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Azidyl Radical Reactivity. $N_6^{\bullet -}$ as a Kinetic Probe for the Addition Reactions of Azidyl Radicals with Olefins[1]

Mark S. Workentin, Brian D. Wagner, Janusz Lusztyk, and Danial D. M. Wayner*

Contribution from Steacie Institute for Molecular Sciences, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, Canada K1A 0R6

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Abstract: The reactivity of the azidyl radical ($N_3^\bullet$) with olefins has been studied in acetonitrile solution using time-resolved UV−vis and infrared (TRIR) laser flash photolysis techniques. Azidyl radicals, formed by electron transfer from azide to excited state ketones, combine with excess azide in acetonitrile in an equilibrium reaction to form the pseudohalogen radical anion $N_6^{\bullet -}$. The visible absorption of $N_6^{\bullet -}$ (λ_{max} = 700 nm) is shown to be an ideal probe for the determination of absolute rate constants for the addition reactions of $N_3^\bullet$ with a variety of alkenes (k_{add}). Bimolecular rate constants for the reactions of $N_3^\bullet$ with a series of ring-substituted styrenes (*p*-CF_3, *m*-CF_3, *p*-Cl, H, *m*-CH_3, *p*-CH_3, *p*-CH_3O) vary between 1×10^6 and 5×10^7 M^{-1} s^{-1}. An excellent correlation of log(k_{add}) with Hammett σ^+ constants ($\varrho^+ = -1.2$, $r = 0.991$) is obtained illustrating the electrophilic nature of the azidyl radical. Rate constants for reaction with α- and β-substituted styrenes and simple alkyl- and alkoxy-substituted olefins vary between 1×10^6 and 1×10^9 M^{-1} s^{-1} and correlate with the ionization potentials (a reflection of the relative HOMO energies) of the olefin. The addition reactions of $N_3^\bullet$ were found to be dominated by polar effects with little contribution from steric factors. TRIR was utilized to follow the fate of azide and azidyl radicals by monitoring the bleach of N_3^-($\bar{\nu}_{max}$ = 2004 cm^{-1}), the decay of $N_6^{\bullet -}$ ($\bar{\nu}_{max}$ = 1842 cm^{-1}), and the concurrent growth of β-azidyl carbon-centered radicals at *ca.* 2100 cm^{-1}. The observation of the latter, which grow in with kinetics identical to the decay of $N_6^{\bullet -}$, combined with the lack of evidence for competing hydrogen atom transfer in the reactions with alkyl olefins (even for 1,4-cyclohexadiene) confirms that reaction of $N_3^\bullet$ with all olefins examined is by addition.

Introduction

The azidyl radical, $N_3^\bullet$, has been used extensively in radiation chemistry studies as a one-electron oxidant of molecules of biological significance.[2−10] This species has a number of properties which make it particularly useful. Firstly, since it exists primarily as a monomer radical in aqueous solution, it is more reactive as an oxidizing agent than the other halogen or pseudohalogen oxidants such as $Br^\bullet$, $Cl^\bullet$, or $SCN^\bullet$ which exist in aqueous solution primarily as the much less reactive dimer radical anions ($Br_2^{\bullet -}$, $Cl_2^{\bullet -}$, and $(SCN)_2^{\bullet -}$, respectively). Secondly, unlike the halogen radical anions which have relatively strong long wavelength UV−vis absorptions, $N_3^\bullet$ does not absorb significantly above 300 nm and, thus, does not interfere with the optical detection of other transients at longer wavelengths. In general, it is assumed that $N_3^\bullet$ reacts in aqueous solution only by electron transfer (eq 1). In this regard it is

$$N_3^\bullet + ArH \rightarrow N_3^- + ArH^{\bullet +} \qquad (1)$$

interesting to note that only recently has the question of the standard potential of the $N_3^\bullet/N_3^-$ redox couple been resolved (1.33 ± 0.01 V vs NHE).[9,10] Obviously, this value is essential in order to understand the kinetics of oxidation of organic substrates by the radical. While this standard potential clearly applies to reactions in aqueous solution, it is not clear, for reactions of azidyl radical with complex biological molecules, that the environment will necessarily be aqueous-like. It has been shown that in less polar solvents the standard potential of the $N_3^\bullet/N_3^-$ couple decreases (*e.g.*, the standard potential decreases by *ca.* 0.5 eV upon changing the solvent from 2,2,2-trifluoroethanol to acetonitrile), while for a large number of delocalized organic radical ions there is little or no solvent effect.[11] Therefore, in less polar solvents or microenvironments the azidyl radical is not as strong an oxidizing agent leaving open the possibility for other reaction channels such as addition to unsaturated bonds (eq 2) or hydrogen atom abstraction (eq 3) to contribute to the oxidation reactions. There is reason to suspect that these reactions may be important under some

$$N_3^\bullet + R_2C{=}CR_2 \rightarrow R_2(N_3)C{-}\dot{C}R_2 \qquad (2)$$

$$N_3^\bullet + RH \rightarrow N_3H + R^\bullet \qquad (3)$$

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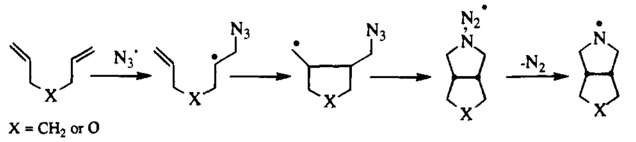
circumstances since: (1) the radical is expected to be electrophilic so polar effects will be important in the transition state and (2) the N_3−H bond is reasonably strong (*ca.* 93 kcal mol^{-1})[12] compared to a large number of C−H bonds. The significance of the first point is that structural changes to an organic molecule which make it more easily oxidized will also stabilize the polar transition state for the addition of an electrophilic radical. Consequently, redox potential/reactivity correlations cannot be taken as proof of electron transfer.

At present, evaluation of the likelihood of processes other than electron transfer occurring in a given system is hampered by the paucity of rate data for the addition and H-atom abstraction reactions of the azidyl radical with organic substrates. In fact, to our knowledge there are no reported direct determinations of absolute rate constants for these reactions in solution. The lack of kinetic data may be, in part, the result of the fact that the azidyl radical only absorbs weakly in the UV (λ_{max} = 274 nm; $\epsilon \approx 2000\ M^{-1}cm^{-1}$)[7,13] with no appreciable absorption above 300 nm. The strength and position of this absorption maximum, which is in a range where many organic substrates absorb, make direct measurement of the kinetics of $N_3^\bullet$ by time-resolved optical detection virtually impossible. Furthermore, monitoring the growth of the absorptions of any transient products formed by H-atom abstraction or addition is often difficult since in many instances they are not readily detectable by laser flash photolysis techniques. Under these circumstances, "probe" techniques have often been used to obtain kinetic information on the reaction of interest.[14,15] Typically, in this technique, a molecule is chosen that reacts with a reactive intermediate to yield a readily detectable species (*i.e.*, the probe). By monitoring the kinetics of formation of the probe as a function of the concentration of other added substrates which will react competitively, kinetic data for the reaction of interest can be obtained.

We have recently demonstrated that azidyl radicals, generated in acetonitrile by electron transfer reactions of azide with organic radical cations[11,16] or aromatic ketone triplets,[17] react with excess azide to form reasonably high equilibrium concentrations of the pseudohalogen radical anion, $N_6^{\bullet-}$. In the present paper we demonstrate the use of the absorption of this species as a probe for the reactivity of $N_3^\bullet$. This initial study is limited to an evaluation of the dynamics of addition reactions of $N_3^\bullet$ to a large variety of olefins in acetonitrile using laser flash photolysis (LFP) techniques with UV−vis and infrared detection. An understanding of the reactivity of the azidyl radical by processes other than electron transfer may provide a basis for evaluating its usefulness as a secondary oxidant in biological studies. Besides the relevance to biological systems, the kinetic data may be of value in synthetic strategies in light of recent results by Kim *et al.*[18] In that study, 5- and 6-exo intramolecular cyclization of alkyl radicals to azido groups was demonstrated to be a viable route to nitrogen heterocycles. Thus, addition reactions of azidyl radicals to suitably designed systems could provide a synthetically useful route to these intermediates as, for example, illustrated in Scheme 1. Clearly, absolute rate constants for the azidyl radical addition are essential in order to exploit these new synthetic alternatives.

Scheme 1



Results

Laser Flash Photolysis with UV−vis Detection. The probe $N_6^{\bullet-}$ was generated by diffusion-controlled electron transfer quenching of acetophenone, benzophenone, or benzil triplets (formed by 308 nm excitation) by tetrabutylammonium azide (eqs 4−6). At concentrations of azide >3 mM, this species

$$\text{ketone} \xrightarrow{h\nu} \text{ketone}^{3*} \tag{4}$$

$$\text{ketone}^{3*} + N_3^- \rightarrow \text{ketone}^{\bullet-} + N_3^\bullet \tag{5}$$

$$N_3^\bullet + N_3^- \rightleftharpoons N_6^{\bullet-} \qquad K_6 = 200\ M^{-1} \tag{6}$$

exhibits a readily detectable, broad absorption centered at 700 nm (inset of Figure 1, $\epsilon = 8140\ M^{-1}\ cm^{-1}$). The assignment of this absorption to $N_6^{\bullet-}$, as well as a study of the dynamics and thermodynamics of its formation has been previously reported.[17] The yield of $N_6^{\bullet-}$, estimated by its optical density, was dependent on the concentration of azide as expected for a species formed in an equilibrium reaction (eq 6). The ketone radical anions also produced in the reaction have long wavelength absorptions that overlap with the absorption of $N_6^{\bullet-}$. These absorptions can be removed by addition of air or oxygen to the solution without affecting the absorption of $N_6^{\bullet-}$, which is itself insensitive to oxygen. For the purpose of the kinetic experiments described below, benzil was used as the sensitizer (results using the other ketones were identical),[19] and solutions were oxygenated and typically contained 10 mM azide. At

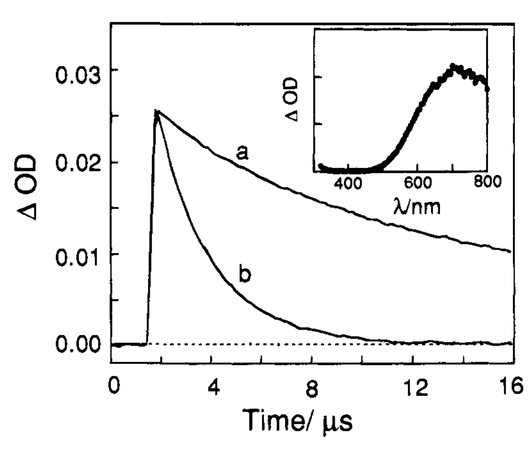


Figure 1. Kinetic traces measured by UV−vis LFP at 700 nm for an oxygen-saturated solution of benzil + 10 mM tetrabutylammonium azide in acetonitrile at 23 °C: (a) without added olefin and (b) in the presence of 17 mM 2,3-dimethyl-2-butene. Inset shows a transient UV−vis absorption spectrum of $N_6^{\bullet-}$ that was measured 1 μs after the 308 nm laser pulse on solution (a) above.

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this concentration, quenching of the sensitizer ketone is instantaneous on our time scale.

In the absence of added quenchers, $N_6^{\bullet -}$ (monitored by its absorption at 700 nm) decays with approximately second-order kinetics with a half-life of *ca.* 10 μs (Figure 1, trace a). Addition of olefin increases the rate of decay, and the kinetics become first order (Figure 1, trace b). The increased rate of decay of the absorption of $N_6^{\bullet -}$ can, in principle, be the result of two mechanistic possibilities: (i) addition of $N_3^{\bullet}$, which is present in equilibrium with $N_6^{\bullet -}$, to the olefin to give the adduct (eqs 7 and 8) or (ii) reaction of $N_6^{\bullet -}$ directly with the olefin, initially forming an intermediate complex which fragments by loss of azide (eqs 9 and 10). The latter mechanism is analogous to what has been reported for the addition reactions of the halogen radical anion $Cl_2^{\bullet -}$ with olefins[20] but in principle may occur as a single elementary step.

$$N_6^{\bullet -} \rightleftharpoons N_3^{\bullet} + N_3^- \qquad (K_6)^{-1} \tag{7}$$

$$N_3^{\bullet} + R_2C{=}CR_2 \rightarrow R_2\dot{C}{-}C(N_3)R_2 \tag{8}$$

$$N_6^{\bullet -} + R_2C{=}CR_2 \rightarrow \left[R_2(N_6^-)C{-}\dot{C}R_2\right] \tag{9}$$

$$\left[R_2(N_6^-)C{-}\dot{C}R_2\right] \rightarrow R_2(N_3)C{-}\dot{C}R_2 + N_3^- \tag{10}$$

Under our experimental conditions, kinetic analysis of the first mechanism (eqs 7 and 8) leads to eq 11, where k_{obs} is the pseudo-first-order rate constant of decay of $N_6^{\bullet -}$, k_0 is the sum of the rate constants of decay in the absence of any added olefin, K_6 is the equilibrium constant for eq 6, and k_8 is the bimolecular rate constant for the process described by eq 8. At a fixed olefin concentration, eq 11 predicts an inverse dependence of k_{obs} on

$$k_{obs} = k_0 + \frac{k_8[\text{olefin}]}{K_6[N_3^-]} \tag{11}$$

$[N_3^-]$. This is indeed what is observed and is illustrated in Figure 2, which shows that the lifetime of $N_6^{\bullet -}$ ($\tau = 1/k_{obs}$), measured in the presence of a fixed concentration of 2,3-dimethyl-2-butene, increases as the concentration of azide increases. For a reaction proceeding by direct reaction of $N_6^{\bullet -}$ (eqs 9 and 10), the kinetics for the decay of $N_6^{\bullet -}$ is predicted to be independent of $[N_3^-]$ and would exhibit a simple linear dependence on olefin concentration.

Absolute bimolecular rate constants for addition of azidyl radical to a variety of alkenes (k_8) were determined from values of the slopes (k_{app}) of the plots derived from eq 11. Plots of k_{obs} versus the concentration of added olefin, at a fixed $[N_3^-]$ (typically 10 mM), were linear. Since the value of K_6 is known to be 200 M^{-1} at 23 °C,[17] the slopes of these plots (k_{app}) yield values of k_8 ($k_8 = k_{app}K_6[N_3^-]$). For a number of the olefins, rate constants were also determined by varying the azide concentration and keeping the olefin concentration fixed. In these cases, plots of k_{obs} versus $1/[N_3^-]$ were also linear (see inset in Figure 2) and led to a value for the slope of k_{app} = $k_8[\text{olefin}]/K_6$. Values of k_8 obtained by the two methods agreed within the experimental uncertainty. Second-order rate constants (k_8) determined for the addition of $N_3^{\bullet}$ to a series of ring-, α-, and β-substituted styrenes are listed in Table 1. Similarly, rate constants for the reaction of $N_3^{\bullet}$ with a variety of simple alkyl- and alkoxy-substituted olefins are listed in Table 2. Electron-deficient alkenes, such as acrylonitrile and methyl methacrylate, were unreactive on the LFP time scale, suggesting the rate constants are less than 10^5 M^{-1} s^{-1}. Each of the rate constants reported contains an associated uncertainty from our previously determined value for K_6.[17] While this increases the error in k_8,

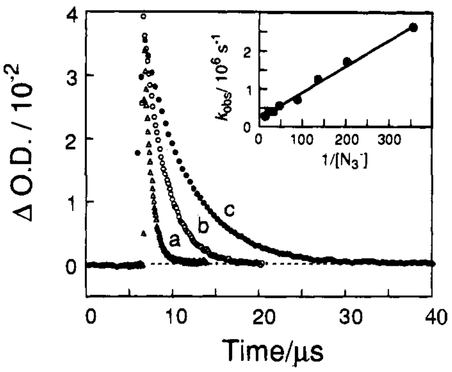
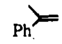
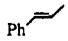
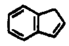
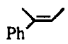
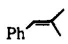
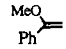
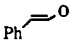
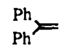


Figure 2. Kinetic traces measured by UV-vis LFP showing inverse dependence of the rate of decay of $N_6^{\bullet -}$ (monitored at 700 nm) on the concentration of added azide at fixed olefin concentration. Kinetics were measured with an oxygen-saturated solution of acetonitrile containing benzil, 10 mM tetrabutylammonium azide, and 8.4 mM 2,3-dimethyl-2-butene with varying concentrations of azide: (a) 21 mM, (b) 46 mM, and (c) 111 mM. Inset shows the linear correlation of k_{obs} with $1/[N_3^-]$.

Table 1. Absolute Rate Constants for the Reaction of Azidyl Radicals with Substituted Styrenes Measured by UV-vis LFP in Acetonitrile Solution at Room Temperature[a]

Substrate	$\sigma^{+\,b}$	$k_8^{\,c}$ /10^6($M^{-1}s^{-1}$)	log (k_8/$M^{-1}s^{-1}$)	IP_a AM1[d] /eV
p-CH_3O-styrene	-0.78	49.0	7.69	8.07 (7.99)[e]
p-CH_3-styrene	-0.31	19.6	7.29	8.34 (8.10)[e]
m-CH_3-styrene	-0.06	9.6	6.98	8.49
styrene	0.00	7.0	6.85	8.55 (8.43)[e]
p-Cl-styrene	0.11	4.8	6.68	8.58 (8.47)[e]
m-CF_3-styrene	0.43	1.5	6.18	8.98
p-CF_3-styrene	0.61	1.2	6.06	9.09
		32	7.51	8.43 (8.19)[e]
		32	7.51	8.29 (8.08)[e]
		22	7.34	8.14
		134 (280)[f]	8.13	8.26
		11	7.05	8.09
		200	8.30	8.37
		1020	9.00	7.99
		86(54)[f]	7.93	8.36 (8.00)[e]

[a] Absolute rate constants were determined from k_{app} values measured by monitoring the decay of $N_6^{\bullet -}$ at 700 nm (see text). Errors in the rate constants are *ca.* 20%. [b] The Hammett σ^+ values are those reported by Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165. [c] $k_8 = k_{app}K_6[N_3^-]$ (see text). [d] AM1-calculated adiabatic ionization potentials (see text). [e] Values in parentheses are experimental gas phase ionization potentials taken from ref 22. [f] TRIR results from the growth of the α-azidyl radical adduct (see text). Errors are *ca.* 50%.

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(19) In some cases when acetophenone or benzophenone was used as the sensitizer, addition of the olefin also quenched the yield of $N_6^{\bullet -}$ via quenching of the triplet precursor. This was not observed when benzil was used as the sensitizer since its triplet energy is lower than that of the alkenes used. Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker Inc.: New York, 1973.

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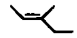
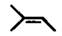
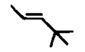
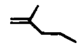
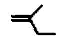
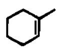
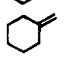
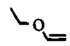
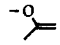
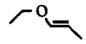
Table 2. Absolute Rate Constants for the Reaction of Azidyl Radicals with Various Olefins in Acetonitrile Measured by UV–vis LFP at Room Temperature[a]

Substrate	$k_8/10^6\ M^{-1}s^{-1}$ [b]	$\log(k_8/M^{-1}s^{-1})$	IP_a/eV [c]	IP_e/eV [d]
	132(100)[e]	8.12	8.23	8.27
	23	7.36	8.60	8.58
	22	7.34	8.59	8.58
	22	7.34	8.64	8.68
	0.40	5.60	8.92	8.91
	0.54	5.73	8.88	8.95
	0.68	5.83	8.96	9.04
	1.6	6.20	9.05	9.08
	1.0	6.0	9.08	9.13
	ca. 0.1	5.0	9.45	9.44
	1.0	6.02	8.86	8.95
	14	7.15	8.54	8.67
	1.7	6.23	8.93	8.93
	2.2	6.34	8.72	8.82
	6.0	6.78	8.61	8.80
	5.4	6.73	8.44	8.64
	96	7.98	8.22	

[a] Absolute rate constants were determined from k_{app} values measured by monitoring the decay of $N_6^{\bullet-}$ at 700 nm (see text). Errors in the rate constants are ca. 20%. [b] $k_8 = k_{app}K_6[N_3^-]$ (see text). [c] AM1-calculated adiabatic ionization potentials. [d] Experimental gas phase ionization potentials taken from ref 22. [e] TRIR results from the growth of the α-azidyl radical adduct (see text).

this error is constant for the series of olefins studied. Included in Tables 1 and 2 are adiabatic ionization potentials (IP_a) calculated using AM1[21] $\{H_f^0(\text{neutral}) - H_f^0(\text{radical cation})\}$ and, where data exists, experimentally determined IP's (IP_e).[22]

When diphenylethylene was used as the quencher, the growth of the substituted diphenylethyl radical (monitored at 330 nm) could be observed, consistent with azidyl radical addition to the alkene (eq 12). For the styrenes, a clear indication of the formation of the benzylic radical adduct could not be obtained because under conditions where the product radicals could be monitored (*i.e.*, in the absence of oxygen) their weak absorptions were obscured by the strong absorption of the sensitizer radical anion (λ_{max} = 350 nm). However, an increase in absorption in the region around 320 nm in the presence of added styrenes was observed and is consistent with a contribution to the absorption from the concurrent formation of benzylic radical adducts. The adduct radicals of all other olefins do not have significant absorptions above 300 nm and hence are inaccessible for study by this method.

$$Ph_2C{=}CH_2 + N_3^{\bullet} \rightarrow Ph_2\dot{C}{-}CH_2N_3 \qquad (12)$$

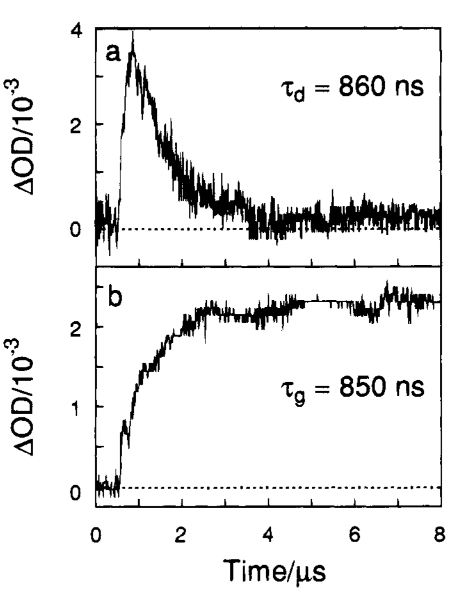


Figure 3. TRIR results for an air-saturated solution of benzil (OD_{308} = 0.3 in 1 mm cell) + 10 mM tetrabutylammonium azide + 20 mM 2,3-dimethyl-2-butene in acetonitrile: (a) decay of $N_6^{\bullet-}$ monitored at 1842 cm^{-1} and (b) growth of the alkyl azide product monitored at 2108 cm^{-1}.

LFP with Time-Resolved Infrared Detection (TRIR). In the present study, IR absorptions of the azidyl moiety are particularly diagnostic and provide a label for the fate of azide in solution. A medium-strength band at 1842 cm^{-1} was previously observed and assigned to $N_6^{\bullet-}$.[17] Azide itself has a strong absorption at 2004 cm^{-1}. The β-azidyl alkyl radical, the expected product of addition of $N_3^{\bullet}$ to an olefin, is expected to exhibit absorptions in the same region as alkyl azides, namely 2080–2120 cm^{-1}.[23,24] The latter two bands in particular are very useful as, in general, the corresponding species do not exhibit characteristic absorptions in the accessible UV–vis region.

The lifetime of the absorption at 1842 cm^{-1} was found to be quenched by olefins. Figure 3a shows the time-resolved absorption at 1842 cm^{-1} of an acetonitrile solution of benzil with the addition of 10 mM azide and 20 mM 2,3-dimethyl-2-butene. A single-exponential fit of the decay gives a lifetime of 860 ns. Concomitant with this decay was a single-exponential growth at 2108 cm^{-1}, shown in Figure 3b, which had a grow-in time of 850 ns. This band is in the region expected for alkyl azides and is assigned to the alkyl azide radical product formed during the addition of $N_3^{\bullet}$ to 2,3-dimethyl-2-butene (eq 13). The identical kinetics observed for the two bands, at all concentrations of olefin, support this assignment. The time-resolved absorption at 2108 cm^{-1} at low olefin concentration (to clearly observe the growth) and the time-resolved IR spectrum of this band at high olefin concentration (to increase the overall signal intensity) are shown in Figure 4, parts a and b, respectively. Similar bands were observed for the quenching of $N_6^{\bullet-}$ by other olefins, including ethyl 1-pro-

(13)

$\bar{\nu}_{max}$ = 2108 cm^{-1}

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(21) Dewar Research Group, J. P. Stewart, *QCPE*, **1986**, *24a,b*.

(22) NISTI Standard Reference Database 25. *NISTI Structures and Properties Database and Estimation Program 1991*; U.S. Department of Commerce: Gaitherburg, MD 20899, 1991.

(23) Lieber, E.; Ramachandra Roa, C. N.; Chao, T. S.; Hoffman, C. W. W. *Anal. Chem.* **1957**, *29*, 916.

(24) Lin-Vien, D.; Colthup, N. B.; Fateley, W. G.; Grasselli, J. G. *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules;* Academic Press, Inc.: San Diego, CA, 1991.

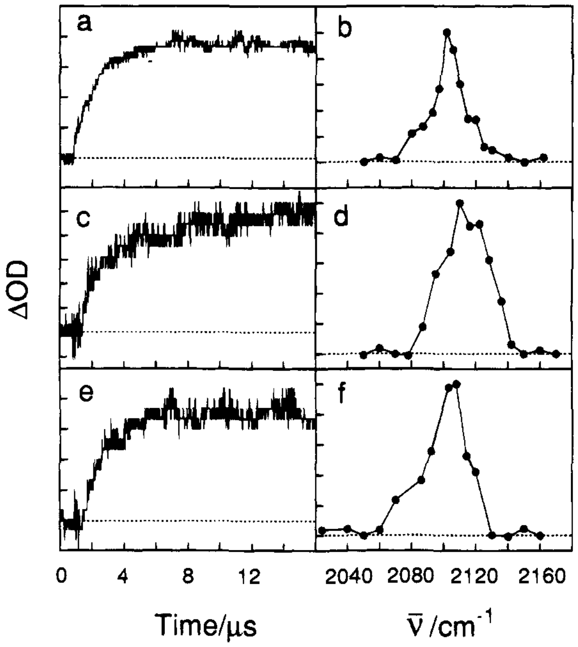

Figure 4. TRIR transient absorption traces (a, c, e) and spectra (b, d, f) obtained for the addition products of an air-saturated solution of benzil (OD_{308} = 0.3 in 1 mm cell) + 10 mM tetrabutylammonium azide with various olefins in acetonitrile: (a) 5 mM and (b) 50 mM 2,3-dimethyl-2-butene, (c) 10 mM and (d) 50 mM ethyl 1-propenyl ether, and (e) 2 mM and (f) 50 mM 2-phenyl-2-butene. The dashed horizontal lines are at ΔOD = 0.

penyl ether (Figure 4c,d) and β-methylstyrene (Figure 4e,f). The position and kinetics of these bands were unaffected by the presence of oxygen in the solution. This implies that conversion of the alkyl radicals to peroxyl radicals does not affect the stretching frequency of the alkyl azide group and, therefore, that there is little interaction between the azido group and the adjacent radical (*i.e.*, the radical is not bridged). There was also very little variation in the observed band positions for the various olefins studied, in agreement with previous observations of alkyl azide stretching frequencies.[23,24]

Measurement of the rate constant of the growth of the alkyl azide product versus olefin concentration allowed for the determination of the bimolecular rate constants for the addition of $N_3^\bullet$ to the olefins (k_8). The relatively weak signals observed, as well as the time resolution of the TRIR system (*ca.* 300 ns), limited the range of olefin concentrations which could be used and made the rate constant determination by this method more difficult than by UV–vis LFP. Rate constants using TRIR obtained from the growth of the alkyl azide band for the reaction of $N_3^\bullet$ with 2,3-dimethyl-2-butene, diphenylethylene, and β-methylstyrene are given in Tables 1 and 2. The agreement between rate constants measured by the two techniques is reasonably good (*i.e.*, within a factor of 2) considering the inherent difficulties in measuring growth kinetics with such weak signals.

The overall fate of the azide in solution also could be followed by this technique. The initial bleaching and partial recovery of the azide (typically *ca.* 65% of the initial bleach) was followed by monitoring the time-resolved absorption of the band at 2004 cm^{-1}. The kinetics of the azide recovery were found to match the kinetics of the decay of $N_6^{\bullet-}$. The percentage of the partial recovery was found to be affected by the addition of olefins to the solution, with less overall azide recovery occurring in the presence of added olefin, indicating that a N_3 group is being consumed in the reaction. This observation, as well as the observation of alkyl azide bands upon addition of the representative olefins studied, is consistent with our conclusion that the quenching of $N_6^{\bullet-}$ occurs via addition of $N_3^\bullet$ to added olefin, as proposed above.

Discussion

In acetonitrile, the visible absorption of $N_6^{\bullet-}$ provides a useful kinetic probe for the investigation of the reactivity of azidyl radicals. The use of the decay of the absorption of $N_6^{\bullet-}$ to probe the kinetics of $N_3^\bullet$ is fundamentally different from the probe techniques employed in time-resolved studies, as originally developed by Scaiano *et al.*[14a] In typical probe experiments, the kinetics of the *formation* of the probe, and the changes in these kinetics as a function of the concentration of an added reactive substrate, are used to obtain kinetic information on the reaction of interest. This particular method requires a probe that is long-lived on the time scale of the experiment and whose growth is readily detectable over a suitable kinetic range (at least an order of magnitude). This methodology has recently been employed by Scaiano *et al.*, who used the growth of the absorption of $Br_2^{\bullet-}$ to probe the kinetics of reactions of the bromine atom.[15] A similar approach cannot be used in the case of $N_6^{\bullet-}$ since its growth is instantaneous at concentrations of azide where its absorption can be easily monitored, a direct result of the relatively low equilibrium constant for formation of $N_6^{\bullet-}$ in acetonitrile at room temperature (K_6 = 200 M^{-1}). Fortunately, analysis of the *decay* kinetics of $N_6^{\bullet-}$ can provide the same information since the probe is formed rapidly and reversibly and since the probe is unreactive toward the substrates (*vide supra*). The key drawback of this approach is the need to know the equilibrium constant for formation of $N_6^{\bullet-}$ (K_6), which is required for the determination of the absolute rate constants. This requirement increases the uncertainty in the k_8 values obtained due to the errors associated with K_6; however, the errors in the relative rate constants remain small.

In most cases when using a probe technique to obtain absolute rate constants for the reaction of another species, information regarding the mechanism or the site of reaction must be obtained from product studies or inferred from the knowledge of the reactivity of the substrates involved. In this regard, TRIR studies provide useful and complementary information to that obtained using UV–vis detection. TRIR provides an advantageous method of monitoring the fate of the N_3 moiety and thus gaining insight into the mode of reaction. Observation of the β-azidyl carbon-centered radical adducts provides clear evidence for addition in these systems (*vide supra*). In principle, the reaction of the azidyl radical with olefins could, in many cases, proceed by hydrogen atom abstraction (eq 3) in competition with addition to the double bond (eq 2). However, a number of observations lead us to conclude that H-atom abstraction does not compete effectively with addition in these systems. For example, the rate constant measured for the reaction of $N_3^\bullet$ with 1,4-cyclohexadiene, whose weak, doubly allylic C–H bonds (BDE = 75 kcal/mole)[25] are particularly suited for H-atom abstraction (BDE(H–N_3) ~ 93 kcal/mol),[12] is only a factor of 2 faster than that measured for cyclohexene, as would be expected for addition solely on the basis of statistical factors due to the presence of the second double bond. Furthermore, only transients formed from addition to the double bond (*i.e.*, the β-azidyl radical adduct) are observed by TRIR experiments with 1,4-cyclohexadiene and the other representative alkenes. In no cases is there evidence for the formation of N_3–H which has a readily detectable IR band at a frequency of 2137 cm^{-1} in acetonitrile under the conditions of these experiments.[26] Unfortunately, since the N_3 stretching frequency of the alkyl

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(25) (a) Tsang, W. *J. Phys. Chem.* **1986**, *90*, 1152. (b) Burkey, T. J.; Majewski, M.; Griller, D. *J. Am. Chem. Soc.* **1986**, *108*, 2218.

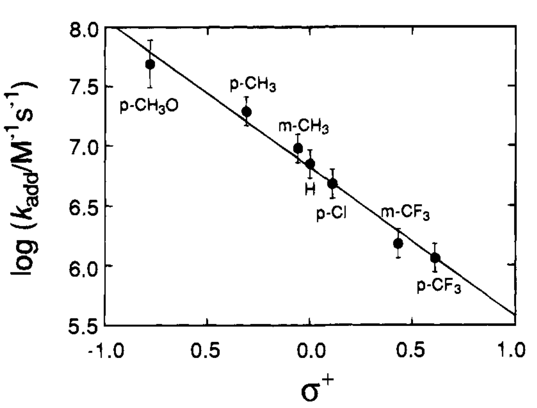


Figure 5. Plot of the variation in the log of the rate constants for azidyl radical addition to ring-substituted styrenes, log(k_{add}), versus Hammett σ^+ values (data from Table 1). The best-fit line determined by least squares analysis is defined by the equation log(k_{add}) = 6.8−1.2σ^+ (r = 0.991).

azidyl radical is independent of substitution, the TRIR studies provide no information regarding the site of reaction.[27]

On the basis of the above discussion, we conclude that the rate constants summarized in Tables 1 and 2 represent those for addition of azidyl radical to the double bond with no measurable contribution to k_8 from H-atom abstraction (*i.e.*, $k_8 = k_{add}$). In general, the rate constants for addition of azidyl radicals to substituted styrenes increase as the olefin becomes more electron-rich. A plot of log(k_{add}) for the reaction of $N_3^\bullet$ with ring-substituted styrenes versus Hammett σ^+ constants is shown in Figure 5. The excellent correlation (r = 0.991) yields a ρ^+ value of −1.2, thus illustrating the electrophilic nature of the addition reaction. A similar correlation (slope = −1.6, r = 0.991) also was obtained for the variation in log(k_{add}) versus the semiempirical AM1-calculated IP$_a$'s for the ring-substituted styrenes. AM1-calculated IP$_a$'s were used in the plot due to the limited IP$_e$ data; however for the styrenes where IP$_e$ exists, there appears to be a regular deviation in their values from those of IP$_a$.

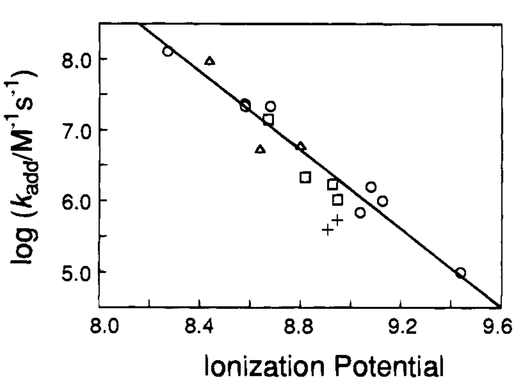
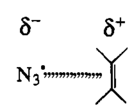


Figure 6. Plot of log(k_{add}) versus experimental gas phase ionization potentials (IP$_e$) for the reaction of azidyl radicals with the alkenes listed in Table 2: (○) acyclic alkyl olefins, (□) cyclic olefins, and (△) alkoxy-substituted olefins. The line is the best fit through all the data points with the exception of 4,4-dimethylpent-2-ene and 3-hexene (+).

The rate constants for the reaction of $N_3^\bullet$ with the olefins in Table 2 also exhibit a reasonable linear correlation with the alkene IP$_e$. This is shown graphically in Figure 6 (slope = −2.8) with the various types of substituted olefins (acyclic, cyclic, and alkoxy substituted) labeled separately. The best-fit line is drawn through the entire data set with the exception of 4,4-dimethylpent-2-ene and 3-hexene. These two points fall below the line and suggest that other factors, including steric effects, may be contributing to the reduced rate constants (*vide infra*). Inasmuch as the IP's reflect the relative HOMO energies of the olefins (as do σ^+),[28] the negative slopes of Figures 5 and 6 indicate that the reactions described here are dominated by the interaction between the SOMO of $N_3^\bullet$ with the HOMO of the olefin with considerable charge transfer interactions in the transition state (Chart 1). The lack of reactivity with electron-deficient alkenes, such as acrylonitrile, in our available time regime indicates that the azidyl radicals are not ambiphilic as has been reported for the (*tert*-butoxycarbonyl)methyl radical and malonyl radical.[29]

Chart 1



Steric effects, influencing the approach of the radical to the olefin, are generally used to explain the regioselective, anti-Markovnikov additions of carbon-centered radicals to olefins.[30,31] Rate constants for addition of these radicals to olefins have also been shown in some cases to be sensitive to steric effects, decreasing as the steric demand at the olefinic carbon center where addition is expected to occur increases.[30,31] However, the effect of substituents appears to be rather minor in the reactivity of $N_3^\bullet$ with alkenes in this study. For example, the rate constants for reactions with α- and β-methylstyrene are identical and indeed greater than that for reaction with styrene, as expected purely on the basis of polar factors. Furthermore, the rate constant for α,β-dimethylstyrene is 4 times greater than that of the singly alkyl-substituted styrenes. Only in the case of β,β-dimethylstyrene, where there are two substituents on the β-carbon (presumably the carbon where

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(26) The value of 2137 cm^{-1} was obtained by titrating a solution of tetrabutylammonium azide (50 mM) in acetonitrile with methanesulfonic acid (pK_a^{DMSO} = 1.6). The band at 2137 cm^{-1} appears at the expense of the asymmetric stretch of N_3^- at 2004 cm^{-1} and is assigned to N_3−H (pK_a^{DMSO} = 7.9), in good agreement with the value of 2140 cm^{-1} reported for N_3−H in the gas phase, see: Dows, D. A.; Pimentel, G. C. *J. Chem. Phys.* **1955**, *23*, 1258.

(27) It is important to emphasize that direct information as to the *site* of addition is unattainable using time-resolved techniques. For addition to diphenylethylene, where the diphenylmethyl radical adduct is observed, or for the reaction of the substituted styrenes, where experimental evidence for the formation of benzylic radical intermediates exists, addition at the α-position can still not be ruled out. For the simple olefins, the assumption would be that the azidyl group will add to the least substituted carbon in an anti-Markovnikov addition as is typically observed in radical reactions with olefins. Shaik and Canadell (Shaik, S.; Canadell, E. *J. Am. Chem. Soc.* **1990**, *112*, 1446) have used a state correlation diagram approach to rationalize the regioselectivity of radical addition to olefins. They concluded that the regiochemistry observed in radical addition reactions is derived from two key properties of the radical and olefin reaction pair: (i) the spin density in the $^3\pi,\pi^*$ state of the alkene and (ii) the relative bond strengths of the two possible C−radical bonds. These factors direct the addition of a radical to an olefin toward (i) the carbon that possesses the largest spin density (which parallels the relative HOMO coefficients of the alkene) and (ii) the olefinic carbon which forms the strongest R−X bond. Often (particularly for the olefins of the present study), these two factors direct the reaction to the same carbon center. Riemenschneider *et al.* (ref 35) have used the magnitude of the atomic orbital (AO) coefficients of the 2p$_z$ orbitals for the two carbon sites in the HOMO of the alkene to predict the site of attack (assuming a HOMO−SOMO interaction). This approach led to the conclusion that addition to the simple alkyl olefins will occur at the least substituted carbon (anti-Markovnikov addition) and at the β-carbon in the alkyl- and ring-substituted styrenes (formation of the benzylic radical).

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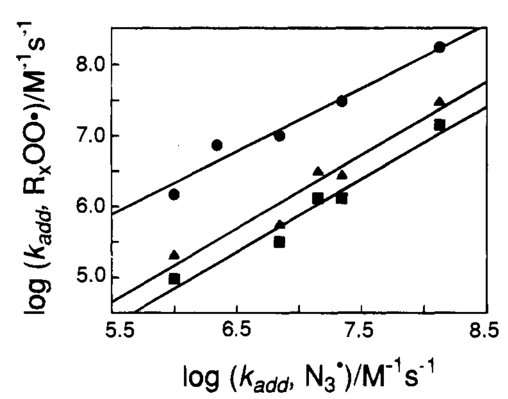

Figure 7. Plot of log(k_{add}) for the reaction of azidyl radicals with a number of olefins (styrene, cyclohexene, 1-methyl-1-cyclohexene, 2-methyl-2-butene, 2,3-dimethyl-2-butene) versus log(k_{add}) for the reaction of (perhaloalkyl)peroxyl radicals (●, $C_4F_9OO^•$; ▲, $CF_3CCl_2OO^•$; ■, $CCl_3OO^•$) with the same olefins (data from refs 32–34). The slopes of these lines are all equal to 1 within experimental uncertainty.

addition will occur), are the rate constants smaller than what might be predicted on the basis of IP. For the reaction of $N_3^•$ with the more simple olefins, the steric effect does not seem to contribute to the same extent since the rate constants correlate well with the IP, increasing as the degree of alkyl substitution increases around the double bond in the series 1-hexene, 2-methylbutene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene. Steric effects may, however, play a role in decreasing the rates of addition with 3-hexene, 3,3-dimethylpent-2-ene, and the cyclic olefins.

Other electrophilic radicals have been shown to follow similar reactivity trends. For example, the rate constants for addition reactions of a number of (perhaloalkyl)peroxyl radicals to a number of olefins have been determined by Neta *et al.*[32–34] For these cases, the reactivity of the peroxyl radicals parallel the reactivity of $N_3^•$ (Figure 7). Relative rate constants determined for reactions of the dicyanomethyl radical with simple alkyl olefins also follow the same general trend of increasing reactivity with increasing substitution.[35] However, in contrast to reactions of $N_3^•$, a significant steric effect was observed in the reactions of dicyanomethyl[36] and, more recently, perfluoroalkyl radicals with β-substituted styrenes.[37] Unfortunately, neither reactions of the (perhaloalkyl)peroxyl radicals with substituted styrenes nor reactions of the perfluoralkyl radicals with more highly substituted olefins have been reported, so further generalization of reactivity trends is not possible at this time.

The difficulty in making quantitative comparisons between different radicals is exemplified by the reactions of $N_3^•$ and n-$C_3F_7^•$. For all of the ring-substituted styrenes reported, n-$C_3F_7^•$ is more reactive than $N_3^•$. This result would imply an earlier transition state for n-$C_3F_7^•$. On the other hand, the 20-fold decrease in the rate of addition of n-$C_3F_7^•$ to β-methylstyrene compared to α-methylstyrene implies a later transition state or different molecular trajectory (or both). Furthermore, the Hammett slopes for addition to ring-substituted styrenes indicate that $N_3^•$ ($\varrho = -1.5$) is more electrophilic than n-$C_3F_7^•$ ($\varrho = -0.53$). The difficulty in comparing these reactions lies in the fact that (1) n-$C_3F_7^•$ is larger than the linear $N_3^•$ and has a different intrinsic steric demand, (2) the addition of n-$C_3F_7^•$ is more exothermic than that of $N_3^•$ which tends to drive the former reaction toward an earlier transition state, and (3) n-$C_3F_7^•$ has a lower electron affinity (EA ≈ 1.8)[38] than $N_3^•$ (EA = 2.7)[39] so the latter should be subject to a larger polar effect (*vide infra*).

Recently, a number of detailed theoretical studies have addressed the dynamics of radical additions to alkenes.[36,40] In general, there is reasonable agreement that the transition state geometries for additions of both electron-rich and electron-deficient radicals in the gas phase imply an angle of attack (*i.e.*, the angle between the C–C bond and the trajectory of the incoming radical) of *ca.* 106–109° with respect to the C–C bond. In a reasonably comprehensive study (including a number of substituted olefins), Wong *et al.* point out that for a given combination of radical and olefin it is difficult to predict the extent to which polar, steric, and enthalpic factors will contribute to the transition state.[40] They find that, even in the gas phase, $HOCH_2^•$ and $NCCH_2^•$ have significantly lower barriers than $CH_3^•$ in additions to a series of olefins. Although these reactions appear to be enthalpy driven, analysis of electron densities are consistent with $HOCH_2^•$ and $NCCH_2^•$ being nucleophilic and electrophilic, respectively. In solution, we have observed that the polar contribution is dominant in the addition reactions of $N_3^•$. This can be understood in the context of the simple configuration mixing model used by Wong *et al.* In that study it is suggested that the polar contribution is governed by the energy of the charge transfer state (E_{CT} = IP − EA). While in the gas phase E_{CT} is on the order of 10 eV, in a polar solvent E_{CT} may be as low as 0.5–2 eV.[40] Thus, since the enthalpic and steric contributions are expected to be essentially solvent independent, polar contributions will become more important as the dielectric constants (static and optical) of the medium increase.

For the reasons mentioned above, a quantitative comparison of reactions of other electron-deficient radicals is difficult. While the reactivity–IP trends are similar (*i.e.*, in the same direction) for a number of radicals, the varying sensitivity to steric effects are not readily rationalized. Since the reactions in solution appear to proceed with barriers that are much less than those calculated in the gas phase, the structures of the transition states are still an open question. As the polar contribution increases (*i.e.*, E_{CT} decreases), the angle of attack is expected to decrease (*i.e.*, approach 90°) in order to maximize the HOMO–SOMO overlap. Unfortunately, there are no theoretical calculations available for addition reactions which include solvation or for reactions with greater polar character (*i.e.*, E_{CT} ≈ 1 eV).

Conclusions

Absolute rate constants for the electrophilic addition of azidyl radicals to a variety of olefins have been measured in acetonitrile at room temperature using the decay of $N_6^{•-}$ as a probe. The use of the *decay* of the probe is in contrast to traditional methods which are based on monitoring the *growth* of the probe. Our method has allowed for the measurement of absolute rate constants for addition reactions of $N_3^•$ which would otherwise be difficult (if not impossible) to obtain. Rates of addition of $N_3^•$ olefins are found to be mainly controlled by polar factors,

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with steric factors playing only a minor role. The magnitude of the rate constants obtained suggests that addition of $N_3^\bullet$ to unsaturated systems can compete with electron transfer reactions of the azidyl radical, particularly in nonaqueous solution or in the more nonpolar environments of proteins and membranes, where electron transfer rate constants will be reduced.

Experimental Section

General. Ketones utilized as sensitizers were commercially available (Aldrich) and purified by recrystallization or distillation prior to use. Tetrabutylammonium azide (TCI) was used as the source of azide since it has high solubility in acetonitrile; however identical results were obtained with NaN_3. Olefins used as quenchers were commercially available (>99%) or prepared by standard procedures and purified by distillation or by passing them through activated alumina immediately prior to use. Acetonitrile was spectroscopic grade (BDH) and used as received. Steady state IR measurements were made on a Nicolet 20BDX FTIR system. UV−vis spectra were recorded on a Varian Cary 3 spectrophotometer.

UV−vis Laser Flash Photolysis Experiments (UV−vis LFP). Nanosecond laser flash photolysis experiments employed the pulses from a Lumonics EX-530 excimer laser (308 nm; 8 ns pulse width; *ca.* 45 mJ/pulse) and a computer-controlled detection system previously described.[41] Solutions typically contained an appropriate amount of the ketone sensitizer such that the optical density at the excitation wavelength was between 0.4 and 0.6 (typically 1 mM). To these solutions was added azide directly as the neat solid or as a standard solution in acetonitrile. For the majority of the kinetic studies (except where noted), the concentration of azide was fixed at 10 mM. Samples were contained in rectangular 7 × 7 mm Suprasil quartz cells. For the kinetic studies, the olefins were added by microliter syringe as a neat liquid or as a standard solution of olefin in acetonitrile. Quenching plots used in the determination of the bimolecular rate constants (see Results) were constructed from the first-order rate constants for decay of the probe measured using at least six to seven substrate concentrations varying by at least a factor of 10 in concentration. Transient absorption spectra were measured employing a flow system which ensured that a fresh volume of sample was irradiated by each laser pulse. Spectra were recorded using N_2, O_2, and air-saturated solutions. The absorbance of $N_6^{\bullet -}$ was unaffected by oxygen; therefore the quenching studies were performed using air- or oxygen-saturated solutions.

Time-Resolved Infrared (TRIR) LFP Experiments. Solutions for the TRIR measurements (prepared to give an optical density of *ca.* 0.3 at 308 nm) were flowed through a 1 mm path length CaF_2 cell. The excitation source was similar to that used in the UV−vis LFP experiments. The IR probe source was a Mutek Model MPS-1000 diode laser system (1500−2280 cm^{-1}). Kinetic traces at a particular IR frequency were obtained by measuring the IR intensity through the sample before, during, and after absorption of the UV laser pulse. Response time of the IR detector was *ca.* 300 ns. Absorption of the excitation pulse caused a shock wave in the kinetic traces, which was dependent on the solution and path length. All kinetic traces were therefore corrected by subtracting the shock wave measured at an IR frequency at which no transient was observed. Spectra were obtained by measuring the individual kinetic traces at 4−10 cm^{-1} increments throughout the region of interest and plotting ΔOD versus wavenumber for a fixed time after the 308 nm laser pulse. Full details of the TRIR system have been given elsewhere.[42,43]

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