of $NiPF_3^+$ reflects the steric crowding involved upon insertion produced by this larger ligand. Much of the chemistry of the NiL^+ ions can be explained by considering the formation of intermediates that would exhibit low steric interactions. The reactivity of $NiCp^+$ with the halobenzenes indicates that this ligand affects the metal ion much differently than either CO or PF_3. Charge transfer to the cyclopentadienyl group to increase its aromatic character may explain why this ion is more reactive than the other NiL^+ species in these examples. In other cases the steric hindrance of the bulky Cp group appears to block reaction pathways.

Acknowledgment. The National Science Foundation (Grant CHE-8722111) is acknowledged for partial support of this work. Also, we thank Professor John Wronka, for assistance in implementation of the frequency-swept detector for the MSU ICR, and Professor James F. Harrison, for helpful discussions and collaborations concerning the nature of transition-metal-ion–ligand bonding.

The Relaxed and Spectroscopic Energies of Olefin Triplets

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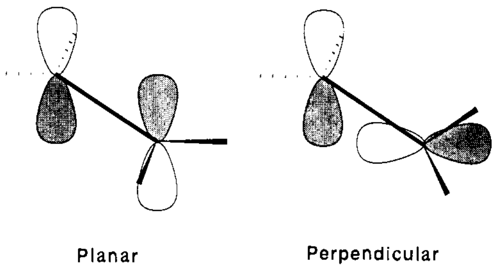
Abstract: The relaxed energies and lifetimes of a series of olefin triplets have been determined by time-resolved photoacoustic calorimetry using a novel cell configuration which allows improved precision. The planar triplet energies of a number of olefins were measured by oxygen and heavy-atom perturbation methods. For styrene triplets, the difference between the relaxed and planar triplet energies varies from 0 to 10 kcal/mol depending on the degree of twisting allowed. Stilbene triplets show a potential surface rather flat between trans and perpendicular geometries. New Benson group equivalents for a number of free radical additivities derived from recent literature values of heats of formation of radicals are tabulated. The energies of acyclic, fully relaxed triplets are in excellent agreement with the values calculated by the Benson method using the new radical group values and the assumption that the triplet is satisfactorily modeled as a "1,2-biradical".

The triplet state of alkenes is an intermediate in many long-known photoreactions, examples including photosensitized cis–trans isomerization,[1,2] photorearrangements,[3] and photocycloadditions.[4] In general, such processes will originate from a thermally relaxed triplet. While transient spectroscopy with standard optical detection allows observation of these species,[5] it does not provide thermochemical information. Normally the excited energies are estimated by spectroscopic methods such as conventional absorption or luminescence. Since the relaxed triplet energies are frequently quite different from vertical energies, i.e., the energies at ground-state geometry, the relaxed energies will frequently be spectroscopically inaccessible due to severe Franck–Condon restriction. To understand the energy surfaces of alkenes better, and particularly to provide thermochemical information from which further considerations of alkene triplet reactivity might follow, we have determined the relaxed triplet energies of a substantial number of related alkenes by time-resolved photoacoustic calorimetry[6,7] (PAC) together with their spectroscopic energies by heavy-atom solvent[8] or oxygen-perturbed[9] absorption. Comparison of the two quantitates the energy difference between the planar and perpendicular forms (sketched below) when the latter is not prohibited by structural constraint.



Experimental Section

Oxygen-perturbed absorption spectra were run on a photodiode array spectrometer (Hewlett-Packard, Model 8450A) with resolution of 1 nm and sensitivity of 10^{-4} in absorbance. The high-pressure sample cell, shown in Figure 1, has a 5-cm light path for vapor samples and 1-cm light path for liquid samples. The spectra of low boiling point samples were taken by placing several drops of the compound under study in the bottom of the high-pressure cell, allowing 5 min for vaporization. In the cases of higher boiling compounds, the spectra were taken in the liquid phase. Normally, 1 mL of solution containing 0.2–0.4 g of compound was placed in a standard 1-cm UV quartz cell which can be placed in the high-pressure cell. The system was then pressurized with 20–40 atm of oxygen. Because the diffusion of oxygen in the liquid phase is very slow, the spectra were recorded after the cell had been gently shaken for 5 min to reach equilibrium. Further shaking produced no further change in the spectra. The spectra under 1 atm were also recorded to provide references. Evaluation of the singlet–triplet absorption spectra were carried out by subtracting the references from the perturbed spectra obtained under high-pressure condition.

External heavy-atom perturbed spectra were also run on the photodiode array spectrometer. Dibromomethane and methyl iodide were used as heavy-atom perturbers. Methyl iodide is a highly light-sensitive

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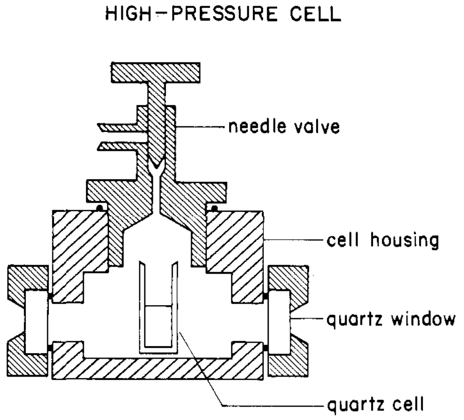

Figure 1. High-pressure absorption cell.

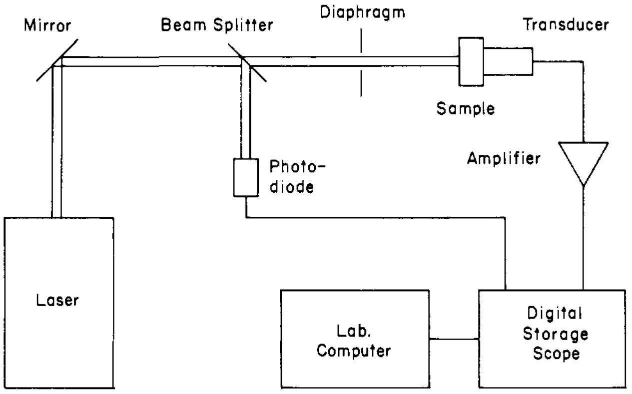

Figure 2. Schematic arrangement of apparatus.

compound. All operations using this compound were performed under red light. The spectra were run under both perturbed and unperturbed conditions. The perturbed spectrum was taken by dissolving 0.2–1.0 g of the compound in 2 mL of methyl iodide or dibromomethane. The reference spectra were taken by dissolving the same amount of compound in 2 mL of cyclohexane. The $S_0 \rightarrow T_1$ absorption spectra were obtained by subtracting the reference from the perturbed spectra.

Photoacoustic Measurements. The scheme of our apparatus arrangement is shown in Figure 2. The output at 337 nm (N_2), 428 nm (N_2^+), or 350 nm (XeF) from a multigas excimer laser (Lumonics, 681S) was used for photoexcitation of the samples. A small fraction of laser output was reflected to a photodiode to generate a trigger signal for a digital storage oscilloscope. The main beam was attenuated and then sent to the photoacoustic cell containing the liquid sample under study.

Our photoacoustic cell is quite different from the conventional design.[6] Instead of right angle irradiation, we use in-line irradiation that allows a larger laser beam area (2 cm^2) (Figure 3). With up to 2-mJ/pulse incident energy, the response is still linear in laser power. The degassed sample flows between a quartz flat and a front surface aluminum mirror spaced 50 ± 5 μm apart by brass shim stock or 150 ± 10 μm apart by microscope glass covers. The brass shim allows higher temporal resolution, while the microscope glass cover permits stronger and more easily interpretable signals. Typically 10–20% of light is absorbed by the sample and the remainder is reflected back by the mirror. Interestingly, even at 30% total absorption the Beer–Lambert law predicts a transient concentration profile uniform to better than ±1% at all penetration depths as a result of the two passes of excitation through the sample. A 0.5-in. diameter piezoelectric transducer (Panametrics A603S, 1 MHz, or A682S, 3.5 MHz) is clamped against the backside of the aluminum mirror to detect the acoustic signal. The output from the transducer is directly fed to a digital storage oscilloscope (Gould 4050) operating at 10 ns per channel, or, if necessary, the signal is first amplified by a wide-band preamplifier (PAR, Model 115) with a gain of 10. Normally 64 or 128 laser pulses were averaged and then transferred to a laboratory computer for analysis. Data collection was completed within 15 min. The drift in laser power during this time was less than 1%. Differences between the T- and E-wave of less than the recorder penwidth (ca. 0.3%) were readily reproduced.

Azulene, 2-hydroxybenzophenone, or ferrocene solution (OD = 4–8 cm^{-1} determined in a 2-mm cuvette) was used as calibration standard for the measurement of the system response. These compounds deposit >99% of energy absorbed as heat on a time scale much shorter than the laser pulse. Following Peters' terminology,[6] we refer to the calibration waveform as the T-wave and the sample waveform as the E-wave. The optical densities of the calibration standard and sample solution were adjusted to be within 1% of one another at the wavelength of excitation, assuring identical energy deposition in the two. A small background acoustic signal from the surface of the mirror (ca. 5% of sample signal in magnitude) was subtracted digitally. During data collection the cell was maintained under a solvent-saturated nitrogen atmosphere.

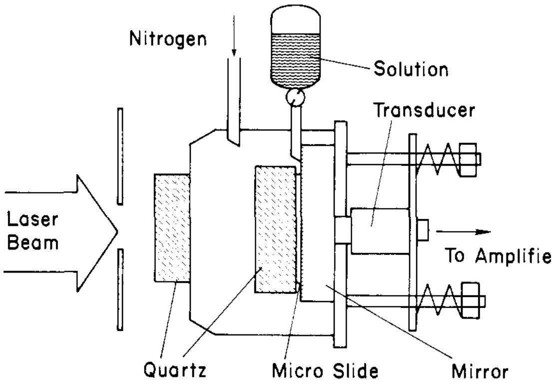

Figure 3. Sample cell for photoacoustic measurements.

The signals were analyzed in a way generally similar to that of Peters[6] after the necessary background subtractions. A fit of the first 2 μs of the acoustic waveform was performed for the determination of the relaxed triplet energies and lifetimes. The E-wave was modeled as a convolution of the actual rates of heat deposition with the T-wave, the latter taken as the instrument response function. The convolution programs were developed as subroutines to a public-domain Marquardt algorithm-based nonlinear least-squares fitting program. The main program estimated adjustments to the parameters and iterated until convergence. Derivatives were calculated numerically. The procedure differs from that of Peters in that our own integration algorithm was more robust, and neither it nor the convergence criteria were under operator control, leading to improved repeatability of data analyses.

The cell design and data reduction algorithm are discussed fully elsewhere.[10]

Kinetic absorption spectroscopy studies were conducted at the Center for Fast Kinetics Research at the University of Texas at Austin using techniques previously described.[11] Experiments for determination of quenching rate used the 355-nm third harmonic of a Nd–YAG Q-switched laser. The lifetime measurement for biacetyl fluorescence used a mode-locked Nd–YAG laser (355 nm, third harmonic).

Materials. Benzophenone, xanthone, *trans*-stilbene, and 4,4′-diacetyl-*trans*-stilbene[12] were recrystallized from ethanol or benzene before use. Biacetyl, cyclohexane, methanol, benzene, dibromomethane, anthracene, azulene, 2-hydroxybenzophenone, 1,1-diphenylethylene, and ferrocene were used as received. 1,1-Diphenylpropene, 1-phenyl-2-methylcyclohexene, 1-phenylcyclopentene, *p*-methoxytrimethylstyrene, 1-phenyl-6-methylcyclohexene, and 1,1-diphenyl-2-methylpropene were synthesized by Misawa,[13] Laboy,[14] and Cao[5] and had been stored in a freezer (ca. −10 °C) in the form of crystals. 1,1-Diphenyl-1-butene was prepared by Dr. Gupta[15] with purity better than 99%. 1-Phenylcyclohexene, indene, 1,2-dihydronaphthalene, styrene, β-methylstyrene, and 2,5-dimethyl-2,4-hexadiene were purified by distillation before use. The colored impurities in *cis*-stilbene and methyl iodide were removed by passing through a silica gel column.

Preparation of 2-Phenylnorbornene.[16] Phenyllithium (47 mL, 2.4 M) was diluted with 150 mL of anhydrous ether. To the phenyllithium solution was added a 150-mL ether solution of 8.5 g of freshly distilled 2-norbornanone at a rate sufficient to maintain a reflux under the protection of nitrogen. After 2.5 h of stirring, 100 mL of water was added. The ether layer was separated and the water layer was washed with portions of ether. The combined ether layer was dried over anhydrous sodium sulfate. After removal of the solvent, the crude 2-phenyl-2-

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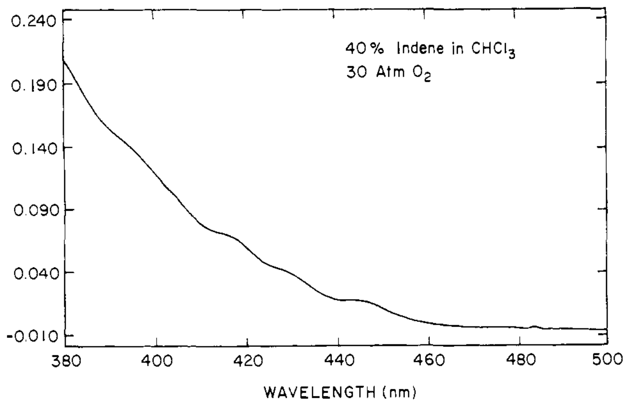

Figure 4. Oxygen-perturbed absorption spectrum of indene.

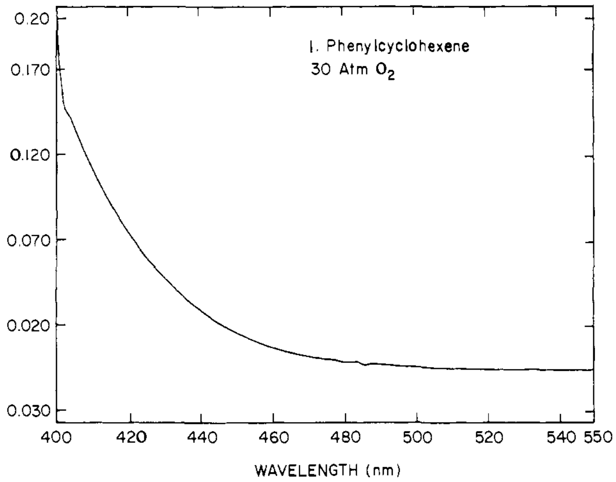

Figure 5. Oxygen-perturbed absorption spectrum of 1-phenylcyclohexene.

norbornanol was distilled at 17 mmHg. The fraction of bp 130–150 °C was collected to yield 8.0 g of colorless oil. The alcohol (8 g) was heated with 4.0 g of potassium bisulfate to 110–125 °C for 80 min. The reaction mixture was poured into 200 mL of cool water and extracted with ether. The ether layer was dried over anhydrous sodium sulfate, the solvent evaporated, and the product distilled, bp 110 °C (10 mmHg), purity 95% by GC. The impurity was 2-phenyl-2-norbornanol and is not expected to impact the measurements made.

Results

Perturbed $S_0 \rightarrow T_1$ Absorptions. Table I shows the triplet energies of a series of alkenes and aromatic hydrocarbons obtained from the oxygen-enhanced and heavy-atom perturbed $S_0 \rightarrow T_1$ absorption spectra. Some compounds such as indene (Figure 4) show marked vibrational structure in $S_0 \rightarrow T_1$ spectra. Their triplet energies were calculated assuming that the longest wavelength maximum observed was the 0,0 transition. Most alkene spectra do not have vibrational structure and the absorption edge is not particularly distinct. The triplet energies of those compounds listed in Table I are derived from the longest wavelength at which light absorption was recorded. For example, the S_0–T_1 transition energy assigned for 1-phenylcyclohexene from Figure 5 (60.8 kcal/mol) corresponds to 470 nm. Since also the $S_0 \rightarrow T_1$ band is often located at the long tail of a charge-transfer complex band, the precision of the triplet energy assignment is limited.[17] We believe our measurements are in general precise to ±10 nm, which corresponds to ±1.3 kcal/mol at 470 nm.

Table I. Spectroscopic Energies for Triplets

compound[a]	E_T (kcal/mol) this work[b]	lit. [ref]
$CH_2=CH_2$	84.0	82.1 [18]
$CH_2=C(CH_3)_2$	80.5	
$CH_2=C(CH_3)C_2H_5$	78.3	
$CH_2=CCl_2$	73.3	
$CH_3CH=C(CH_3)_2$	77.2	
$(CH_3)_2C=C(CH_3)_2$	75.8	
isoprene	60.0	60.1 [19]
$(CH_3)_2C=CHCH=C(CH_3)_2$	57.2	60.5 [19]
benzene	83.8 (83.6[c])	84.2 [20]
toluene	82.1 (82.4[c])	82.3 [17]
naphthalene	60.5	60.6 [20]
cyclopentene	79.4	
1-phenylcyclopentene	58.9	59.6 [22]
1-anisylcyclopentene	58.9	
cyclohexene	81.2 (80.5[c])	
1-methylcyclohexene	75.2	
1-phenylcyclohexene	60.8	
1-phenyl-2-methylcyclohexene	63.5	
1-phenyl-6-methylcyclohexene	62.1	
1,2-diphenylcyclohexene	55.0	
diphenylacetylene	62.7	62.5 [20]
$PhCH=CH_2$	64.9 (60.8[d])	61.8 [20]
$CH_2=C(CH_3)Ph$	61.7 (61.5[d])	62.2 [22]
trans-$PhCH=CHCH_3$	60.5	60.2 [23]
$AnCH=C(CH_3)_2$	59.5	
$Ph_2C=CH_2$	60.8	
$An_2C=CH_2$	60.2	
$Ph_2C=CHCH_3$	60.2	
$Ph_2C=C(CH_3)_2$	60.8	
trans-stilbene	51.0 (51.1[d])	50.7 [20]
cis-stilbene	55.5	54.4 [24]
indene	64.1	
1,2-dihydronaphthalene	60.5	
norbornene	72.3	
2-phenylnorbornene	57.2	

[a] An = anisyl = *p*-methoxyphenyl. [b] Observed by oxygen perturbation except the values in blanks. [c] Dibromomethane as perturber. [d] Methyl iodide as perturber.

Although the effect of heavy-atom perturbation is about two orders of magnitude weaker than that of oxygen perturbation,[25] the triplet energies obtained from heavy atom perturbation are generally consistent with those from oxygen perturbation. Where larger differences exist, e.g., styrene, the lower energy is the preferred value. The present results actually agree with those of Evans,[21] Kellogg,[19] Phillips,[17] and Salisbury[22] more closely than the precision limit above.

We assign the spectroscopic energies we report to the planar olefin triplet in which only relaxation of the C=C stretch in T_1 occurs. We know of no rigorous proof that this is so, but the only significant alternative would be the inclusion of a certain amount of twisting. The data show essentially the identical energy (59–61 kcal/mol) for styrene, β-methylstyrene, phenylcyclopentene, phenylcyclohexene, and 1,2 dihydronaphthalene, a series containing the same styrene chromophore throughout but in which the ability to twist varies widely. If torsion were significant, substantial variation of energy would have been expected.

Analysis of Photoacoustic Signals. Irradiation of benzophenone (ca. 0.07 M) or xanthone (ca. 2 × 10^{-3} M) solution containing 0.03–0.15 M olefin gives an acoustic waveform (E-wave) which is deconvoluted assuming three sequential heat decays:

$$\text{sensitizer} \xrightarrow{337 \text{ or } 350 \text{ nm}} {}^1(\text{sensitizer})$$

$$^1(\text{sensitizer}) \xrightarrow{\phi_1,\, \tau_1} {}^3(\text{sensitizer})$$

$$^3(\text{sensitizer}) + \text{olefin} \xrightarrow{\phi,\, \tau_2} {}^3(\text{olefin}) + \text{sensitizer}$$

$$^3(\text{olefin}) \xrightarrow{\phi_3,\, \tau_3} \text{olefin}$$

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Table II. Relaxed Energies and Lifetimes of Olefin Triplets

compound	solvent	sensitizer	E_T (kcal/mol)	lifetime (ns) PAC	lifetime (ns) KAS[a] [ref]
styrene	cyclohexane	xanthone	51.2 ± 2.0	22.1 ± 0.6	24 [27]
$PhCH{=}CHCH_2$	cyclohexane	benzophenone	53.2 ± 2.4	26.4 ± 0.6	27 [27]
$AnCH{=}C(CH_3)_2$	cyclohexane	xanthone	51.6 ± 2.3	38.6 ± 1.5	46.5 [5]
$Ph_2C{=}CH_2$	cyclohexane	benzophenone	52.1 ± 1.8	34.2 ± 2.3	40 [32]
$Ph_2C{=}CHC_2H_5$	benzene	benzophenone	51.3 ± 1.4	46.4 ± 0.9	47 [14]
$Ph_2C{=}C(CH_3)_2$	cyclohexane	benzophenone	49.7 ± 1.6	110.6 ± 0.6	113 [15]
1-phenylcyclohexene	cyclohexane	benzophenone	56.4 ± 0.7	62.4 ± 1.7	56 [5]
1-phenylcyclopentene	cyclohexane	xanthone	59.2 ± 0.2		
1,2-dihydronaphthalene	cyclohexane	xanthone	61.0 ± 0.2		
indene	cyclohexane	xanthone	65.3 ± 0.2		
2-phenylnorbornene	cyclohexane	xanthone	53.8 ± 0.2		
trans-stilbene	cyclohexane	benzophenone	46.5 ± 0.9	62.0 ± 1.0	59 [35]
	cyclohexane	biacetyl	46.4 ± 1.6	56.8 ± 2.2	
cis-stilbene	cyclohexane	benzophenone	42.0 ± 1.5	62.0	63 [35]
4,4′-diacetylstilbene	methanol		48.4 ± 1.2	111.0 ± 2.2	115.5 [12]
	benzene		49.0 ± 0.4	88.7 ± 1.2	
2,5-dimethyl-2,4-hexadiene	cyclohexane	benzophenone	53.1 ± 1.9	48.7 ± 3.1	44 [44]

[a] KAS = kinetic absorption spectroscopy.

Table III. Triplet Energies Measured by PAC

compound	sensitizer	solvent	excitation wavelength, nm	E_T (kcal/mol) PAC	E_T (kcal/mol) ref 26
anthracene	biacetyl	cyclohexane	428	42.8 ± 1.2	42.0[a]
naphthalene	benzophenone	cyclohexane	337	59.6 ± 0.1	60.9[a]
benzophenone		acetonitrile	337	68.3 ± 0.1	69.2[b]
benzophenone		benzene	337	66.1 ± 0.2	68.6[a]

[a] In nonpolar solvent. [b] In polar solvent.

where τ_1, τ_2, and τ_3 are the decay rates and ϕ_1, ϕ_2, and ϕ_3 are the fractions of photon energy released in each decay. The olefin triplet energy, E_T, is given by $E_T = (1 - \phi_1 - \phi_2)E$, where E is the energy of the photon. During the convolution process, three of the six parameters are known and held constant, and the others are fit using the least-squares fitting routine. The fraction ϕ_1 in the first decay is fixed based on the triplet energy of the sensitizer. The decay rate, τ_1, is fixed at 0.1 ns because the intersystem crossing of the sensitizer is very fast and the transducer cannot resolve the heat decay faster than 1 ns. The second decay rate is also fixed using the triplet–triplet energy transfer rate constant either measured by kinetic absorption spectroscopy or calculated assuming a diffusion-controlled triplet energy transfer rate. At the olefin concentrations we employed, a small deviation from the assumed diffusion controlled rate does not lead to a significant error in the resulting olefin triplet energies.

Biacetyl, unlike benzophenone, has a significant lifetime in the first excited singlet state. The lifetime we measured in cyclohexane using picosecond laser excitation is 12.0 ns, and agrees with the reported value (11.5 ± 1.5 ns).[26] When biacetyl was used as sensitizer, a four-step sequential decay process was assumed:

$$\text{biacetyl} \xrightarrow{428\text{ nm}} \text{biacetyl } (S_1, v > 0)$$

$$\text{biacetyl}(S_1, v > 0) \xrightarrow{\phi_1, \tau_1} \text{biacetyl}(S_1, v = 0)$$

$$\text{biacetyl } (S_1, v = 0) \xrightarrow{\phi_2, \tau_2} {}^3(\text{biacetyl})$$

$$^3(\text{biacetyl}) + \text{olefin} \xrightarrow{\phi_3, \tau_3} \text{biacetyl} + {}^3(\text{olefin})$$

$$^3(\text{olefin}) \xrightarrow{\phi_4, \tau_4} \text{olefin } (S_0)$$

ϕ_1, ϕ_2, and τ_1 are known and are held constant in deconvolution; τ_2, 12 ns measured by picosecond excitation, is also held constant. The triplet energy of olefin, E_T, is given by $E_T = (1 - \phi_1 - \phi_2 - \phi_3)E$.

For both three- and four-sequential decay processes, no more than three parameters were fit in the deconvolution. Figure 6 shows an example of the acoustic waveforms and residuals. The experimental results determined by PAC are summarized in Table II. The values given in Table II with 90% confidence limits are $\mu \pm t\sigma/n^{1/2}$, where μ is the average of n (typically 5–7) experimental runs, σ is the standard deviation, and t is as needed for 90% confidence depending on n.

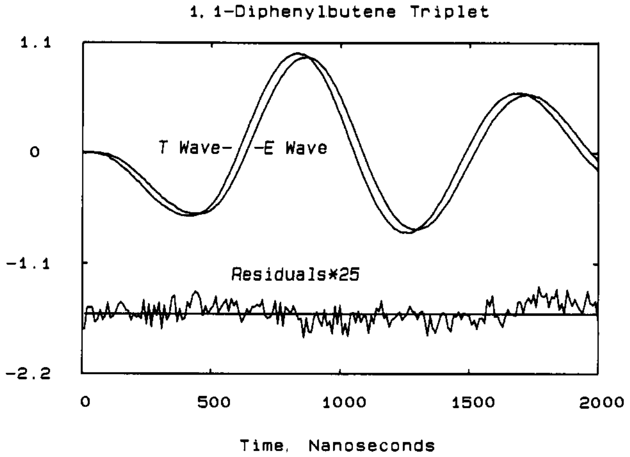

Figure 6. A representative photoacoustic waveform: 1,1-diphenylbutene. Amplitude of T-wave is normalized; E-wave is shown to the same scale, and residuals are shown amplified by a factor of 25.

Test of Accuracy. Measurements of Well-Known Triplet Energies. Deconvolution of the acoustic waveform generated by irradiation of benzophenone in acetonitrile without quencher gives a triplet energy of benzophenone (68.3 ± 0.1 kcal/mol) which agrees well with the literature value.[28] We also checked our system using naphthalene and anthracene as quenchers, and the results are summarized in Table III. Excitation at 337 nm of the cyclohexane solution of naphthalene using benzophenone as sensitizer gives the triplet energy of naphthalene (59.6 ± 0.1 kcal/mol); using biacetyl as sensitizer, the 428-nm (N_2^+) excitation

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of anthracene gives triplet energy of anthracene (42.8 ± 0.2 kcal/mol). It can be seen that our PAC results reproduce literature values[28] of triplet energies of naphthalene and anthracene and energy of benzophenone in acetonitrile with error less than ±1.5 kcal/mol. The energy of benzophenone in benzene determined by PAC is 2.5 kcal/mol lower than the value measured by phosphorescence spectroscopy in glassy matrix at liquid nitrogen temperature (68.6 kcal/mol). The difference substantially exceeds the combined errors. This is not a contradiction, since Singer[29] has suggested reversible triplet exciplex formation between triplet benzophenone and benzene. While we believe our results provide additional evidence for the triplet exciplex, we caution that benzophenone phosphorescence in fluid solution is about 1 kcal/mol red-shifted with respect to the matrix spectra in several solvents in which exciplex formation seems unlikely.[30] This would indicate a lower stabilization energy for the exciplex, barely over our error limits. Similar to the exciplex between acetone triplet and benzene[31a], this triplet exciplex also forms very quickly since deconvolution did not give any component for slow decay. In contrast, the exciplex between cyclohexanone and *o*-xylene appears to form slowly.[31b] We do not understand the reason(s) for the difference among the ketone–arene systems in the rates of exciplex formation.

Styrenes. Since the lifetime of styrene triplet is quite short (24 ns[27]), the results for styrene triplet in Table II were determined with the 3.5-MHz transducer which has higher temporal resolution than the 1.0-MHz transducer. The triplet decay times of indene, 1,2-dihydronaphthalene, 2-phenylnorbornene, and 1-phenylcyclopentene are longer than 1 μs, and the 1 MHz transducer does not respond to them. Therefore no third decays were observed. For acyclic styrenes, 99 ± 2% of absorbed energy is released as heat which was detected by the transducer. The relaxed triplet state of styrene, β-methylstyrene, and 1-anisyl-2-methylpropene have energies of 51.2 ± 2.0, 53.2 ± 2.4, and 52.0 ± 2.3 kcal/mol, respectively, as determined by PAC. The values are each about 8–10 kcal/mol lower than the corresponding spectroscopic values obtained from perturbed absorption spectra. In the case of 1-phenylcyclohexene, owing to the formation of trans isomer, only 79.6 ± 1.5% of absorbed energy is released and detected by the 1-MHz transducer, and the remainder is attributed to strain energy of *trans*-1-phenylcyclohexene as previously reported.[32] Using the quantum yield for the trans isomer formation (0.36 ± 0.01[32]), the strain energy can be calculated from the unreleased energy. Our results on strain energy (47.0 ± 3.0 kcal/mol) and triplet energy (56.4 ± 0.7 kcal/mol) agree well with literature values[32] and have better precision. The differences between relaxed energies and spectroscopic energies are negligible for 1-phenylcyclopentene, indene, and 1,2-dihydronaphthalene.

1,1-Diphenylalkenes. In the deconvolution procedure for 1,1-diphenyl-1-butene triplet, the quenching rate, 2.15×10^9 M^{-1} s^{-1}, measured by kinetic absorption spectroscopy, was held constant. Similar to acyclic styrenes, the relaxed energies of 1,1-diphenylethylene (52.1 ± 1.8 kcal/mol) and 1,1-diphenyl-1-butene (51.3 ± 1.4 kcal/mol) are about 8 kcal/mol lower than their spectroscopic values. The lifetime of 1,1-diphenylethylene, 34.2 ± 2.3 ns determined by PAC, is shorter than the reported value.[33a] The triplet lifetime of 1,1-diphenyl-1-butene is in excellent agreement with that measured by kinetic absorption spectroscopy (47 ns). In the case of 1,1-diphenyl-2-methylpropene, the quenching rate of benzophenone triplet by the olefin was determined by kinetic absorption spectroscopy. Since the rate, 1.47×10^9 M^{-1} s^{-1}, is relatively slow, the value for the triplet energy required a small correction for hydrogen abstraction from cyclohexane by benzophenone triplet. The lifetime, 110.6 ± 0.6 ns, agrees very well with the kinetic absorption spectroscopic result (113 ns); the relaxed energy, 49.7 ± 1.6 kcal/mol, is comparable with those of 1,1-diphenylethylene and 1,1-diphenyl-1-butene. 1,1-Diphenylethylene triplet has a fully twisted geometry (90°) when relaxed, as suggested by Görner[33a] and Bonneau.[33b] The relaxed triplet energies of 1,1-diphenylethylene and substituted 1,1-diphenylethylenes we studied are all significantly lower than their spectroscopic energies, and we believe these large energy differences correspond to this kind of high degree of relaxation.

4,4′-Diacetyl-*trans*-stilbene. Since the intersystem crossing between S_1 and T_1 in this case is efficient, values for this compound were determined without sensitizer, and analysis was performed assuming a two-sequential heat decay mechanism. The triplet energies with 337-nm (N_2 laser) excitation were 48.4 ± 1.2 kcal/mol (methanol) and 49.0 ± 0.4 kcal/mol (benzene). The triplet lifetime depends on solvent, values in methanol (111.0 ± 2.2 ns) and benzene (88.7 ± 1.2 ns) differing somewhat. The former agrees with that determined in methanol by kinetic absorption spectroscopy (115.5 ns);[12] no such value is available for benzene. If hydrogen bonding to the polar carbonyl groups somewhat increased the contribution of the more conjugated planar structure, a lifetime increase would be expected. In each solvent, 95 ± 1% of absorbed energy was released as heat. The remainder is attributed to the fluorescence emission, for which we measured a quantum yield of 0.013,[34] and trans–cis isomerization energy. The given relaxed energies are the lower limits. If internal conversion occurred in 4,4′-diacetyl-*trans*-stilbene, the relaxed energies as the results of deconvolution would be even higher.

Stilbenes. We studied stilbene triplets generated from the trans isomer either with benzophenone sensitization at 350 nm (XeF laser) or with biacetyl sensitization at 428 nm (N_2^+ laser). Energies were respectively 46.5 ± 0.9 and 46.4 ± 1.6 kcal/mol. The value with benzophenone sensitization was determined using the quenching constant measured by kinetic absorption spectroscopy. Two experiments were performed with biacetyl sensitization. Using low concentration of *trans*-stilbene (5.56×10^{-3} M), the rate constant for quenching of biacetyl triplet by *trans*-stilbene was obtained (4.35×10^9 M^{-1} s^{-1}); using higher concentration of *trans*-stilbene (0.07 M), and constraining τ_3 in deconvolution according to the already obtained quenching rate constant, the triplet energy can be determined with better precision. The lifetime with benzophenone sensitization, 62.0 ± 1.0 ns, agreed well with the reported value.[35] Probably because of the influence of high concentration of biacetyl (0.25 M), the triplet lifetime of *trans*-stilbene (56.8 ± 2.2 ns) measured with biacetyl sensitization was slightly shorter. The 350-nm excitation for *cis*-stilbene required a small correction for light directly absorbed by *cis*-stilbene. The quenching rate of benzophenone triplet by *cis*-stilbene in cyclohexane (5.04×10^9 M^{-1} s^{-1}) was determined by kinetic absorption spectroscopy and was similarly held constant in deconvolution. The relaxed triplet energy, 42.0 ± 1.5 kcal/mol, is relative to the cis ground state, and therefore corresponds to a 4.5-kcal/mol difference in enthalpy between the trans and the cis isomers.

Discussion

Peters and Goodman[32,36] reported the first examples of determination of the relaxed energies of olefin triplets by pulsed, time-resolved photoacoustic calorimetry. They claimed the enthalpy sensitivity can approach ±1 kcal/mol,[37] but actually the precision reported for their values is 3–4 kcal/mol.[32,36] With our improved PAC cell, the acoustic signals increase by 10^2 in magnitude. Together with our improved deconvolution routine, the precision limits are about ±2 kcal/mol for short-lived triplets (<50 ns) and are even better for long-lived olefin triplets. Good results have been obtained in our laboratories for triplets with lifetimes

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as short as 12–15 ns, although the error of 2–4 ns is more apparent since it is in such a case a large percentage of the value. This seems to be about as fast as the apparatus will allow, since delta-function decays often show up as 2–4 ns. It is perhaps surprising that decays nearly as fast as the temporal resolution of the digitizer can be measured even this well, until one remembers that the time information is essentially contained in a phase shift, the enthalpy information in an amplitude, and all 200 points contribute to the determination of each.

Our values reproduce well-known triplet energies to ±1–1.5 kcal/mol. Although the precision limits on energies by the PAC method are somewhat greater than those by another direct method, i.e., Gorman's equilibration technique[38] (±0.2–0.3 kcal/mol), PAC is the only way directly to study those cases in which the transient lifetimes are not long enough to reach equilibrium. Therefore, most of our values for the relaxed energies are the first experimental results.

Styrene Triplets. The "azulene effect"[39] and lifetime[5] studies on acyclic styrene triplets have indicated that the relaxed states prefer the twisted geometry. The relaxed energies we now report for acyclic styrene triplets (ca. 52 kcal/mol) are significantly lower than their planar triplet energies (ca. 60 kcal/mol). This reflects the fact that acyclic styrene triplets can fully twist. Our values for triplet lifetimes of styrene and β-methylstyrene are in excellent agreement with reported values measured by kinetic absorption spectroscopy.[27] The rotational barriers around carbon–carbon double bonds of ground-state acyclic styrenes have not been determined. The thermal transition state of S_0 as estimated using Benson's method[40] is nearly isoenergetic with the relaxed triplet state for acyclic styrenes. The differences between spectroscopic energies and relaxed energies are sensitive to constraints which affect the capability of the triplet to twist about the double bond. Inability to access the perpendicular conformation should decrease the energy difference. The relaxed energy of 1-phenylcyclophexene (56.4 ± 0.7 kcal/mol) is somewhat lower than its planar triplet energy (60.8 kcal/mol). As noted by Peters et al.,[32] 1-phenylcyclohexene triplet should be only partially twisted in its relaxed state as a result of the ring constraint. The capacity for the highly constrained triplets of 1-phenylcyclopentene, indene, and 1,2-dihydronaphthalene to relax should be negligible. No obvious energy differences between relaxed and planar states were found, consistent with that expectation.

Studies of sensitized photodimerization[41] have placed the rates of reaction of triplet state with the corresponding ground state in the order of indene (5×10^7 M^{-1} s^{-1}) > 1,2-dihydronaphthalene (4×10^6 M^{-1} s^{-1}) > 1,1-diphenylethylene (nonreactive). This is consistent with our relaxed triplet energies with the order of indene (65.3 kcal/mol) > 1,2-dihydronaphthalene (61.0 kcal/mol) > 1,1-diphenylethylene (52.1 kcal/mol), since the higher the relaxed energy the more powerful the driving force for the reaction. The observation is even more striking when other possible factors are considered. Both intermediate biradical stability and lack of steric hindrance at the reacting termini would suggest that 1,1-diphenylethylene would be the most, not the least, reactive.

From the structural point of view, the triplet of 2-phenylnorbornene is highly constrained and can hardly be twisted. However, we found the relaxed energy was 3.4 kcal/mol lower than the spectroscopic energy (53.8 vs. 57.2 kcal/mol). We think that some relaxation path other than twisting, such as pyramidalization, may cause the energy difference. Gorman[42] has found a similar result on norbornene, but his value placed the relaxed triplet energy more than 14 kcal/mol below its planar energy. As shown by Gorman,[42] his relaxed triplet energy is not relative to the relaxed ground state. The experiment involved measurement of energy transfer rates from norbornene to various arenes, and thus probably more closely represents the vertical energy gap between the relaxed norbornene triplet and the ground-state surface.

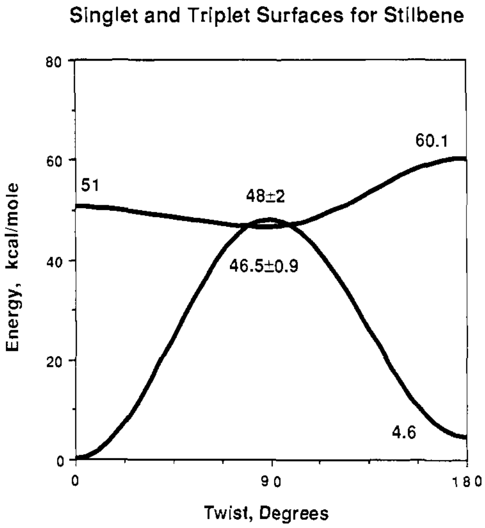

Figure 7. Sketch of S_0 and T_1 energies of stilbene as a function of twist angle; ground-state parameters from ref 43.

For lack of suitable sensitizer, our attempt to reexamine the relaxed energy of norbornene triplet by PAC did not succeed. However, the spectroscopic energy (72.3 kcal/mol) shows a substantial decrease compared to cyclohexene (80.5 kcal/mol) or even tetramethylethylene (75.8 kcal/mol). We note that 2-phenylnorbornene also has a somewhat low spectroscopic energy.

We note that the indene triplet (64.1 kcal/mol) is about 4 kcal/mol above the other styrenic triplets as measured spectroscopically and also that the relaxed energy (65.3 kcal/mol) is similar. As with diacetylstilbene, any undetected energy wastage would result in too low a triplet energy, so the anomalously high energy must be real. However, we have no explanation yet.

Stilbene Triplets. A recent triplet quenching experiment performed by Saltiel placed the relaxed energy of stilbene triplet at least 3 kcal/mol below the transition state for thermal cis–trans isomerization (48 ± 2 kcal/mol relative to trans).[43] With either benzophenone or biacetyl sensitization, we found the relaxed triplet energy of *trans*-stilbene is about 2.5 kcal/mol higher than the upper limit estimated by Saltiel (<44 kcal/mol). PAC study on *cis*-stilbene afforded the relaxed energy of 42.0 ± 1.5 kcal/mol relative to cis ground state, and 46.6 ± 1.5 kcal/mol relative to trans ground state after correction for 4.6 kcal/mol heat of ground-state cis–trans isomerization.[43] The total amount of energy absorbed at 350 nm which was released as heat was 98 ± 2% from *trans*-stilbene and 101 ± 2% from *cis*-stilbene, consistent with the values (96.5 and 102.3%, respectively) expected from the known[1] triplet decay fraction for stilbene and the enthalpy of ground-state isomerization.[43] The average of three values for the relaxed stilbene triplet energy is 46.5 ± 0.9 kcal/mol which is 1.5 kcal/mol lower than the thermal transition state. The upper limit estimated by Saltiel is substantially outside our error limits and the value may thus be rejected. Since the combined error for energy difference between relaxed triplet state and the thermal transition state, ±2.5 kcal/mol, is greater than the energy difference, the conclusion that S_0 and T_1 for stilbene must cross is unwarranted. Another photoacoustic determination of stilbene triplet energy[36] places trans at 44 ± 2 and cis at 44 ± 3 kcal/mol, the latter translating into 48.6 ± 3 kcal/mol vs. the trans ground state. The average of these two values is 46 ± 3 kcal/mol relative to trans. These results are therefore quite consistent with ours even though they were initially taken to corroborate the Saltiel estimate.

The result of 4,4′-diacetylstilbene suggests that the S_0 and T_1 curves are unlikely to cross in this case. Even though there is no

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Table IV. New Benson Group Equivalents[a]

group	ΔH_f (kcal/mol)	ref compd	ref
${}^{\bullet}C(C)(H)_2$	38.75	C_2H_5	47a,b
${}^{\bullet}C(C)_2(H)$	41.18	*i*-Pr, *s*-Bu	47b
${}^{\bullet}C(C)_3$	41.85	*t*-Bu	47a,c
${}^{\bullet}C(C_B)_2(H)$	24.98	Ph_2CH	49
${}^{\bullet}C(C_B)_2(C)$	26.86	Ph_2CCH_3	49
${}^{\bullet}C(C_B)(H)_2$	25.8	$PhCH_2$	47d
${}^{\bullet}C(C_B)(C)(H)$	27.7	$PhCHCH_3$	49

[a] Uncertainty ±1 kcal/mol.

Table V. Energies of 1,2-Biradicals

compound	*E*(biradical)[a] (kcal/mol)	*E*(triplet) (kcal/mol)
styrene	53.2	51.2
β-methylstyrene	53.5	53.2
1,1-diphenylethylene	51.35	52.1
1,1-diphenylbutene	50.92	51.3
1,1-diphenyl-2-methylpropene	51.6	49.7
trans-stilbene	48.9[b]	46.5
2,5-dimethyl-2,4-hexadiene	52.3	53.1

[a] The enthalpy difference between the 1,2-biradical and the ground state of olefin calculated by the Benson method using the group equivalents in Table IV. [b] The ground state was taken to have 7 kcal/mol additional resonance stabilization: Streitwieser, A., Jr. *Molecular Orbital Theory for Organic Chemists*; Wiley: New York, 1961; p 243.

measurement of the thermal activation energy for cis–trans isomerization, it seems unlikely to be higher than the 48 kcal/mol for stilbene. Accordingly, the measured triplet energy, ca. 49 kcal/mol, is higher than the expected thermal transition state.

Oxygen-perturbed absorption places the planar triplet energy of *trans*-stilbene at 51 kcal/mol. Our PAC values are somewhat (4.5 kcal/mol) below the planar energy. Therefore, the triplet potential energy surface is rather flat in the region between trans and the perpendicular geometry (Figure 7).

Diene Triplets. The relaxed triplet energy of 2,5-dimethyl-2,4-hexadiene (53.1 ± 1.9 kcal/mol) is significantly lower than the spectroscopic value (ca. 60 kcal/mol). We believe that this corresponds to twisted allylmethylene structure.[44] The "available" energy estimated by Gorman[38a] by triplet excitation transfer to anthracene was about 11 kcal/mol lower than ours. Since the lifetime of the diene triplet is so short (48.7 ± 3.1 ns), Gorman did not observe energy-transfer equilibration. That the "available energy" is so much lower than the true relaxed energy must be due to the extreme difference in relaxed geometries for T_1 and S_0 of 2,5-dimethyl-2,4-hexadiene. Caldwell noted a similar effect in excitation transfer from isoprene to the stilbenes.[45] The generalization of these observations is that energy transfer should be slower than predicted from the exothermicity when the donor must undergo a substantial change in geometry.

Another photoacoustic measurement performed by Goodman placed the relaxed energy at 45 kcal/mol,[36] which is still much lower than our value, even though the lifetime (49 ± 3 ns) is in agreement with ours. Since for another similar acyclic diene, piperylene, Goodman found a relaxed triplet energy of 53 kcal/mol,[36] we think the discrepancy probably arises from the lower precision of their experiment.

The 1,2-Biradical Model. Caldwell has proposed a "1,2-biradical" model structure for relaxed acyclic olefin triplets.[46] The implication of this formalism is that the thermodynamic and possibly the chemical kinetic properties of such triplets will be adequately represented by the consideration of the two ends separately. While the present results speak only to the thermodynamic aspect, they do provide substantial support for the model.

The model would require that the relaxed energies be satisfactorily reproduced by considering them as resulting from (e.g.) the dissociation of two hydrogens from the dihydro derivative, with no modification of the resultant hypothetical energy to take any possible interaction of the termini into consideration. Equivalently and just as conveniently, the Benson group additivity method of estimation could be used if group equivalents for appropriate radical models for the termini were available. The original Benson monograph[40] does, in fact, offer a number of such group equivalents. However, the most recent work[47] has called into question the values which depend on the halogenation techniques which undergirded much of the data for free radical thermochemistry available at that time. A recent frequently cited compilation[48] of bond dissociation energies and free radical thermochemistry also depends partly on halogenation data. We are convinced by the arguments adduced most recently[47] that the true values for free radical heats of formation, and thus also BDE's, are typically 3 kcal/mol or so higher than the widely promulgated earlier values. We have accordingly used only recent results[47a–c,49] which do not involve halogenation to generate the new values of group equivalents listed in Table IV.

Table V lists the (gas phase) heats of "isomerization", *E*(biradical), of the reactants to (twisted) triplet, as estimated by the Benson method but with the new values of free radical group equivalents, for comparison to the measured triplet energies. The comparison is spectacular. The average difference between the two is 1.2 kcal/mol, well, within the error limts of any of the values. No systematic difference is apparent. Tsang[47a] has already pointed out the *E*(biradical) for ethylene as 63.5 kcal/mol, about 1.5 kcal/mol below the thermal isomerization transition state; we note the best calculated values for the relaxed (perpendicular) ethylene triplet[50] are about 1 kcal/mol above the calculated singlet. To excellent precision, then, the 1,2-biradical model is clearly justified for both simple and conjugated alkenes.

While the question of whether the S_0 and T_1 surfaces of olefin triplets cross in general cannot be answered by the present observations, we note that the use of the 1,2-biradical model was reasonably successful early on[40] in predicting the activation energies of isomerization of a number of alkenes, i.e., in locating the perpendicular singlet on S_0. Since it also succeeds in predicting relaxed alkene triplet energies, it follows that there cannot be a gross difference between the S_0 perpendicular maximum and the T_1 perpendicular minimum in general. However, the new radical thermochemistry, plus the fact that neither conditions nor substrates of the thermal isomerizations and our photoacoustic measurements coincide, invites a fresh study of this point.

Other Intermediates. If olefin triplets are well described thermochemically as 1,2-biradicals, any triplet intermediate with canonical radical sites separated farther than vicinal should be even better so represented, and indeed has usually been considered in this way in organic mechanistic studies. A recent thermochemical study of 1,3-biradical formation[51] also shows a successful comparison with Benson estimates, and agreement is even better when those data are reanalyzed in light of the more recent free radical thermochemistry. Reestimation of the energy of the valerophenone-derived Norrish II 1,4-biradical shows an energy of 61.8 kcal/mol above valerophenone, compared to 65 ± 3 kcal/mol reported.[6] We are encouraged that most of all triplet-state photoreactions can in principle successfully be analyzed in this way and that wider use of such thermochemical analysis will lead to novel mechanistic insights. A study of the triplet state

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di-π-methane reaction in which both the present data and such insights become crucial will be reported separately.[52]

Summary

We have improved the technique of time-resolved photoacoustic calorimetry and have used it to determine the relaxed energies and lifetimes of a series of olefin triplets. Compounds with transient lifetimes as short as 20 ns can be resolved. The time-resolved photoacoustic calorimetry is a quick and reliable technique for determination of the relaxed transient energy. Results indicate that acyclic olefin triplets are well described by the "1,2-biradical" structure.

Acknowledgment. We thank Professor Kevin S. Peters for providing exemplary software, advice, and assistance at the outset of this work. This work was supported by the National Science Foundation (Grant CHE-8516534) and the Robert A. Welch Foundation. Kinetic absorption spectroscopy was performed at the Center for Fast Kinetic Research at The University of Texas at Austin, supported by NIH Grant RR-00886 from the Biotechnology Branch of the Division of Research Resources and by The University of Texas. We thank Dr. S. C. Gupta for the sample of 1,1-diphenyl-1-butene.

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Electron Affinities of Cyclic Unsaturated Dicarbonyls: Maleic Anhydrides, Maleimides, and Cyclopentenedione

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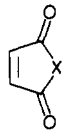
Abstract: The electron affinities of 20 cyclic diones, mostly substituted maleic and phthalic anhydrides and maleimides and phthalimides, were determined by measuring gas-phase electron-transfer equilibria involving these compounds and reference compounds whose electron affinities were determined previously. A pulsed high pressure mass spectrometer (PHPMS) was used. The substituent effects for the anhydrides are similar to those observed earlier for the benzo- and naphthoquinones but somewhat larger. Comparison with the reduction potentials in solution permits the evaluation of the solvation energies of the radical anions in dimethylformamide. Significant decreases of solvation exothermicity with increasing electron affinities of the precursor neutral compounds are observed.

It has been known for some time that the cyclic unsaturated dicarbonyl compounds of structures I and II can capture electrons and form stable radical anions.[1-4] In particular the maleic anhydride (I, X = O), phthalic anhydride (II, X = O), maleimide (I, X = NH) and phthalimide (II, X = NH) radical anions are known to form by one-electron reductions of the neutral parent compounds in solution.[1,2] Also in the gas phase, long-lived negative ions have been observed,[4] and some electron affinities have been determined. Compounds I and II resemble the benzo- and napthoquinones with regard to electron capture. Thus, they also act as similar electron acceptors in charge-transfer complexes and also, but to a much lesser extent, have biological significance as electron carriers.[5]



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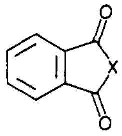

II

X = (O, NH, CH_2)

Recently, we reported the determination of a large number of electron affinities[6,7] which were obtained by measuring electron-transfer (et) equilibria, see reaction 1, in the gas phase with

$$A^- + B = A + B^- \quad (\mathrm{et}) \qquad (1)$$

$$e + B = B^- \quad (\mathrm{a}) \qquad (2)$$

$$\Delta G^\circ = -RT \ln K \qquad (3)$$

$$-\Delta H_a^\circ(\mathrm{B}) \approx \mathrm{EA(B)} \qquad (4)$$

a pulsed electron high pressure mass spectrometer (PHPMS).[8] The ΔG_1° and ΔH_1° values obtained by making measurements with a number of compounds can be combined into a scale of relative electron attachment free energies ΔG_a° and ΔH_a°, see eq 2. By calibrating the scale to the literature value for ΔG_a° and ΔH_a° of one compound (SO_2, primary standard), the rest of the absolute values are obtained.[6] In general, the structures and internal motions of B and B^- are very similar, which leads to very similar heat capacities $c_p(B)$ and $c_p(B^-)$. As a consequence, the electron affinity, which relates to electron attachment at 0 K, and the enthalpy change ΔH_a°, at 298 K, are numerically very similar such that EA ≈ $-\Delta H_a^\circ$ within 1-2 kcal/mol. Thus, not only ΔG_a° and ΔH_a° values are obtained but also fairly accurate EA. The ΔG_a° and the ΔH_a° are of interest in their own right, since in many actual experimental situations (thermal energies) it is these quantities and not the EA that are relevant.

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