and tungsten[29] are comparable to those for ruthenium[9] and osmium.

The explanation of the stability of the $Fe(CO)_4$ unit in the presence of CO and $Fe(CO)_5$ is based upon spin conservation rules. The $Fe(CO)_4$ complex has been characterized as possessing a ground-state triplet electronic configuration so that its reactions with either singlet CO or singlet parent to produce singlet $Fe(CO)_5$ or singlet $Fe_2(CO)_9$, respectively, are formally spin-forbidden.[8] The facile CO addition reactions for $Fe(CO)_2$ and $Fe(CO)_3$ are evidence to support the notion that all the mononuclear iron photofragments are ground-state triplets.[30] However, spin selection rules may also play a role in some polynuclear forming reactions of $Fe(CO)_3$.[25] The reaction of $Fe(CO)_3 + Fe(CO)_5$ to form the bridged form of $Fe_2(CO)_8$ is facile, suggesting that the ground state of this form of $Fe_2(CO)_8$ is a triplet.[25] Formation of the unbridged form of $Fe_2(CO)_8$ from these same reactants is currently under study.[25] Spin conservation rules suggest that the $Ru(CO)_3$ and $Ru(CO)_4$ fragments are likely to possess ground-state electronic singlet configurations on the basis of the magnitude of their reaction rate constants. A singlet ground-state configuration for $Ru(CO)_4$ has been predicted as lowest in energy based on Hartree–Fock–Slater molecular orbital calculations.[31] Low-spin configurations are most often observed for second- and third-row transition-metal complexes. For third-row transition elements, it has been noted that spin-selection rules can break down from effects such as large spin–orbit coupling.[32] Indeed, this trend is evident in the atomic electronic spectra of the transition elements.[33] For example, very few of the most intense spectral lines for first-row metals arise from spin-forbidden transitions, whereas for third-row elements, transitions that give intense spectral features do not show a significant bias toward following spin-selectron rules. The assumption that the $Os(CO)_3$ and $OsCO)_4$ species possess ground-state singlet electronic states cannot be concluded solely on the basis of evidence from rate constants. However, our observations are compatible with that assignment.

Conclusions

The transient infrared spectroscopy study of unsaturated osmium carbonyl complexes generated by 248-nm photolysis of $Os(CO)_5$ has shown that $Os(CO)_3$ and $Os(CO)_4$ species are the nascent photoproducts. With 248-nm irradiation, the predominant photoproduct of $M(CO)_5$ is $Fe(CO)_2$ for iron and $M(CO)_3$ for ruthenium and osmium. The average metal carbonyl bond dissociation energy for loss of three CO ligands is larger for ruthenium and osmium than for iron. Two dinuclear osmium carbonyl complexes, $Os_2(CO)_8$ and $Os_2(CO)_9$, are formed by reactions of the unsaturated photofragments with parent $Os(CO)_5$; $Os_2(CO)_8$ had not been reported previously. There is evidence for formation of trinuclear osmium clusters from reaction of $Os_2(CO)_8$ with $Os(CO)_5$. The tendency for cluster formation for osmium is reflected in the additional depletion of $Os(CO)_5$ between UV pulses that is several times the amount photolyzed. The bimolecular rate constants for reaction of $Os(CO)_3$ and $Os(CO)_4$ with CO are 7.6 ± 0.9 and $5.5 \pm 0.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, respectively. These are the same magnitude as those observed for the corresponding ruthenium complexes and 10^3 larger than that observed for the reaction of $Fe(CO)_4$ with CO. The rate constant for formation of $Os_2(CO)_8$ is $2.7 \pm 0.9 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} and is similar to that for $Fe_2(CO)_8$. All photofragments for the group 8 pentacarbonyls have very short gas phase lifetimes except for $Fe(CO)_4$. Slow reaction rates for $Fe(CO)_4$ are explained on the basis of spin selection rules. Ruthenium carbonyl photofragments are thought to have singlet electronic ground states. The behavior of $Os(CO)_x$ photofragments is consistent with spin conservation during reactions with CO or parent. However, due to enhanced spin–orbit coupling in heavy metals, spin states are expected to have significantly less effect on reaction rate for osmium species than for iron or even ruthenium. Thus it is premature to conclude that the ground states of $Os(CO)_x$ fragments *must* be singlets based on this kinetic evidence, though their behavior is compatible with this conclusion.

Acknowledgment. We are indebted to G.-Y. Kiel and Prof. J. Takats for providing the $Os(CO)_5$ for this study. We thank the National Science Foundation for support of this work under NSF Grant CHE 88-06020 and we acknowledge support of the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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Excited-State Calorimetry Studies of Triplet Benzophenone Using Time-Resolved Photothermal Beam Deflection Spectroscopy

P. E. Poston and J. M. Harris*

Contribution from the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112.
Received June 21, 1989

Abstract: Photothermal beam deflection spectroscopy is found to be a useful method for determining the kinetics and energetics of photochemical and photophysical processes. The accumulation of heat from the reaction and decay of excited states is observed with a step-response function on time scales from nanoseconds to milliseconds. Using this method, we study hydrogen abstraction from ethanol by triplet benzophenone and determine the rate constant of this reaction to be $1.43\ (\pm 0.08) \times 10^6$ M^{-1} s^{-1}. From the relative amplitudes of the photothermal transients, we derive the enthalpy of the photoproducts and estimate the C–H bond dissociation energy of benzhydrol and the O–H bond energy of the ketyl radical to be 87 (±2) and 95 (±2) kcal/mol, respectively. We also investigate the intensity dependence of heat released from triplet benzophenone to determine the influence of excited-state absorption on the calorimetric results. The data are fit to a four-level, excited-state absorption model, and the triplet excited-state absorption cross section of benzophenone at 322 nm is found to be $2.7\ (\pm 0.5) \times 10^{-17}$ cm^2.

Photothermal spectroscopy with pulsed-laser sources is developing into a powerful method for determining nonradiative, excited-state quantum yields and decay kinetics of molecules in solution. The measurement is a specific example of photocalorimetry where the heat given off by the decay of excited states and/or photoproducts is observed as an increase in the sample temperature. Early photocalorimetry experiments produced excited states with a continuous source and detected the temperature

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rise with a thermocouple or thermistor.[1-3] The first experiments to examine the time dependence of excited-state heat release utilized the photoacoustic effect, where the temperature rise from a flashlamp or modulated excitation source creates a time-dependent volume expansion in the sample, which was measured with millisecond time resolution using a microphone.[4,5] More recently, photoacoustic spectroscopy with pulsed lasers has been used to detect the heat generated by two-step excitation of photochemical intermediates,[6-9] where the excited-state kinetics were obtained from the signal amplitude dependence on a picosecond time delay between excitation pulses[6,7] or from its nonlinear dependence on excitation intensity.[8,9]

Photoacoustic spectroscopy with a pulsed laser and a high-band-width piezoelectric transducer[10] allows the time dependence of the heat release from excited states to be measured directly with submicrosecond time resolution.[11-16] This method has been used, for example, to observe the kinetics and energetics of photochemical reactions of benzophenone excited triplet states[11,12] and quenching of this excited state by iodide[13] and alkene triplet energy acceptors[12,14] and to determine energetics and yields in excited-state organometallic reactions.[15,16] While the nanosecond time resolution[17] of this method is very powerful, the instrument signature on the heat signal is not ideal for determining the excited-state kinetics of the sample. The first limitation is that the impulse response is an envelope of a nearly single frequency waveform dominated by the acoustic resonances of the cell and transducer. Extracting the excited-state kinetics requires that the signal be deconvoluted from the instrument response; the uncertainty of extracting more than two kinetic parameters can be large due to the single-frequency character of the signal, which can be described in large part by a single amplitude and phase. The second limitation of the instrument response relates to its lack of any low-frequency amplitude, which limits its sensitivity to the nonradiative decay of long-lived (>1 μs) excited states or photoproducts.[14]

The limitations of the photoacoustic measurement derive from the adiabatic conditions under which a pressure wave is generated.[10] The only heat that contributes to the photoacoustic response is that which is released on the time scale of sound propagation across the excitation zone in the sample. Given typical conditions for this experiment, where the laser beam spot size is 100 μm and the sound velocity in the sample is 10^3 m/s, the photoacoustic sensitivity is expected to fall off for heat produced on time scales greater than 100 ns. An alternative approach to measuring the time-dependent heat release is to detect the lowering of the solvent density with increasing temperature within the excitation zone. The solvent density is lower after the pressure wave leaves the excitation zone, and this higher temperature, lower density condition persists for a much longer time, governed by thermal conductivity from the heated region (typically ≥10 ms). While the rise time of this density change is limited by propagation of sound out of the excitation zone with similar response-time characteristics as the resulting photoacoustic wave,[17] the temperature and density changes in the excitation region are sensitive to the accumulation of heat released into the sample for times ranging over a much larger time window spanning 6 orders of magnitude, from nanoseconds to milliseconds.

The lower solvent density arising from the change in temperature creates a refractive index gradient in the sample, which can be detected by its effect on a probe laser beam which passes through the sample. If the beam centers of the excitation and probe lasers coincide, the refractive index gradient corresponds to a thermal lens in the sample,[18] which increases the rate at which the probe laser beam expands as it propagates beyond the sample. An early application of thermal lens spectroscopy to photocalorimetry was the absolute determination of luminescence quantum yields of fluorescent dye molecules.[19] More recently, the thermal lens method has been used to observe the formation and decay of singlet oxygen[20-23] and to measure excited triplet state lifetimes in solutions of phthalazine[24] and benzophenone.[25]

In this work, we utilize a related photocalorimetry method, photothermal beam deflection spectroscopy,[26-28] to study the energetics of the reaction of the excited triplet state of benzophenone with ethanol. Photothermal beam deflection senses the temperature-dependent, refractive index gradient at the edge of the excitation region and produces a change in the propagation direction of a probe laser beam. The beam deflection method has temporal response characteristics similar to thermal lens spectroscopy since the heat is detected under isobaric conditions. While the sensitivities of these two techniques are comparable, a particular advantage of the beam deflection method is that it is much less dependent on the excitation laser producing a Gaussian spatial intensity profile, which makes it well suited for excitation with pulsed lasers having higher order transverse mode characteristics, such as nitrogen, Nd:YAG, and pulsed dye lasers.

Using photothermal beam deflection spectroscopy, we determine the rate constant for hydrogen abstraction from ethanol by triplet benzophenone, and from the preexponential factors, which describe the photothermal transients, we derive the enthalpy of the photoproducts. We also investigate the intensity dependence of heat released from triplet benzophenone and show how excited-state absorption influences the calorimetric results. The dependence of the observed heat on excitation intensity is fit to a simple four-level model, which allows the excited-state absorption cross section at the laser wavelength to be determined.

Theory

Kinetics of the Heat Produced by Triplet Benzophenone. The heat released from photoexcited benzophenone is found to depend nonlinearly on excitation intensity. This phenomenon can be attributed to optical absorption by the excited triplet state of the molecule, the absorption cross section of which is determined by measuring the ratio of the heat released quickly to that released slowly, versus laser intensity. The fast component is defined as

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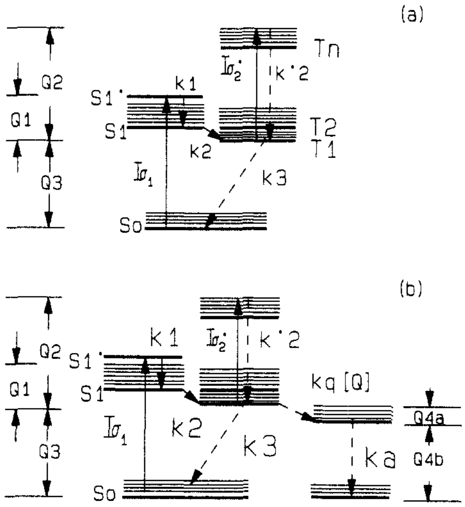

Figure 1. (a) Four-level model of the excited-state manifold of benzophenone. Laser excitation at a rate $I\sigma_1$ is followed by the release of heat, Q_1, from rapid internal conversion, k_1, and intersystem crossing, k_2, to the triplet manifold. During the laser pulse, the lowest triplet state also can be pumped at a rate $I\sigma_2$ to an upper triplet level, T_n. T_n decays with a rate, k_2', to T_1 releasing heat, Q_2. This is followed by relaxation of triplet to ground state at a rate k_3 and the release of heat, Q_3. (b) Four-level model of benzophenone combined with quenching to a photoproduct. Quenching occurs at a rate $k_q[Q]$, releasing heat, Q_{4a}, and producing photoproducts. These intermediates can further decay or react at a rate k_4, releasing heat, Q_{4b}.

heat released on a time scale short compared to the development of a density gradient in the probe beam region ($t < 100$ ns). The fast heat derives from the initial relaxation to the lowest vibrational level of the excited singlet state, from the vibrational relaxation, which follows intersystem crossing, and from further excitation of the triplet state population; all of these processes produce heat on a time scale limited by the laser pulse duration. The slow heat component, in turn, is generated by the relaxation of the lowest lying triplet state upon its return to the ground state.

To relate the calorimetric data to the molecular photophysics, we begin with an energy level diagram for benzophenone, as shown in Figure 1a. The spectroscopy and photophysics of this molecule are well established, having been investigated by polarized absorption spectroscopy, flash photolysis, and picosecond spectroscopy.[29-34] Upon excitation to either the $^1(n,\pi^*)$ or S_1 state, or to the $1(\pi,\pi^*)$ or S_1' state, intersystem crossing to the triplet manifold occurs with unity quantum yield over 5–15 ps, depending on the solvent and excitation wavelength employed.[30,32,34] Internal conversion and vibrational relaxation to the lowest lying, $^3(n,\pi^*)$, or T_1 triplet state[33] occurs within 20–50 ps, which includes any reorientational relaxation of the solvent around the excited solute.[34] The results of these investigations allow us to model, on a nanosecond time scale, the nonradiative relaxation of excited benzophenone using a four-level kinetic model,[35] as shown in Figure 1a. This model also accounts for subsequent absorption by T_1[36,37] during the laser pulse, to an upper excited triplet state, T_n.

Several approximations appropriate for benzophenone photophysics simplify the excited-state kinetics. The decay of the triplet state population is much slower than the rates of internal conversion and intersystem crossing, $k_3 \ll k_1,k_2$, and these rates are also faster than the excitation rate, $I\sigma_1 \ll k_1,k_2$. Similarly, stimulated emission from S_1' can be neglected since $k_1 \gg I\sigma_1$. Finally, the lifetime of the upper excited triplet state population is much smaller than the laser pulse duration, $1/k'_2 \ll t_0$, so that a steady-state approximation can be used for T_1 and T_n during the laser pulse. These assumptions result in the following expressions for the normalized-state populations arising from excitation with constant intensity, I, in quanta cm^{-2} s^{-1}, over the laser pulse duration, $t_0 \ll 1/k_3$:

$$S_0(t) = \exp(-I\sigma_1 t) \tag{1a}$$

$$S_1(t) = (I\sigma_1/k_2)[\exp(-I\sigma_1 t) - \exp(-k_2 t)] \tag{1b}$$

$$T_1(t \le t_0) = [k'_2/(k'_2 + I\sigma_2')][1 - \exp(-I\sigma_1 t)] \tag{1c}$$

$$T_n(t \le t_0) = [I\sigma_2'/(k'_2 + I\sigma_2')][1 - \exp(-I\sigma_1 t)] \tag{1d}$$

The heat produced by each of these states, as identified on Figure 1a, is determined by integrating the formation and decay of the state populations, each weighted by the energy released from the decay

$$Q_1(t > t_0) = (h\nu - E_{T_1})[1 - \exp(-I\sigma_1 t_0)] \tag{2}$$

$$Q_2(t > t_0) = [h\nu I\sigma_2'/(1 + I\sigma_2'/k_2')]\{t_0 - [1 - \exp(-I\sigma_1 t_0)]/I\sigma_1\} \tag{3}$$

$$Q_3(t > t_0) = E_{T_1}[1 - \exp(-I\sigma_1 t_0)][1 - \exp(-k_3 t)] \tag{4}$$

where E_{T_1} is the triplet energy of benzophenone, σ_1 is the absorption cross section of the singlet state, σ_2' is the triplet absorption cross section, Q_1 is the heat released from internal conversion and intersystem crossing, Q_2 is the heat released by the excited triplet state, and Q_3 is the heat released from the lowest triplet state. The fast heat terms, represented by Q_1 and Q_2 in eq 2 and 3, produce heat only during the laser pulse. These were determined by integrating the decay of S_1' and T_n from $t = 0$ to t_0, assuming a constant laser intensity over the pulse duration. The slow heat released, Q_3, was determined by integrating the decay of the lowest triplet state population and by assuming that the heat released from this state during the laser pulse is negligible, since $t_0 \ll 1/k_3$. The quantum yield for nonradiative decay of the benzophenone triplet state is assumed to be unity, since the yield of phosphorescence is quite small, having been found to be ≤2% in carbon tetrachloride solution at room temperature.[38]

The ratio of fast heat to the total slow heat released from benzophenone, $Q_f/Q_s = (Q_1 + Q_2)/Q_3(t=\infty)$, can be measured as a function of laser intensity and used to determine the influence of triplet state absorption on the release of heat from this molecule. Taking the ratio of the sum of eq 2 and 3 to eq 4 results in the following expression, which is accurate to second order:

$$Q_f/Q_s = \frac{(h\nu - E_{T_1})}{E_{T_1}} + \frac{h\nu I\sigma_2' t_0 k_2'}{2E_{T_1}(k_2' + I\sigma_2')(1 - I\sigma_1 t_0/2)} \tag{5}$$

This approach is similar to a recently published photocalorimetry method[39] for determining excited-state absorption in solid-state materials, except that the slow heat signal in this case, arising from a common decay path, provides an internal standard, which can be used to ratio out fluctuations in photothermal response.

Enthalpy and Kinetics of Photoproduct Formation. The energetics of heat production by excited benzophenone in the presence of a triplet state quencher is outlined in Figure 1b. Adding triplet state quenching to the photophysics requires that the quantum yield for the triplet state decay be incorporated in the Q_3 term and that two additional sources of heat, Q_{4a} and Q_{4b}, from the formation and decay of the photoproduct, be included in the calorimetric model. Equations 2 and 3 describing the fast heat derived from intersystem crossing and triplet state absorption

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remain unchanged. The equations for the time evolution of heat into Q_3, Q_{4a}, and Q_{4b}, for $t \geq t_o$, are

$$Q_3 = Q_3(\infty)[1 - \exp(-k_d t)] \quad (6)$$

$$Q_{4a} = Q_{4a}(\infty)[1 - \exp(-k_d t)] \quad (7)$$

$$Q_{4b} = Q_{4b}(\infty)\{1 + [k_a/(k_d - k_a)] \exp(-k_d t) - [k_d/(k_d - k_a)] \exp(-k_a t)\} \quad (8)$$

where the decay rate of the benzophenone triplet state is $k_d = (k_3 + k_q[\mathrm{Q}])$, where [Q] is the quencher concentration, k_q is the second-order rate constant for quenching, and k_a is the rate constant for the decay of the acceptor species. If this species is not stable, then its decay rate is finite, and the population of intermediates vary as the convolution of formation and decay processes. The accumulated heat, Q_{4b}, is equal to the acceptor energy times the integrated rate of this decay[40] as shown in eq 8. The final, accumulated heat magnitudes observed at $t = \infty$ from each of the heat producing processes are

$$Q_3(\infty) = E_{\mathrm{T}_1}[1 - \exp(-I\sigma_1 t_o)]/(1 + k_q[\mathrm{Q}]/k_3) \quad (9)$$

$$Q_{4a}(\infty) = (E_{\mathrm{T}_1} - E_a)[1 - \exp(-I\sigma_1 t_o)]k_q[\mathrm{Q}]/(k_3 + k_q[\mathrm{Q}]) \quad (10)$$

$$Q_{4b}(\infty) = E_a[1 - \exp(-I\sigma_1 t_o)]k_q[\mathrm{Q}]/(k_3 + k_q[\mathrm{Q}]) \quad (11)$$

The initial triplet population at the end of the laser pulse from eq 1c is $\mathrm{T}_1(t{=}t_o) = [1 - \exp(-I\sigma_1 t_o)]$. Under the experimental conditions, the conversion to population T_1 is essentially complete, and the exponential terms, $[1 - \exp(-I\sigma_1 t_o)]$, are approximately equal to 1.

Photothermal Beam Deflection Response. In order to determine the temperature distribution in the solvent, the above equations for the time-dependent deposition of heat by each donor excited state must be multiplied by the spatial distribution of excited states, which is assumed to be nearly Gaussian in the region of the sample that is interrogated by the probe laser

$$N_d(r') = (2\alpha_d E_o/\pi\omega_o^2 h\nu) \exp(-2r'^2/\omega_o^2) \quad (12)$$

where α_d is the sample absorptivity at the excitation laser wavelength, E_o is the laser pulse energy, ω_o is the beam spot size, and $h\nu$ is the photon energy. The time-dependent temperature distribution in the solvent resulting from the heat deposition is the integral over time and space of the product of excited-state density and the rate of heat deposition convoluted with the heat transport out of the excitation region[41,42]

$$\mathrm{T}(r,t) = \int_0^t \int_0^\infty 2\pi r' \sum (\mathrm{d}Q_i/\mathrm{d}t')\, G(r',r,t-t')\, N_d(r',t')\, \mathrm{d}r'\, \mathrm{d}t' \quad (13)$$

where Q_i are the heat terms Q_1 through Q_{4b}, $G(r',r,t-t')$ is the Green's function for thermal diffusion in a cylindrical coordinate system, ρ is the solvent density, C_p is the heat capacity of the solvent at constant pressure, and D is the thermal diffusion constant of the solvent. Under the conditions where the time evolution of Q_i occurs on a much faster time scale than the time constant for heat transport out of the excitation beam, the convolution integral is simplified, and the temperature distribution is given by:

$$\mathrm{T}(r,t) = 2E_o\alpha_d/[\pi\rho C_p h\nu(8Dt + \omega_o^2)] \exp[-2r^2/(8Dt + \omega_o^2)]\sum Q_i \quad (14)$$

A probe laser beam propagating through the heated sample in the z direction, parallel with the excitation beam, will experience a deflection of its propagation direction in the x direction by an angle, $\phi(x,t)$, which depends on the offset, x, between the probe beam center and the origin or excitation beam center[28]

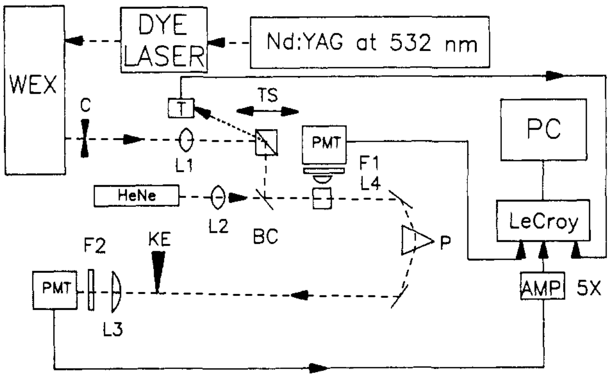

Figure 2. Photothermal beam deflection experiment. WEX is the "wavelength extender" or second harmonic generator, L1–L4 are lenses, F1 and F2 are filters, T is a trigger photodiode, TS is a translation stage, BC is a beam combiner, P is a prism, PMT's are photomultiplier tubes, and KE is a knife edge.

$$\phi(x,t) = -[8\alpha E_o x b(\partial n/\partial T)/\rho C_p \pi n h\nu(8Dt + \omega_o^2)^2] \exp[-2x^2/(8Dt + \omega_o^2)] \times \{A_\infty + A_d \exp(-k_d t) + A_a \exp(-k_a t)\} \quad (15)$$

where b is the path length through the sample and $\partial n/\partial T$ is the change in the solvent refractive index with temperature and where the final signal amplitude is $A_\infty = [Q_1 + Q_2 + Q_3(\infty) + Q_{4a}(\infty) + Q_{4b}(\infty)]$, the amplitude associated with the donor decay rate constant is $A_d = [Q_{4b}(\infty)k_a/(k_d - k_a) - Q_{4a}(\infty) - Q_3(\infty)]$, and the amplitude associated with the acceptor decay is $A_a = [-Q_{4b}(\infty)k_d/(k_d - k_a)]$.

Experimental Section

The experimental configuration used is shown in Figure 2. A QuantaRay Model DCR-2A Nd:YAG laser with a filled-in beam was frequency doubled to 532 nm and used to side-pump a QuantaRay Model PDL-2 dye laser. The laser dye used was DCM, and the laser was tuned to an output of 644 nm. The dye laser output was, in turn, frequency-doubled in angle-tuned KDP to an output of 322 nm, corresponding to the lowest energy n-π* transition in benzophenone. The 20-Hz laser pulse train was reduced by a Uniblitz chopper to 1.25 Hz, and directed onto a UV turning prism mounted on a precision translation stage. Lateral motion of the translation stage had the effect of changing the pump–probe separation. Adjustment of the translation stage allowed the deflection signal to be optimized and provided a precise measurement of the excitation beam spot size from the positions of maximum signal,[43] corresponding to $x = \pm\omega_o/2$.[44] The excitation beam profile, determined by scanning the excitation beam across the probe beam and measuring the probe beam deflection, was found to be distorted from a Gaussian near its center but was smooth and near-Gaussian on one side, which was chosen for beam deflection studies. The pump beam was combined with a HeNe probe beam, horizontally polarized to reduce reflective losses, and directed onto the sample. The pump and probe beams were made parallel and in the same plane by initial collinear alignment using pinholes. The laser beams were then passed through a prism to disperse the pump and probe wavelengths. The probe beam was half-blocked by a knife edge before being focused onto a red-sensitive Hammamatsu Model R929 photomultiplier tube (PMT). The base of the PMT was wired for a nanosecond rise-time response.[45] A similarly wired PMT was also positioned next to the sample to collect phosphorescence at 430 nm using a 25-mm-diameter band-pass filter from Ditrich (fwhm 10 nm).

Photothermal and phosphorescence signals were taken simultaneously by a LeCroy Model 9400 digitizing oscilloscope. A total of 200 signal transients was acquired and averaged from the phosphorescence and photothermal channels. All signals were passes through Belden 9222 triaxial cable with one end of the exterior sheath floating relative to ground, in order to reduce the Q-switch radio frequency noise. The

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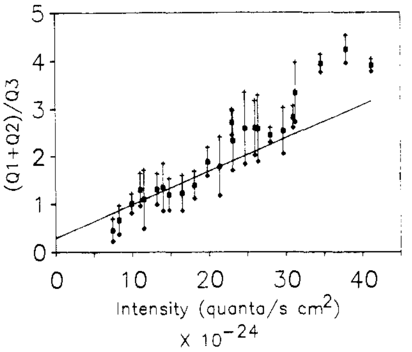

Figure 3. Intensity dependence of the ratio of fast to slow heat released from benzophenone and the least-squares fit of the first 10 points to eq 17.

photothermal signal was passed through a bucking circuit to reduce the offset, and the offset signal was amplified by a gain of 5. The scope was triggered using a reflection from the turning prism on the translation stage directed to a photodiode. Data were transferred from the scope to an IBM PC-XT computer through a National GPIB board using routines written in C. The photothermal transients were fit to the following response by nonlinear least squares using a Marquardt algorithm[46] written in FORTRAN:

$$Y(t) = A_1 - A_2 \exp(-t/\tau_1) - A_3 \exp(-t/\tau_2) \qquad (16)$$

For the excited triplet state studies, the pump laser pulse energies were varied from 250 μJ to 1.25 mJ. The probe beam spot size was 60 μm, and two pump beam spot sizes were used, 425 and 165 μm; for these two conditions, the offsets between the pump and probe beams were $x = 212$ and 132 μm, respectively. The pump laser pulse duration was measured by scattering light into a fast PMT, and a value of 4 ns was obtained. The benzophenone samples were 1.4×10^{-4} M in carbon tetrachloride and exhibited a decadic absorbance at the laser wavelength of approximately 1.4×10^{-2} cm^{-1}. Sample solutions were held in a 4-cm-path-length cell equipped with a side arm to allow degassing by freeze-pump-thawing. The sample absorbance was kept low so that there would be no depth dependence of the kinetic equations (eq 1a-d) and so that self-quenching of the benzophenone triplet states, observed at higher concentrations, would be avoided. Quencher concentrations in solution ranged from 0 to 60 mM. Baker grade benzophenone was used without purification. The concentration of benzophenone was kept constant so that any quenching impurities in the sample would not vary. USI Chemical Co. 200 proof ethanol was also used without further purification.

Three replicate samples were prepared and studied for each data point reported. In the quenching work, the first millisecond of data was digitized to cover the time region in which thermal diffusion was not apparent in the signal, only the deposition of heat. Each sample was subjected to four freeze-pump-thaw cycles, pumped to a base pressure of approximately 40 μTorr. Nonlinear and linear least-squares fits of the signal amplitudes to theory were weighted inversely by the variance of the observed results.[46] The uncertainty of the parameters reported are 95% confidence limits.

Results and Discussion

Excited-State Absorption by Triplet Benzophenone. The influence of excited triplet state absorption on the heat produced by photoexcited benzophenone can be seen in the ratio of the fast to slow heat, Q_f/Q_s, as a function of excitation laser intensity, plotted in Figure 3. As a check on the consistency of the measurements, two independent data sets are plotted together in Figure 3, representing results gathered using two different excitation spot sizes, 425 and 165 μm; the observed intensity-dependent behaviors of the two data sets are indistinguishable. The increase in the fast-heat amplitude with increasing laser intensity, relative to the amplitude from the slow triplet state decay, is suggestive of a higher order excitation process. The 10, lowest intensity data points were fit to eq 5 by nonlinear least squares. The positive deviation of the Q_f/Q_s ratio from a nearly linear response at the higher intensities has no physical meaning within the triplet state absorption model, as discussed below. The two unknown parameters in eq 5 determined from the best fit, the triplet absorption cross section at 322 nm, and the decay rate of the upper triplet state were found to be $\sigma_2 = 2.7\ (\pm 0.5) \times 10^{-17}$ cm^2 and $k_2' \geq 10^{12}$, respectively. The observed triplet cross section compared favorably with the triplet absorption cross section, which can be inferred from published results.[36,37] A strong, transient absorption band at 325 nm is shown in Figure 1 of ref 36 and Figure 2 of ref 37. Assuming that the benzophenone molecules were completely photolyzed in these studies, the measured absorptivity would correspond to a triplet absorption cross section in the range of $2-3 \times 10^{-17}$ cm^2, which agrees with the results of the present work.

The decay rate of the upper triplet state is a lower bound since the weighted residuals were insensitive to larger values of this parameter. The lifetime of the upper excited triplet states of benzophenone has recently been estimated from the photobleaching yield in benzene to be between 1 and 10 ps,[47] in agreement with the present results. Given the triplet absorption cross section and excited-state decay rate, a saturation intensity can be calculated by applying steady-state conditions to the excited-state populations. Under these conditions, the saturation intensity for the triplet state excitation is $I_{sat} = k_2'/\sigma_2'$, which for the above results is $I_{sat} \geq 4 \times 10^{28}$ protons s^{-1} cm^{-2}, a value much higher than the laser intensities employed. The insensitivity of the fit to k_2' is consistent with the essentially linear dependence on laser intensity, which can be seen by determining the ratio of Q_f/Q_s to only first order in laser intensity

$$Q_f/Q_s = [(h\nu - E_{T_1}) + h\nu I \sigma_2' t_0]/E_{T_1} \qquad (17)$$

where no dependence on k_2' is observed. Such a large value for the decay of the upper excited triplet would make the yield of fluorescence extremely small, lending support to a model where only nonradiative decay of the upper triplet is considered.

This four-level model for excited-state absorption and decay also predicts that, in the limit of zero laser intensity, the ratio, Q_f/Q_s, converges on $Q_1/Q_3 = (h\nu - E_{T_1})/E_{T_1}$, as seen in both eq 5 and 17. This limit has a physical meaning since the heat from the triplet state absorption is from a second-order (sequential two-photon) excitation process while the production of excited singlet states from the ground-state population is linear with photon flux. The data in Figure 3 are observed to converge on this limit at low laser intensities. The weighted least-squares fit of the first 10 data points to eq 17 results in an intercept of 0.29 ± 0.04. At the 322-nm excitation wavelength, the theoretical value for Q_1/Q_3 is 0.295 for benzophenone, which is within the uncertainty of the observed intercept.

The positive deviation from a linear response at high intensities is not consistent with the proposed four-level model. If saturation of the triplet state absorption were taking place, the ratio of fast to slow heats would be expected to fall below a linear response and level out at higher intensities. The observed behavior at higher excitation intensities is probably due to the onset of a second excited-state absorption process, most likely in the excited singlet state manifold. The scatter in the results at the highest intensities and a lack of information about the high-energy spectroscopy of benzophenone preclude a definitive assignment. The success of the four-level model at lower intensities, however, makes it possible to use it as a basis for measuring the energetics of triplet state photochemical reactions, even in the presence of triplet state absorption contributing to the fast-heat amplitude. This concept is applied to the determination of the enthalpy and kinetics of benzophenone photoreduction by hydrogen abstraction from ethanol, as discussed in the next section.

Energetics of Hydrogen Abstraction by Triplet Benzophenone. Hydrogen abstraction, from a variety of substrates, including aromatic, saturated, and unsaturated hydrocarbons and alcohols, by triplet benzophenone has been studied extensively.[48-54] The

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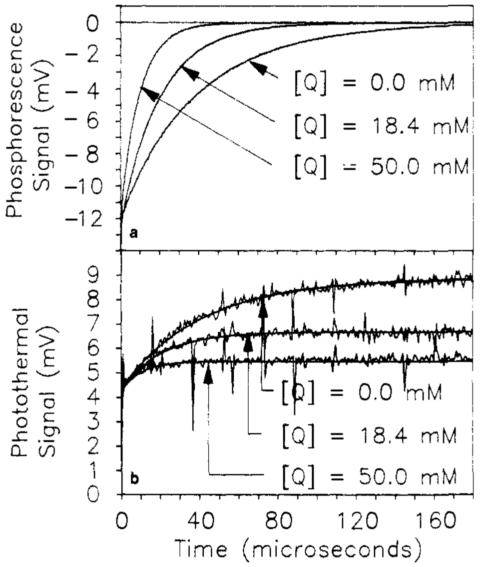

Figure 4. Representative phosphorescence (a) and photothermal (b) transient signals from the decay of benzophenone excited states. The smooth curve through the photothermal data is the best fit to eq 16 where $A_3 = 0$. Decreasing lifetime of benzophenone triplet state with increasing ethanol concentration is observed in both the photothermal and phosphorescence data.

photoreduction of benzophenone in ethanol has been investigated by flash photolysis, providing evidence for the following reaction scheme:[51-52]

$$^1(C_6H_5)_2CO \xrightarrow{h\nu} {}^1(C_6H_5)_2CO^* \tag{18}$$

$$^1(C_6H_5)_2CO^* \rightarrow {}^3(C_6H_5)_2CO^* \tag{19}$$

$$^3(C_6H_5)_2CO^* + CH_3CH_2OH \rightarrow (C_6H_5)_2\dot{C}OH + CH_3\dot{C}HOH \tag{20}$$

$$CH_3\dot{C}HOH + CH_3\dot{C}HOH \rightarrow CH_3CHO + CH_3CH_2OH \tag{21}$$

$$(C_6H_5)_2\dot{C}OH + (C_6H_5)_2\dot{C}OH \rightarrow \text{benzpinacol, isobenzpinacol} \tag{22}$$

Following intersystem crossing, triplet benzophenone is reduced in hydrogen-donating solvents to produce the ketyl and ethoxy radicals. On a longer time scale, these intermediates decay along paths dominated by homomolecular reactions, where ethoxy radicals undergo disproportionation and ketyl radicals couple to form benzpinacol and isobenzpinacol products.[52,54,55]

Having monitored the formation and decay of benzophenone triplet states using photothermal beam deflection, the method is now used to determine the rate constant and energetics of hydrogen abstraction by this species from ethanol in carbon tetrachloride. Representative photothermal beam deflection transients are plotted in Figure 4a, along with the nonlinear least-squares fits to eq 16. There is only one exponential present in the data since the decay of the radical photoproducts is on a much longer time scale than that of the measurement ($k_a \gg 1$ ms). A negligible change in the temperature distribution around the probe beam over this time scale is indicated by the flat plateau in the signal response; the step response of the photothermal beam deflection method makes the further exothermic or endothermic decay of photoproducts, on time scales as long as milliseconds, easily detected as a deviation from this flat signal plateau.

Table I. Benzophenone Triplet Lifetimes versus Ethanol Concentration Photothermal and Phosphorescence Results[a]

	photothermal		phosphorescence	
[Q], mM	τ, μs	s, μs	τ, *ms*	s, μs
0.0	41.5	0.3	40.0	0.8
8.55	29.6	2.0	25.9	1.1
18.4	19.8	0.4	19.2	0.6
28.7	14.0	0.2	13.7	0.6
38.6	12.7	0.4	12.5	0.1
50.0	9.5	0.4	9.6	0.1

[a] Each lifetime and standard deviation determined from the average of three determinations.

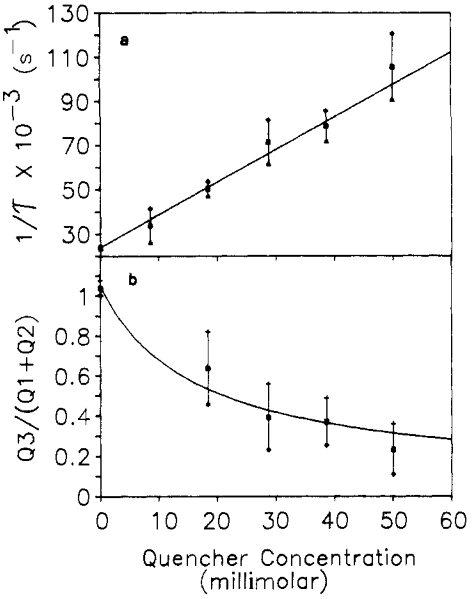

Figure 5. (a) Stern-Volmer plot of the rate of heat accumulation from the decay of benzophenone triplet states versus ethanol concentration. (b) Preexponentials as a function of quencher concentration. The weighted least-squares fit to eq 23 is also plotted.

The decay of benzophenone phosphorescence is also measured, as shown in Figure 4b, in order to check the photothermal results. The benzophenone triplet lifetimes determined by both methods are summarized in Table I. The phosphorescence and photothermal lifetimes are found to agree within the uncertainty of the two measurements, which are of the same order of magnitude. A Stern-Volmer plot of the triplet decay rate, measured by the photothermal method, versus ethanol concentration is shown in Figure 5a to be linear, with a rate constant for triplet state quenching determined by a weighted least-squares fit to be $k_q = 1.43\ (\pm 0.08) \times 10^6\ M^{-1}\ s^{-1}$. This result indicates that quenching of benzophenone triplet state by ethanol is about 1000 times slower than diffusion controlled. The measured rate constant is similar in magnitude to the value, $7 \times 10^5\ M^{-1}\ s^{-1}$, which can be estimated[56] from the lifetime of benzophenone triplet state in pure ethanol.[51b] Some disagreement between these results is expected since the diffusion-controlled collision frequency does not scale linearly with concentration to the limit of neat quencher.[57]

The preexponential values determined from the photothermal transients, as a function of quencher concentration, can be used to estimate the enthalpy of the radical photoproducts. Since the hydrogen abstraction reaction takes place on a time scale much slower than the laser pulse duration, the fast-heat signal is not sensitive to quencher concentration and provides an internal standard for the measurement. Since the decay of the radical products is slow on the time scale of the 1-ms observation, k_a is taken as zero, and the amplitude associated with the slow-heat release from eq 15 simplifies to $A_d = [-Q_{4a}(\infty) - Q_3(\infty)]$. Sub-

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stituting the expressions for these amplitudes from eq 9 and 10 and using the assumptions of eq 17 to describe the fast heat, the ratio of slow to fast heat amplitude is predicted to vary with quencher concentration according to the following expression:

$$Q_s/Q_f = \frac{E_{T_1}k_3 + (E_{T_1} - E_a)k_q[\mathrm{Q}]}{[(h\nu - E_{T_1}) + h\nu I\sigma_2{}'t_o](k_3 + k_q[\mathrm{Q}])} \qquad (23)$$

When the excitation photon and triplet state energies are known and the values for k_3 and k_q obtained independently from the Stern–Volmer plot above are used, the enthalpy of the radical photoproducts, $E_a = \Delta H$, can be determined from Q_s/Q_f versus ethanol concentration, plotted in Figure 5b along with the best fit of the data to eq 23.

The enthalpy of the ethoxy and ketyl radical photoproducts relative to ethanol and ground state of benzophenone, thus determined, is $\Delta H = 63.7$ (±2) kcal/mol. Using this value, the C–H bond dissociation energy of ethanol,[58] and the triplet energy of benzophenone from its phosphorescence spectrum, one can estimate the O–H bond energy of the ketyl radical relative to the benzophenone triplet state. This bond energy is useful in predicting the reactivity of the triplet benzophenone toward hydrogen abstraction:[49]

$$(C_6H_5)_2\dot{C}OH + CH_3\dot{C}HOH \rightarrow$$
$$(C_6H_5)_2C{=}O + CH_3CH_2OH \qquad \Delta H = -64\ \mathrm{kcal/mol} \quad (24)$$

$$CH_3CH_2OH \rightarrow CH_3\dot{C}HOH + \dot{H} \qquad \Delta H = +90\ \mathrm{kcal/mol} \quad (25)$$

$$(C_6H_5)_2C{=}O \rightarrow (C_6H_5)_2\dot{C}\text{–}\dot{O} \qquad \Delta H = +69\ \mathrm{kcal/mol} \quad (26)$$

$$(C_6H_5)_2\dot{C}OH \rightarrow (C_6H_5)_2\dot{C}\text{–}\dot{O} + \dot{H} \qquad \Delta H = +95\ \mathrm{kcal/mol} \quad (27)$$

The resulting O–H dissociation energy, thus determined, is 95 (±2) kcal/mol, which is smaller than the value of 104 (±3) kcal/mol estimated by Walling and Gibian.[49] This previous estimate was based on a thermochemical cycle requiring knowledge of the C–H bond dissociation energy of benzhydrol, which was predicted[49] to lie between the C–H bond energies of triphenylmethane (ca. 75 kcal/mol) and toluene (77–85 kcal/mol). Our result for the O–H bond energy of ketyl radical, above, would require the C–H bond dissociation energy of the alcohol to be 87 (±2) kcal/mol, which is at the high-energy end of the predicted range.

Rothberg et al.[11] carried out a similar study of the energetics of hydrogen abstraction by triplet benzophenone from aniline using photoacoustic spectroscopy. Their calorimetric results for this reaction were consistent with a benzhydrol C–H bond dissociation energy of 78 kcal/mol, the best estimate of Walling and Gibian. This result was based on measurements made at a single, high concentration of aniline (0.3 M) in air-saturated ethanol,[11] which would not reveal any side reaction that might compete for the decay of the excited-state population, such as quenching by oxygen[59] in the air-saturated solvent. Finite yield from this or other processes could lower the measured product energy compared to free radicals, which would, in turn, lower the estimated benzhydrol bond dissociation energy. Further investigation of these energetics is warranted. A particularly interesting experiment would be to measure the energetics of hydrogen abstraction by triplet benzophenone from benzhydrol.[60] Since the products of this reaction are two ketyl radicals, one could use the measured enthalpy of the reaction together with the heats of formation of the benzhydrol and benzophenone to determine both the O–H bond dissociation energy of the ketyl radical and the C–H bond dissociation energy of benzhydrol independently, from the same data. Studies along these lines are in progress in our lab.

Summary. We have shown that photothermal beam deflection spectroscopy is a useful method for determining the kinetics and energetics of photochemical and photophysical processes. The accumulation of heat from the reaction and decay of excited states can be observed with a step-response function on time scales from nanoseconds to milliseconds. Using this method, we investigate the intensity dependence of heat released from triplet benzophenone, using the slow decay of the triplet population as an internal standard. The dependence of the observed heat on excitation intensity is fit to a simple four-level model, which allows the excited-state absorption cross section at the laser wavelength to be determined. We also use this method to estimate the rate constant for hydrogen abstraction from ethanol by triplet benzophenone. The preexponential factors are determined from the photothermal transients using the fast-heat amplitude from vibrational relaxation, intersystem crossing, and triplet state absorption as an internal standard. From these preexponential factors, we derive the enthalpy of the photoproducts and estimate C–H and O–H bond dissociation energies of benzhydrol and the ketyl radical product, respectively.

Acknowledgment. We thank Dr. Xiao Rong Zhu for discussions concerning the excited-state absorption model, Hans Morrow for constructing the sample cells, and Dale Heisler for assistance with signal processing. This research was supported in part by the National Science Foundation, through Grant CHE85-06667, and by Dow Chemical.

Registry No. $(C_6H_5)_2CO$, 119-61-9; CH_3CH_2OH, 64-17-5; $(C_6H_5)_2CHOH$, 91-01-0; $(C_6H_5)_2\dot{C}OH$, 4971-41-9.

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