM $O_2^{\bullet -}$. [d] Trichlorotoluene (35 mM), 2 mM $O_2^{\bullet -}$. [e] 1-Bromobutane (700 mM), 1 mM $O_2^{\bullet -}$.

Table II. Chemiluminescence at 1268 nm from the $O_2^{\bullet -}$–CCl_4–^2H_2O System

CCl_4 (mM)	added ^2H_2O (mM)	rel emission[b]
1.3		348 ± 25
1.3	6.8	370 ± 22
	6.8	−1 ± 6
	68	2 ± 11

[a] The initial $O_2^{\bullet -}$ concentration was 1 mM. The acetonitrile solvent contained 4.2 mM water before any additions. [b] Arbitrary units.

et al.[2] for Cl-containing halocarbons. The latter group found that the addition of large amounts of H_2O to suspensions of KO_2 in either CCl_4 or Freon-113 increased the $^1O_2$ production.[2] They attributed the increased $^1O_2$ yield to the H_2O-induced dismutation of $O_2^{\bullet -}$.[2] Alternative explanations exist for their data, however. The addition of large amounts of water to KO_2–halocarbon suspensions will induce the dissolution of KO_2 for enhanced reactivity with the halocarbon and will cause the rapid decomposition of KO_2. The O_2 evolution from the KO_2 particles will increase the reactant mixing rate, which will increase the rate of the surface reaction between KO_2 and the halocarbon. The H_2O-induced decomposition of KO_2 may also heat the reaction mixture and thereby increase the rate of the $O_2^{\bullet -}$/halocarbon reaction.

With 1-bromobutane, $^1O_2$ was produced only when the halocarbon was in large excess. This is consistent with a competition between reaction 3 (producing $^1O_2$ via a Russell mechanism[8]) and reaction 4, which consumes peroxyl radicals. The polyhalogenated

$$RO_2^\bullet + O_2^- \rightarrow RO_2^- + O_2 \qquad (4)$$

halocarbons have been shown to have a more complex reaction mechanism with $O_2^{\bullet -}$ in which there is a sequential removal of halogen atoms. Singlet oxygen is generated in these reactions even when the halocarbons are not in large excess. One explanation for this observation is the production of $^1O_2$ from the reactions of $O_2^{\bullet -}$ with various partially halogenated intermediates.

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Bimodal Inclusion of Nitroxide Radicals by β-Cyclodextrin in Water As Detected by Electron Spin Resonance

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The most important factor regulating the stability of cyclodextrin inclusion complexes[2] is the charge and the direction of inclusion. With respect to the direction two-way inclusion has been suggested by many investigators.[3-7] This report deals with the detection of bimodal inclusion of a nonsymmetric[8] nitroxide radical into β-cyclodextrin (cycloheptaamylose, β-CD) by electron spin resonance (ESR).

Recently various kinds of artificial molecular receptors which can form inclusion complexes have been reported.[9] Most of them have structures capable of including a substrate by two different ways. It should be noted that enzyme activities could be greatly affected by the presence of bimodal inclusion. In CD's the importance of bimodal inclusion has been discussed from the viewpoint of the driving force for molecular recognition.

Magnetic resonance techniques have been the major tool for the detection of the structure of CD inclusion complexes in solution.[3-5,10,11] However, NMR spectroscopy has failed to separate

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