Determination of the Energies and Lifetimes of Triplet 1,4-Biradicals Involved in [2 + 2] Photocycloaddition Reactions of Enones with Alkenes Using Photoacoustic Calorimetry

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It is known that triplet 1,4-biradical intermediates play a critical role in [2 + 2] photocycloaddition reactions of enones with alkenes en route to formation of products.[1,2] Recently, Weedon and co-workers[2,3] succeeded in trapping such species using selenium hydride. However, very little is known about the energetics and lifetimes of these biradicals. Using "radical clocks" as probes, Rudolph and Weedon[4] estimated that the lifetime of biradicals produced from cyclopentenone and vinylcyclopropane was on the order of 50 ns. Caldwell, Schuster, and co-workers used time-resolved photoacoustic calorimetry (PAC) to determine the average energy (47.4 kcal/mol) and lifetime (37 ns) of the mixture of head-to-head (HH) and head-to-tail (HT) triplet 1,4-biradicals implicated in the photodimerization of cyclopentenone.[5] This technique, which is based on the measurement of time-resolved thermal relaxation of electronically excited states,[6-10] allows the simultaneous determination of the energetics and dynamics of short-lived (>15 ns) transient species and is especially useful in cases where the transient is difficult to detect using time-resolved absorption spectroscopy. In earlier work using PAC, Peters and co-workers determined that the triplet 1,4-biradical obtained from valerophenone by intramolecular H-abstraction had a lifetime of 85 ± 10 ns and an energy (relative to the ground-state ketone) of 65 ± 3 kcal/mol;[7] the biradical lifetime was in excellent agreement with that determined by Caldwell using transient absorption spectroscopy (TAS).[11]

Taking advantage of the simplicity of the PAC technique, we have determined energies and lifetimes of a series of 1,4-biradicals derived from the [2 + 2] photocycloaddition of isophorone (**1**), 3-methyl-2-cyclohexen-1-one (**2**), testosterone acetate (**3**), and (*R*)-(−)-4,4a,5,6,7,8-hexahydro-4a-methyl-2(3H)-naphthalenone (**4**) to a variety of alkenes in acetonitrile. UV excitation of enones gives singlet states which decay very efficiently to produce π,π^* triplet states. These triplet states are intercepted by alkenes to produce a mixture of triplet 1,4-biradicals which after a spin flip either close to products or fragment to regenerate starting materials.[1,2] As in the prior studies on triplet 1,4-biradicals cited above, deconvolution of the experimental waveforms for time-resolved heat evolution (E-wave) was performed against a calibration standard (T-wave), allowing the simultaneous determination of the lifetimes and energies of the triplet 1,4-biradicals; the corresponding parameters for the enone triplets in the absence of alkenes as well as the rate constants for quenching by alkenes of the enone triplets are already known.[12-14] In the overall scheme, the fractional heat loss ϕ_1 results from the relaxation at the rate of $1/\tau_1$ of the initially generated singlet to the enone triplet state; ϕ_2 is the fractional heat released at rate $1/\tau_2$ upon formation of biradicals from reaction of the enone triplet with the ground state alkene; ϕ_3 (which should equal $1 - \phi_1 - \phi_2$) is the fractional heat loss upon biradical decay to reactants and products, and τ_3 is the biradical lifetime. As in the study of the predimerization biradicals derived from cyclopentenone, τ_1 is fixed at 0.1 ns,[12,15] ϕ_1 is known,[13] the enone triplet lifetime $\tau_2 = (k_q[\text{alkene}] + 1/\tau_0)^{-1}$,[16] and the other three parameters (ϕ_2, ϕ_3, τ_3) are allowed to vary independently. The details of the methodology are presented in ref 6 and 9. The assumption is made that all triplet quenching leads to biradicals, since the triplet energies of alkenes are typically much higher than those of relaxed enone triplets;[12,18] in the case of alkenes where triplet energy transfer from enones is a possibility, e.g., acrylo- and fumaronitrile, it has been demonstrated that quenching by triplet energy appears not to be important and that the Schenck mechanism (adduct formation) still operates.[19] On this basis, the quantum yield for formation of biradicals $\Phi_{\text{bir}} = k_q[\text{alkene}]\,(k_q\,[\text{alkene}] + 1/\tau_0)^{-1}$.

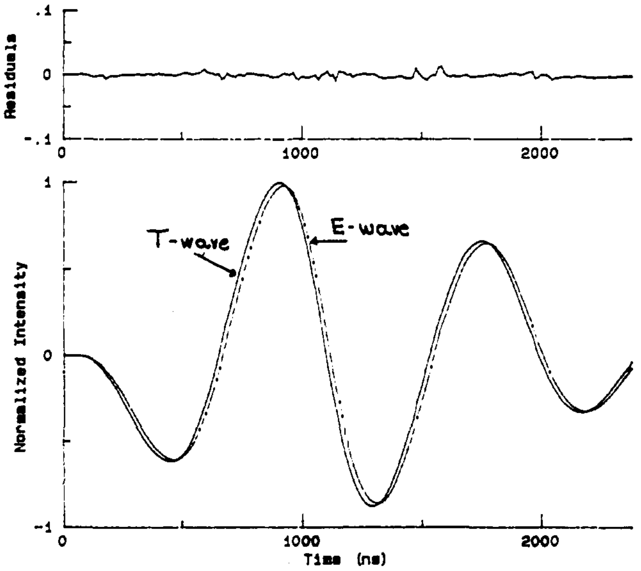

Figure 1. Residuals (upper) from deconvolution of the waveform (lower) from irradiation of **2** at 308 nm in the presence of acrylonitrile in acetonitrile (E-wave). The T-wave is the transducer response to the calibration standard, 2-hydroxybenzophenone. Sixteen shots are averaged to give the composite waves illustrated here. The experiment was repeated four times with fresh samples.

Figure 1 demonstrates a representative PAC trace from a single

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(14) Rate constants for quenching of isophorone (3,5,5-trimethylcyclohexenone) triplets by alkenes have been determined to be nearly the same as those for 3-methylcyclohexenone.

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(16) The values for τ_0 are those for the enone at infinite dilution in acetonitrile. To the extent that triplet self-quenching (i.e., quenching of the triplet by the ground state) occurs, the triplet lifetimes prior to addition of alkene would be reduced. However, the rate constant for triplet self-quenching is only ca. $1.1 \times 10^7\ M^{-1}\ s^{-1}$ for cyclohexenone[17] and is probably somewhat less for the substituted compounds. The triplet lifetime of **2** in acetonitrile is unchanged between between 0.013 and 0.09 M and thus is unlikely to be significantly reduced at 0.2 M, the concentration used in the present experiments. A similar situation holds true for the other enones.

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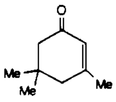
experiment using 3-methylcyclohex-2-en-1-one (**2**) and acrylonitrile. The experimental wave (E) was obtained from excitation of **2** (0.19 M, 308 nm, XeCl excimer laser, 2–3 mJ/pulse, 2-Hz repetition rate) in the presence of the alkene (0.49 M) in nitrogen-outgassed acetonitrile solution and was deconvoluted against the T-wave acquired from excitation of 2-hydroxybenzophenone (0.003 M) under the same conditions. The kinetic and enthalpic fitting parameters in this case are $\phi_1 \equiv 0.25$ (fixed, corresponding to the triplet energy of **2** of 68.7 kcal/mol);[12,13] $\phi_2 = 0.23$; $\phi_3 = 0.51$; $\tau_1 \equiv 0.1$ ns (fixed, from an estimate of the rate of intersystem crossing of the singlet excited state of **2** to its triplet state;[15] τ_2, the triplet lifetime of **2** in the presence of the alkene = 11.5 ns using $\tau_0 = 74$ ns and $k_q = 1.5 \times 10^8$ M^{-1} s^{-1}, as previously determined by TAS;[12,16] τ_3, the average lifetime of the mixture of triplet 1,4-biradicals = 13.7 ns. The average energy of the HH and HT triplet 1,4-biradicals relative to the ground-state enone is given by $[(1 - \phi_1 - \phi_2)/\Phi_{\text{bir}}]E_{h\nu} = 57.5$ kcal/mol, where $\Phi_{\text{bir}} = 0.84$, and $E_{h\nu} = 92.92$ kcal/mol at 308 nm. Note that values for the energies and lifetimes of triplet biradicals given in Table I are averages of at least four independent experiments of the type illustrated here.

The energies and the lifetimes of the mixture of triplet 1,4-biradicals derived from the [2 + 2] photocycloaddition of **1** (0.18 M), **2** (0.2 M), **3** (0.16 M), and **4** (0.14 M) with a variety of alkenes are summarized in Table I. Alkene concentrations minimize the triplet enone lifetime, τ_2. The results indicate that both electron-deficient and electron-rich alkenes lead to triplet 1,4-biradicals. Although the energies of these triplet 1,4-biradicals do not show any obvious trend, the lifetimes seem to be dependent on the alkene substituents. Thus, the biradicals produced from fumaronitrile and acrylonitrile have considerably shorter lifetimes than the biradicals derived from electron-rich alkenes. The very long lifetimes for the biradicals derived from 2,3-dimethyl-2-butene are unexpected but reproducible. The range of lifetimes (determined by TAS) of 1,4-triplet biradicals derived from the Norrish Type II reaction is also quite large, from 24 to 2200 ns depending on biradical structure and the solvent.[11,20] For **1** and **2** with 2,3-dimethyl-2-butene and **4** with cyclopentene, the triplet 1,4-biradical energies could not be accurately determined due to the low quantum yields for their formation.

Heats of formation of HH and HT biradicals for the systems studied, calculated by Benson's group equivalency technique,[21] are in good agreement with the experimental values reported in Table I. There may well be large differences in the lifetimes of the individual HH and HT triplet 1,4-biradicals, but our measurements provide no information on this point. On the basis of Weedon's studies with cyclopentenone,[2,3] it is likely that HH and HT biradicals are also formed in approximately equal amounts from cyclohexenones, but this also is not known with certainty. It is premature to draw definitive conclusions about the factors which determine the lifetimes and the energies of these triplet 1,4-biradicals. Future experiments will include variations of solvent polarity, temperature, and alkene structure, in order to establish the dependence of biradical lifetime and energy on these factors.

Table I. Energies and Lifetimes of 1,4-Biradicals Derived from the [2 + 2] Photocycloaddition of Enones and Various Alkenes



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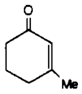

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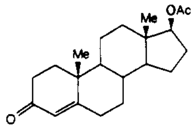

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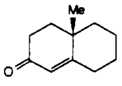

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enone	alkene	ϕ_{bir}[a]	E_{bir} (kcal/mol)	τ (ns)
1	fumaronitrile[b]	0.83	50.1 ± 5.9	25.9 ± 1.6
	acrylonitrile[c]	0.85	55.0 ± 7.9	28.8 ± 2.9
	cyclopentene[d]	0.76	42.2 ± 7.2	172.8 ± 14.3
	cyclohexene[d]	0.68	56.5 ± 1.1	130.4 ± 13.6
	2,3-dimethyl-2-butene[e]	0.38	see text	398.3 ± 135.4
2	fumaronitrile[b]	0.82	48.5 ± 9.4	30.5 ± 9.7
	acrylonitrile[c]	0.84	51.8 ± 8.9	14.8 ± 1.7
	cyclopentene[d]	0.77	33.8 ± 7.4	76.7 ± 8.1
	cyclohexene[d]	0.66	40.4 ± 2.5	74.5 ± 8.7
	2,3-dimethyl-2-butene[e]	0.37	see text	903.1 ± 111.5
3	cyclopentene[f]	0.99	44.4 ± 5.6	59.2 ± 5.6
4	cyclopentene[g]	0.18	*h*	*h*

[a] Quantum yields of biradicals: see text. [b] [alkene] = 0.13 M. [c] [alkene] = 0.49 M. [d] [alkene] = 8.89 M. [e] [alkene] = 7.90 M. [f] [alkene] = 5.5 M. [g] [alkene] = 9.8 M. [h] Not detectable.

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