J. Am. Chem. Soc. 1982, 104, 5109–5114

Laser Photolysis Study of the Reactions of Alkoxyl Radicals Generated in the Photosensitized Decomposition of Organic Hyponitrites[1]

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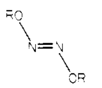
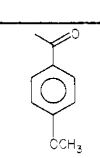
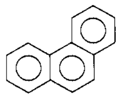
Abstract: The triplet photosensitized decomposition of organic hyponitrites produces alkoxy radicals in good yields. For example, the quenching of *p*-methoxyacetophenone triplets by di-*tert*-butyl hyponitrite in benzene at 27 °C occurs with $k_q = 1.41 \times 10^8$ M^{-1} s^{-1}, and ~50% of the quenching events lead to a pair of *tert*-butoxy radicals. Steric effects play an important role in the kinetics of the quenching process; e.g., phenanthrene triplets are quenched 23 times faster by di-2-phenylethyl hyponitrite than by di-*tert*-butyl hyponitrite. The 2-phenylethoxy radicals undergo efficient β-cleavage to yield $Ph\dot{C}H_2$ radicals with log $(k_\beta/s^{-1}) = 10.89 - 4830/\theta$, with $\theta = 2.3RT$ in cal/mol. The rate is markedly enhanced by polar solvents. The reaction of alkoxy radicals with diphenylmethanol is also sensitive to steric effects and occurs with rate constants (benzene, 27 °C) of 5.8×10^6 and 2.6×10^7 M^{-1} s^{-1} for *tert*-butoxy and 2-phenylethoxy radicals, respectively.

Introduction

The reactions of alkoxy radicals continue to be the subject of considerable attention.[3-9] The great majority of these studies have centered on *tert*-butoxy radicals, reflecting the fact that their most common precursor, di-*tert*-butyl peroxide, is safe, easy to handle and purify, and commercially available. Quite frequently the direct photodecomposition of the peroxide can be used as a *tert*-butoxy radical source, although the sensitized process is also viable, and, indeed, quite efficient.[10,11] Di-*tert*-butyl hyponitrite ($Bu^tON_2OBu^t$) has been known for a number of years, and its thermal decomposition has been widely used as a *tert*-butoxy source.[12,13] A few other hyponitrites (RON_2OR) are known but have received considerably less attention,[14] and, in particular, their photosensitized decomposition has not been examined.[12,14] Our very limited knowledge of the reactivity of alkoxy radicals other than *tert*-butoxy is based on competitive studies mainly using alkyl hypochlorites[15,16] or, in the case of methoxy, pulse radiolytic experiments.[17-19]

Organic hyponitrites show only very weak absorptions at $\lambda >$ 290 nm, thus making the possibility of a photosensitized cleavage particularly attractive. At our excitation wavelength (337.1 nm) only a minor fraction of the incident excitation pulse can be absorbed by the hyponitrites; direct photodecomposition experiments are not viable under these conditions. The photosensitized process is in fact the only way in which the study reported herein could be carried out at present in our laboratories.

Table I. Triplet Quenching by Different Hyponitrites in Benzene at 27 °C

 R ≡	 k_q[a]/M^{-1} s^{-1}	 k_q[a]/M^{-1} s^{-1}
Bu^t	$(1.41 \pm 0.37) \times 10^8$	$(4.32 \pm 1.00) \times 10^6$ [b]
$Ph(CH_3)CH$	$(3.68 \pm 0.16) \times 10^8$	$(1.94 \pm 0.09) \times 10^7$
$(CH_3)_2CH$	$(5.52 \pm 1.44) \times 10^8$	$(6.81 \pm 2.04) \times 10^7$
$CH_2(CH_2)_4CH$	$(6.12 \pm 1.73) \times 10^8$	$(7.34 \pm 0.46) \times 10^7$
$PhCH_2$	$(1.36 \pm 0.25) \times 10^9$	$(7.98 \pm 2.12) \times 10^7$
$PhCH_2CH_2$	$(6.76 \pm 0.71) \times 10^8$	$(1.01 \pm 0.11) \times 10^8$

[a] Error limits correspond to 95% confidence (2σ). [b] In toluene.

Table II. Triplet Energy Dependence of the Rates of Quenching in Benzene

sensitizer	E_t[a]	$k_q(Bu^tON_2OBu^t)$[b]	k_q-(Bu^tOOBu^t)[c,d]
p-methoxyacetophenone	72.5	$(1.41 \pm 0.37) \times 10^8$ [f]	7.9×10^6 [e]
benzophenone	68.6	$(4.75 \pm 0.98) \times 10^7$ [f]	3.4×10^6
phenanthrene	61.9	$(4.32 \pm 1.00) \times 10^6$ [f,g]	1.8×10^6
anthracene	42	$\leqslant 5 \times 10^5$ [h]	9.7×10^4

[a] Triplet energy in kcal/mol. [b] At 27 °C in units of M^{-1} s^{-1}. [c] At 25 °C in units of M^{-1} s^{-1}. [d] From ref 10. [e] Value of *p*-methoxypropiophenone. [f] 95% confidence error limits. [g] In toluene. [h] No quenching observed.

This work was undertaken in order to examine two different aspects of the problem. First, we wanted to study the photosensitized process itself and compare it with the analogous process in the case of dialkyl peroxides. In addition, because organic hyponitrites are a convenient source of a variety of alkoxy radicals, we wanted to examine the effect of structural changes on their reactivity.

Results

All the experiments reported herein have been carried out under oxygen-free conditions using the pulses from a nitrogen laser (337.1

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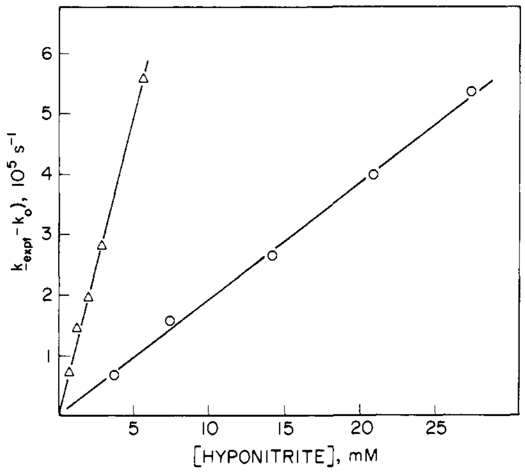


Figure 1. Quenching of phenanthrene triplets (benzene, 27 °C) by di-1-phenylethyl hyponitrite (○) and di-2-phenylethyl hyponitrite (△); corrected for triplet decay (k_d) in the absence of quencher.

nm, ~8 ns, up to 10 mJ) for excitation. Details on the instrument[20] and the techniques for the study of alkoxy radicals can be found elsewhere.[5,21]

In order for the organic hyponitrites to undergo photosensitized decomposition, it is a necessary condition that they ought to quench the excited photosensitizer. Only triplet sensitizers have been examined in this work, and the next section deals with this aspect of the problem.

Quenching of Triplet States. The quenching of the triplet states of *p*-methoxyacetophenone and of phenanthrene by a series of hyponitrites was examined in benzene at 27 °C. The details of these experiments are similar to those reported in the case of peroxide quenching.[10] Briefly, the triplet state T–T absorptions were monitored at, or near, the corresponding maximum, i.e., at 400 and 483 nm for *p*-methoxyacetophenone and phenanthrene, respectively. The incident dose was kept low enough that the triplet decay followed clean first-order kinetics, and the dependence of the rate constant for decay upon quencher concentration was examined for five to nine quencher concentrations. The corresponding bimolecular rate of quenching is then obtained from a plot of the pseudo-first-order rate constant for triplet decay as a function of quencher concentration. Figure 1 shows representative plots and Table I summarizes the data. The large error limits of some of the measurements (e.g., for diisopropyl hyponitrite) reflect to some extent the limited availability of these materials and the unstable (and explosive!) nature of some of these substrates.

Given the number of parameters and aspects that we wanted to examine, our study of the triplet energy dependence of the rates of quenching is more limited than in our earlier work with di-*tert*-butyl peroxide,[10] but the same features are apparent, even if the rates are considerably faster. Table II summarizes the results of a series of experiments with di-*tert*-butyl hyponitrite.

Another aspect of the quenching process examined was its temperature dependence for a couple of representative examples. Figure 2 shows the Arrhenius plots, while the corresponding parameters are given in Table III. The data at the lower temperatures are subject to larger errors as a result of solubility problems.

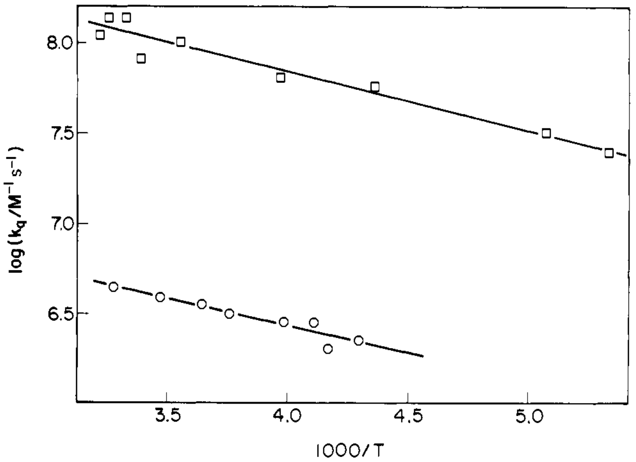
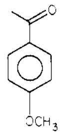
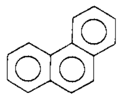


Figure 2. Arrhenius plots for the quenching of *p*-methoxyacetophenone (□) and phenanthrene (○) by $Bu^tON_2OBu^t$ in toluene.

Table III. Arrhenius Parameters for Triplet Quenching by Di-*tert*-butyl Hyponitrite in Toluene

	sensitizer	
parameter		
E_a, kcal/mol	1.43 ± 0.34	1.36 ± 0.33
log (A/M^{-1} s^{-1})	9.08 ± 0.30	7.62 ± 0.27
k_q/M^{-1} s^{-1} at 27 °C	1.09 × 10^8	4.32 × 10^6

Cleavage of $PhCH_2CH_2\dot{O}$ Radicals. When a solution of *p*-methoxyacetophenone and di-2-phenylethyl hyponitrite in benzene is irradiated in the laser system, the transient absorption spectrum observed corresponds to that of $Ph\dot{C}H_2$, showing its strong band at 317 nm and a weaker one at 306 nm, in good agreement with its reported spectrum.[22] Benzyl radical is the expected product according to the mechanism of reactions 1 and 2, where S stands for sensitizer.

$$S^* + (PhCH_2CH_2O)_2N_2 \xrightarrow{k_q} S + N_2 + 2PhCH_2CH_2O\cdot \quad (1)$$

$$PhCH_2CH_2\dot{O} \xrightarrow{k_\beta} Ph\dot{C}H_2 + CH_2O \quad (2)$$

The kinetics of reaction 2 can be studied directly in our laser system provided that the 2-phenylethoxy radical can be generated in a process considerably faster than its own decay. Since we assume (vide infra) that radical generation is concurrent with the decay of the triplet sensitizer, it becomes straightforward to decide whether the condition mentioned above is fulfilled. For example, when the decomposition of di-2-phenylethyl hyponitrite (0.112 M) is sensitized by *p*-methoxyacetophenone in benzene at 27 °C, the triplet lifetime of the sensitizer (monitored at 400 nm) is 14 ns, while the buildup of $Ph\dot{C}H_2$ takes place with a lifetime of 44 ns. We believe that this value reflects the kinetics of reaction 2, which under these conditions takes place with $k_\beta = 2.3 \times 10^7$ s^{-1}.

The temperature dependence of reaction 2 was examined in chlorobenzene, which provides an adequate temperature range. These experiments were carried out using a solution containing 0.09 M hyponitrite and 0.004 M *p*-methoxyacetophenone. The corresponding Arrhenius plot is shown in Figure 3. Least-squares analysis of the data leads to

$$\log (k_\beta/\text{s}^{-1}) = (10.89 \pm 0.26) - (4830 \pm 300)/\theta$$

where θ is $2.3RT$, in units of cal/mol.

Polar solvents are known to increase the rate of β-cleavage of alkoxy radicals.[15] We made an attempt to measure this effect quantitatively by repeating the experiment described above using 1-propanol as solvent. While the generation of $Ph\dot{C}H_2$ was quite evident, its rate of formation was beyond the time resolution of the experiment (ca. 15 ns). Therefore, while this experiment does not provide a quantitative measure of the rate enhancement, it does provide a direct confirmation of earlier conclusions by Walling and Wagner.[15]

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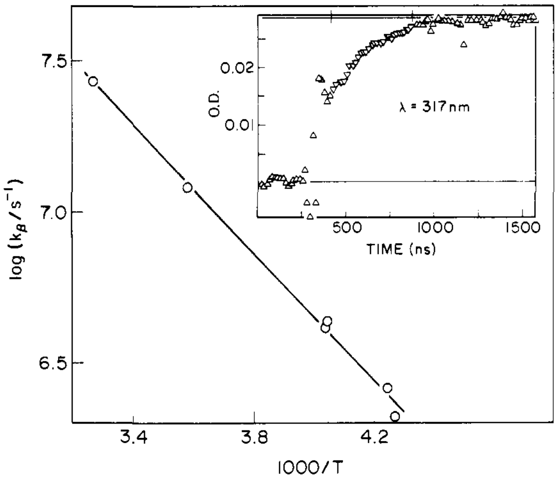

Figure 3. Arrhenius plot for the β-cleavage of $PhCH_2CH_2O\cdot$ radicals in chlorobenzene in a sample containing 0.004 M *p*-methoxyacetophenone and 0.101 M di-2-phenylethyl hyponitrite. Insert: Buildup of $Ph\dot{C}H_2$ observed at 247.7 K. The first few points after laser excitation are affected by scattered light (down) and some absorption by the sensitizer triplet (up). The markers indicate the region used for the kinetic calculations.

Given the relative lack of success in the experiment above, we examined the effect of small amounts of ethanol on the kinetics of reaction 2 in chlorobenzene at −35 °C. We found that the rate of cleavage is enhanced considerably. At the highest ethanol concentration used (0.434 M), the observed overall cleavage rate is 1.07×10^7 s^{-1}, which compares with 1.87×10^6 s^{-1} in chlorobenzene under the same conditions. The values of k_β follow a reasonably linear dependence (correlation coefficient 0.992) with $[C_2H_5OH]$ and lead to a formal bimolecular rate constant for induced β-cleavage of 1.9×10^7 M^{-1} s^{-1} in chlorobenzene at −35 °C.

Rates of Hydrogen Abstraction from Diphenylmethanol. The reaction with diphenylmethanol was chosen as a test system since earlier studies have already demonstrated[5,21] that the formation of the easily detectable[23] $Ph_2\dot{C}OH$ radical makes this system a particularly convenient one. As in the example of the β-cleavage described above, the sensitizer triplet lifetime is required to be considerably shorter than that of the alkoxyl radicals. The latter is given simply by the kinetics for the buildup of $Ph_2\dot{C}OH$, according to the mechanism of reactions 3 to 5.[5,21]

$$S^* + (RO)_2N_2 \xrightarrow{k_q} S + N_2 + 2RO\cdot \qquad (3)$$

$$RO\cdot + Ph_2CHOH \xrightarrow{k_a} ROH + Ph_2\dot{C}OH \qquad (4)$$

$$RO\cdot \xrightarrow{k_d} \text{pseudo-first-order decay} \qquad (5)$$

Reaction 5 includes all other modes of decay, such as β-cleavage, hydrogen abstraction from molecules other than diphenylmethanol, etc. As before, the excellent absorption properties of triplet *p*-methoxyacetophenone make it extremely easy to verify that this criterion is met, by simply monitoring the triplet decay at 400 nm. It should be noted that as steric factors increase, the concentration of hyponitrite required also increases (Table I); as a result of solubility and precursor availability, only four substrates leading to *tert*-butoxy, cyclohexyloxy, benzyloxy, and 2-phenylethoxy could be examined. The last one presents some specific problems and will be discussed in some detail later.

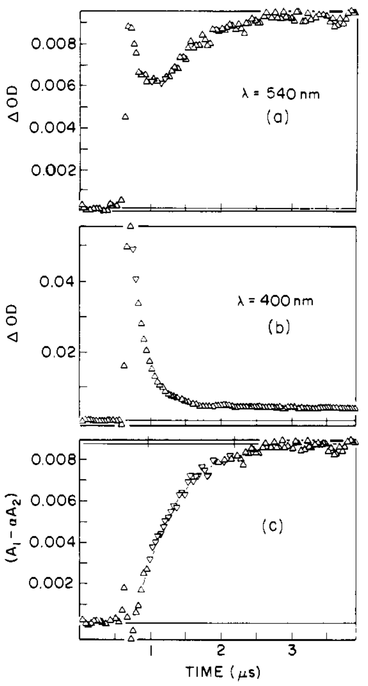

Figure 4. Traces obtained at 540 nm (a) and 400 nm (b) upon laser excitation of a benzene solution (27 °C) containing 0.016 M *p*-methoxybenzophenone, 0.0195 M dicyclohexyl hyponitrite, and 0.202 M diphenylmethanol. The bottom trace corresponds to a deconvolution according to eq 9 (see text). The markers at the top of trace c show the segment used for the kinetic calculations.

In order to determine k_a it is necessary to monitor the formation of $Ph_2\dot{C}OH$ for different concentrations of diphenylmethanol in much the same manner as in our earlier studies.[5,21,24] However, a new problem arises in these systems: the easy detectability of triplet *p*-methoxyacetophenone, which facilitates the experiments mentioned above, also produces signals (even at 540 nm) that interfere with the measurement of the buildup of $Ph_2\dot{C}OH$. Figure 4a shows a typical trace obtained at 540 nm. The initial decay corresponds to the triplet sensitizer which leads to an absorption minimum roughly at the time at which the concentration of alkoxy radicals (not detectable under these conditions) reaches a maximum. The buildup following the minimum is due to the formation of $Ph_2\dot{C}OH$ which in a longer time scale (not shown) decays with second-order kinetics. While Figure 4a is typical as far as the signal-to-noise ratio is concerned, it is among those traces where the triplet decay overlaps more, both in signal intensity and in time scale with the generation of $Ph_2\dot{C}OH$. The time profile for the formation of $Ph_2\dot{C}OH$ can be easily deconvoluted if a wavelength can be found where triplet decay is the predominant (not necessarily the only) detectable process. Measurements of this type can be easily obtained in the 400-nm region and typically lead to virtually noise-free traces such as that shown in Figure 4b. The deconvolution is based upon the following ideas: let A_1 and A_2 be the transient optical densities at two different wavelengths (400 and 540 nm, respectively, in this case), C^A and C^B the concentrations of species A and B (triplet sensitizer and $Ph_2\dot{C}OH$, respectively, in this example), and the various ϵ values the corresponding extinction coefficients for each species at each wavelength. Equations 6–8 show the corresponding relationships:

$$\alpha = \epsilon_1{}^A/\epsilon_2{}^A \qquad (6)$$

$$A_1 = \epsilon_1{}^A C^A + \epsilon_1{}^B C^B \qquad (7)$$

$$A_2 = \epsilon_2{}^A C^A + \epsilon_2{}^B C^B \qquad (8)$$

Multipling eq 8 by α and subtracting from (7) leads to:

$$A_1 - \alpha A_2 = (\epsilon_1{}^B - \alpha\epsilon_2{}^B)C_B \qquad (9)$$

Thus, if the value of α can be determined, a time profile according to eq 9 will have the shape corresponding to the evolution of the concentration of B, C_B. In our case α is simply the ratio of extinction coefficients for the triplet sensitizer at 400 and 540 nm, respectively, and it corresponds to the ratio of experimental optical densities following the laser pulse and before significant triplet decay takes place. Figure 4c shows the trace according to eq 9 derived from Figures 4a and 4b. The data were processed

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Table IV. Rate Constants for the Reaction of Alkoxy Radicals with Diphenylmethanol at 27 °C

radical	solvent/source	k_a/M^{-1} s^{-1}
$Bu^tO\cdot$	C_6H_6:Bu^tOOBu^t (1:2)[5,24]	7.2×10^6
$Bu^tO\cdot$	neat C_6H_6/hyponitrite	$(5.8 \pm 0.3) \times 10^6$
$\overline{CH_2(CH_2)_4CH}O\cdot$	neat C_6H_6/hyponitrite	$(9 \pm 2) \times 10^6$
$PhCH_2O\cdot$	neat C_6H_6/hyponitrite	$(1.34 \pm 0.24) \times 10^7$
$PhCH_2CH_2O\cdot$	neat C_6H_6/hyponitrite	2.6×10^7[a]

[a] Determined by a competitive technique (see text), error is difficult to estimate but probably around 30–40%.

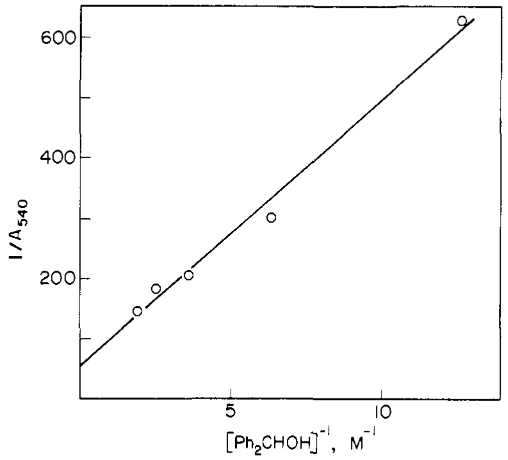

Figure 5. Plot according to eq 11 (benzene, 27 °C) for the reaction of 2-phenylethoxy radical with diphenylmethanol.

in a similar manner for cyclohexyloxy, benzyloxy, and *tert*-butoxy, although in the last case the signals were adequate enough to be processed even without deconvolution. Table IV summarizes the data.

As mentioned before, the case of the 2-phenylethoxy radical is somewhat different. The short lifetime of this radical (see previous section) prevents a detailed study of the build-up traces for $Ph_2\dot{C}OH$, which is also produced in relatively low yields. The yield of ketyl radicals (A_{540}) after the alkoxy radical decay is complete follows the following proportionality:

$$A_{540} \propto \frac{k_a[Ph_2CHOH]}{k_\beta + k_a[Ph_2CHOH]} \qquad (10)$$

Equation 10 does not include the possibility of hydrogen abstraction from the solvent and/or radical precursors. This is reasonable in view of the very short radical lifetime. Thus, if we introduce a constant a, we obtain

$$\frac{1}{A_{540}} = a + \frac{ak_\beta}{k_a[Ph_2CHOH]} \qquad (11)$$

That is, the ratio k_β/k_a will be given by the slope-to-intercept ratio of a plot of A_{540}^{-1} vs. $[Ph_2CHOH]^{-1}$. Figure 5 illustrates the plot obtained in benzene at 27 °C and leads to $k_\beta/k_a = 0.87$ M, from which we calculate $k_a = 2.6 \times 10^7$ M^{-1} s^{-1}. While the value is based on a competitive (or Stern–Volmer) type of approach, we believe that, since the value of k_β was determined under identical experimental conditions, and using the same technique, the absolute value of k_a is probably quite reliable.

Since all experiments in this section rely on the monitoring of $Ph_2\dot{C}OH$ radicals, and the ones with $PhCH_2CH_2O\cdot$ upon the measurement of the yield of ketyls, we thought it as important to establish that no $Ph_2\dot{C}OH$ radicals were produced via hydrogen abstraction by triplet *p*-methoxyacetophenone, the sensitizer used. Blank experiments in the absence of hyponitrite showed that no photoreduction takes place in the short time domain (<100 ns) in which the sensitization process usually occurs. The result is consistent with the low reactivity expected of carbonyl triplets with low-lying π,π^* states.[25-27]

Yields of Alkoxy Radicals. The experiments described in the last two sections clearly show that the quenching of the triplet sensitizers is accompanied by the generation of alkoxy radicals; however, they do not provide a clear estimation of the yield of alkoxys generated per quenching event.

In order to determine the fraction of quenching events that lead to alkoxy radical generation, we carried out matched experiments in which the *p*-methoxyacetophenone triplet was quenched to the same extent by appropriate concentrations (estimated from the data in Table I) of hyponitrite and di-*tert*-butyl peroxide in the presence of 0.094 M diphenylmethanol. Since the efficiency is known from earlier studies in the case of the peroxide,[10] it is straightforward to determine the value for the hyponitrite. For example, for $Bu^tON_2OBu^t$ we found that 50% of the quenching events lead to a pair of "out-of-cage" *tert*-butoxy radicals. The yield of "out-of-cage" alkoxys in the thermal decomposition of $Bu^tON_2OBu^t$ is strongly solvent dependent.[12] For alkanes with viscosity similar to that of benzene, only 10–20% cage effect is expected, suggesting that in the triplet sensitization (where a triplet rather than a singlet radical pair is probably produced) part of the inefficiency occurs in the triplet quenching process. The values for other hyponitrites are 0.22 and 0.35 for dibenzyl and dicyclohexyl hyponitrites, respectively.

On the Possibility of Singlet Quenching. In the case of ketone sensitizers, intersystem crossing is usually quite fast, and as a result singlet quenching does not need to be taken into consideration. In the case of aromatic molecules the singlet lifetimes are long enough that singlet quenching becomes a definite possibility. This was examined in the case of phenanthrene where the singlet lifetime is ca. 60 ns.[28] While it is clear that hyponitrites do lead to some singlet quenching (as detected by the decrease in triplet phenanthrene yields), the effect is not predominant. For example, in the case of dibenzyl hyponitrite (benzene, 27 °C) a 0.005 M concentration decreases the triplet yield by 16%.

Discussion

Generation of Alkoxy Radicals. Quite clearly the photosensitized decomposition of organic hyponitrites provides a convenient source of alkoxy radicals for kinetic studies. Our choice of sensitizers deserves some comment; the factors taken into consideration included the rather high triplet energy, relative unreactivity toward alkoxy radicals, and easy excitation with a nitrogen laser (337.1 nm); especially important, we looked for triplets that would not be good hydrogen abstractors. *p*-Methoxyacetophenone and phenanthrene fulfill these conditions. In addition, we wanted triplet states that would be easily detectable, so that the overall process, including sensitizer behavior, could be easily monitored. While similar conditions should probably be given consideration in other studies, the choice may obviously be different.

Table I, particularly the phenanthrene data, shows that the quenching process is largely controlled by steric factors.[29] One conspicuous inversion is observed in the case of *p*-methoxyacetophenone sensitization: the rate for dibenzyl hyponitrite is higher than could be expected. We can only speculate that perhaps in this particular system the triplet energy of the hyponitrite may be relatively low and that electronic energy transfer may be playing a limited role. Unfortunately, almost nothing is known about the spectroscopy of hyponitrites (which do not seem to resemble azo compounds), thus making it difficult to be conclusive. The fact that only 22% of the quenching events leads to alkoxy radicals may be directly related to the energy transfer mechanism.

Attempts to correlate the rate constants with the steric effect parameter, E_s,[30] lead to the expected trends, but the correlation

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coefficient is usually rather low. The best correlation between log k_q and E_s was obtained for the phenanthrene data in Table I and led to a slope of 1.04 ($r = 0.947$).

The effect of triplet energy on the rate constants for quenching parallels that observed in the case of di-*tert*-butyl peroxide although the rates are considerably higher for the hyponitrites (Table II).[10] Part of the rate enhancement may be due to a decrease in steric requirements in the case of the hyponitrite, although mechanistic effects may also play a role. We note that the effect of triplet energy on rates is too small to be the result of electronic-to-electronic energy transfer.[31]

The data in Table III show that the changes in rate constant which result from triplet energy changes are not the result of increased activation energy, but rather, they reflect more stringent entropic requirements as the energy available is reduced. It should be noted that both sensitizers in Table III are able to provide energy in excess of that required for the thermal decomposition.[12] As pointed out earlier, the knowledge of the spectroscopy of hyponitrites is so limited that it is impossible to be conclusive regarding the mechanism of reaction, which may be similar to that in the case of peroxides (transfer to a repulsive state) or involve the intermediacy of a so far undetected intermediate (exciplex?) which leads to the radical products.

As pointed out in the Results section, we have assumed that the formation of alkoxy radicals occurs concurrently (or virtually without delay if an intermediate was involved) with the decay of the triplet sensitizer. One could, in fact, conceive an alternative mechanism in which the cis isomer of the hyponitrite would be generated in the quenching process (by analogy with some azoalkanes)[32] and would then decompose thermally to generate molecular nitrogen and alkoxy radicals. We do not favor such a mechanism for the following reasons: (a) if we accept that electronic-to-electronic energy transfer does not occur, then the triplet photosensitized formation of ground-state cis isomer would be spin-forbidden; (b) hyponitrites are considerably more labile than azoalkanes, and the probability of a long-lived intermediate seems less likely; and (c) in the case of the di-2-phenylethyl hyponitrite (where such an intermediate would have more effect on our interpretation), the cis isomer would be required to cleave in 44 ns (benzene, 27 °C), while, in order to match the experimental kinetics, the 2-phenylethoxy radical would then be required to have a lifetime <10 ns, so that its disappearance would not be rate controlling for the formation of $PhCH_2$.

Cleavage of $PhCH_2CH_2O\cdot$ Radicals. The value of k_β obtained in this study (2.3×10^7 s^{-1} in benzene at 27 °C) seems consistent with earlier competitive studies. For example, Walling and McGuiness[33] report k_β/k_a of ca. 250 M at 40 °C for the $PhCH_2C(CH_3)_2O\cdot$ radical, where the reference molecule is cyclopentane. If we assumed that $Bu^tO\cdot$ is a good model for $PhCH_2C(CH_3)_2O\cdot$ and taking the rate of abstraction at 40 °C as 1.07×10^6 M^{-1} s^{-1},[5,34] we estimate $k_\beta = 2.7 \times 10^8$ s^{-1}, somewhat higher than our value, as could be anticipated from the change in α-substitution.

The preexponential factor obtained [log (A/s^{-1}) = 10.89] is rather low and less than the simple, theoretical transition state value (13.3) or prefered values for the analogous cleavage of benzyl radicals from alkyl benzenes (14.6–15.9).[35,36] The low value measured in our case suggests that a substantial degree of solvent organization occurs at the transition state. About −4.6 gibbs/mol (i.e., one order of magnitude in the A factor) can be ascribed to freezing out of a rotation about the benzyl carbon atom in the transition configuration, but the overall effect is too large to be due to this factor alone. Our solvent studies confirm earlier reports[15] of dramatic effect of solvent polarity upon k_β/k_a ratios.[15,37] The source of these effects on the rates may be via destabilization of the alkoxy or stabilization of the transition state for its β-scission. The second explanation is acceptable to the extent that the transition state resembles the ketone product, since reagents which accelerate β-scission also complex with the ketone.[15,37] On the other hand, the rapid rate of β-scission in the present case argues for an early transition state which resembles the starting alkoxy radical.

Intermolecular Reactivity of Alkoxy Radicals. Table IV illustrates the reactivity of several alkoxy radicals toward diphenylmethanol. Steric effects seem to be quite important in these reactions; thus, *tert*-butoxy radicals, which are usually regarded as highly reactive species, are the least reactive radicals among the alkoxys examined here.

The difference between the two lines at the top of Table IV is particularly interesting. The difference of about 20% can conceivably be the result of the accumulation of random and systematic errors; however, it is tempting to try to justify the change in k_a on the basis of solvent effects. The value obtained using peroxide as a *tert*-butoxy precursor was obtained in a solvent containing only 33% benzene, while the hyponitrite value results from measurements in neat benzene. It has been proposed[15] that aromatic solvents associated with $Bu^tO\cdot$ (perhaps through reversible ring addition), thus reducing their reactivity.[38] Our results are entirely consistent with this suggestion, although the effect may not be large enough to completely rule out error accumulation.

Conclusion

In summary, the sensitized decomposition of organic hyponitrites provides a convenient source of alkoxy radicals. Sensitizers in the 60–75-kcal/mol triplet energy range seem quite adequate. The sensitization process and the reaction of alkoxys are quite sensitive to steric effects.

Finally, a note of caution: while hyponitrites are very convenient radical sources when structural changes are desired, they are also unstable and their handling and preparation requires careful safety precautions.[39] Those interested in using this technique should familiarize themselves with these problems (see Experimental Section).

Experimental Section

Materials. Benzene (Aldrich, Gold Label) was purified by washing with sulfuric acid, sodium bicarbonate solution, and water, then dried, and distilled from CaH_2 under nitrogen. Other solvents were of the highest purity commercially available and were used as received.

Alkyl hyponitrites were prepared from the corresponding alkyl bromide or iodide and silver hyponitrite according to published procedures.[12,40] The new hyponitrites[41] were characterized by elemental analysis or mass spectra, and by characteristic strong IR absorption near 1000 cm^{-1}. They were purified by low-temperature crystallization from methanol. Sodium hyponitrite, from which silver hyponitrite was prepared, was usually synthesized from sodium, benzophenone, and nitric oxide in toluene–dimethoxyethane or toluene–tetrahydrofuran by a procedure given in a preliminary communication.[42] *Caution*: This reaction has been carried out several dozen times since then by seven individuals on scales up to 16 L without difficulty. *Recently, however, an injurious fire and explosion occurred during the workup of a scaled-up run starting with 10.4 mol of sodium in a 12-L flask.* Although the cause of the accident is not known and may have involved an ignition source elsewhere in the hood, this reaction should obviously be carried out with extreme care. During workup by slow addition of water, the mixture should be stirred under a nitrogen atmosphere until it is certain that any unreacted pieces of sodium have completely dissolved and a two-phase system is obtained.

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The use of alcohols to quench the reaction is not recommended because they do not dissolve sodium hyponitrite and may cause the latter to coat any unreacted pieces of sodium present in the mixture. A related literature preparation with pyridine[43] gave an impure, pyrophoric product. Two other procedures[44,45] for making sodium hyponitrite have succeeded in our laboratory but have not been used on a routine basis.

Laser Photolysis. All laser photolysis experiments were carried out under oxygen-free conditions. The samples (typically 1 mL) were excited with the pulses from a Molectron UV-24 nitrogen laser. Our system has been fully interfaced with a PDP11/03L computer which controls the experiments, gathers the data, and provides suitable processing, storage, and hardcopy facilities. Further details have been published elsewhere.[20]

Acknowledgment. Thanks are due to Mr. S. E. Sugamori for his technical assitance. One of us (G.D.M.) thanks the National Research Council of Canada for the support as a guest worker.

Registry No. *t*-BuON=NOBu-*t*, 14976-54-6; Ph(CH$_3$)CHON=NOCH(CH$_3$)Ph, 82522-46-1; (CH$_3$)$_2$CHON=NOCH(CH$_3$)$_2$, 82522-47-2; *c*-C$_6$H$_{11}$ON=NO-*c*-C$_6$H$_{11}$, 82522-48-3; PhCH$_2$ON=NOCH$_2$Ph, 19657-56-8; PhCH$_2$CH$_2$ON=NOCH$_2$CH$_2$Ph, 82522-49-4; *t*-BuO·, 3141-58-0; *c*-C$_6$H$_{11}$O·, 3384-35-8; PhCH$_2$O·, 26397-37-5; PhCH$_2$CH$_2$O·, 40355-55-3; *p*-methoxyacetophenone, 100-06-1; phenanthrene, 85-01-8; diphenylmethanol, 91-01-0; benzophenone, 119-61-9; anthracene, 120-12-7.

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Laser Raman and Infrared Spectra, and X-ray Crystal Structure of *trans*-Di-*tert*-butyl Hyponitrite

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Abstract: The molecular structure of *trans*-di-*tert*-butyl hyponitrite has been determined from a single-crystal, low-temperature X-ray study. The compound crystallizes in a monoclinic space group $P2_1/c$ with two molecules per unit cell. The molecule has N=N, N—O, and O—C distances of 1.252 (5), 1.380 (6), and 1.471 (7) Å, respectively, and an N=N—O angle of 106.5 (3)°. The IR and Raman band assignments were made with the aid of $^{15}N/^{14}N$ isotopic substitution. The Raman spectra allowed unique assignment of the ν_{NO} and ν_{CO} stretching modes. These overlap in the ^{14}N spectrum to give the characteristic, IR-active band at 990 cm^{-1}. The Raman active $\nu_{N=N}$ is assigned at 1509 cm^{-1}.

Introduction

Alkyl hyponitrites have been known for a number of years as useful, low-temperature sources of alkoxy radicals.[2] A number of very significant studies of solvent and pressure effects on cage recombination[3] and of free-radical chain oxidations[4] and polymerizations[5] have been carried out with di-*tert*-butyl or dicumyl hyponitrites. The total literature on hyponitrites is sparse, however, as compared with the literature on the closely related azoalkanes.

Although the crystal structures of some interesting cis[6] and trans[7] organometallic hyponitrites have been determined, the trans geometries of the simple alkyl derivatives have only been inferred on the basis of the vibrational spectra of sodium[8] and silver[8a] hyponitrites from which the organic hyponitrites were synthesized. A study of the dipole moments of two alkyl hyponitrites also supported the trans structure.[9]

We now report the X-ray crystal structure of an organic hyponitrite for the first time. The IR and Raman vibrational spectra are assigned using $^{15}N/^{14}N$ isotopic substitution, and the results are completely consistent with the space group and trans structure found in the single crystal analysis. Solution (CHCl$_3$) and solid-state Raman spectra are similar and indicative of the trans structure.

Experimental Section

X-ray Study. Colorless, transparent, rectangular parallelepiped crystals of di-*tert*-butyl hyponitrite were obtained from pentane solution upon cooling. The compound was prepared by Traylor's procedure from silver hyponitrite and *tert*-butyl bromide.[2c] A 250-MHz ^{1}H NMR scan of the product in CDCl$_3$ gave no indication of major impurities or isomers.

X-ray diffraction data were collected with a computer-controlled Syntex P2$_1$ four-circle diffractometer [Mo Kα ($\bar{\lambda}$ = 0.71073 Å)] at −50 °C. Initially 25 reflections (range 6° ≤ 2θ ≤ 31°) were used to calculate cell constants. Axial photographs and systematic absences in the 1045 reflections indicated the monoclinic space group $P2_1/c$ with $Z = 2$. Final cell parameters were a = 5.739 (2), b = 10.870 (5), c = 8.762 (4) Å, β = 108.13 (3)°, corresponding to a cell volume of 524.0 (4) Å^3. The calculated density, 1.10 g/cm^3, and the measured density, 1.05 (4) g/cm^3

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