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Photodissociation of Highly-Excited Triplet State of Benzophenone Studied by a Time-Resolved Thermal Lensing Technique

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Two-step photo-absorption processes of benzophenone and photodissociation of the highly-excited triplet state have been investigated in solution by the time-resolved thermal lensing technique. Two-step absorption processes at 308 nm are found to be composed of the first $S_1 \leftarrow S_0$ absorption followed by a rapid intersystem crossing to T_1 and the second $T_n \leftarrow T_1$ absorption. The quantitative analysis of time-resolved thermal lensing signals leads to an unexpected result that only 51±6% of the photon energy absorbed by the molecule in T_1 has been detected as the heat released back to the system. This observation could be explained by a model that a fast photodissociation of benzophenone takes place from T_n. The chemical evidence and energy consideration support the dissociation into two phenyl radicals and a carbon monoxide molecule.

The photodissociation of carbonyl compounds has been widely investigated in both the gas and liquid phases. The simplest carbonyl compound, H_2CO, is known to decompose into H_2+CO, $H+HCO$, and $2H+CO$ fragments in the excitation to the S_1 state.[1] The photochemical behavior of acetone as the simplest kenone, $(CH_3)_2CO$, has been extensively studied. Acetone dissociates into methyl and acetyl radicals in the photolysis at 266 nm.[2] The VUV irradiation in the gas phase leads to the fission of two C–CO bonds yielding two methyl radicals and a CO molecule.[3] Benzene is formed as the initial dissociation products of benzaldehyde after the photo-excitation to the S_2 state.[4] Normal aromatic ketones have their triplet states around 70 kcal mol^{-1} (1 kcal mol^{-1}=4.184 kJ mol^{-1}) above the ground states. Since C–CO single bond energy ranges between 60 and 100 kcal mol^{-1}, the α-cleavage (so-called "Norrish Type I" reaction)[5] takes place for some triplet ketones in the solution. For example, the excitation to the S_1 state of dibenzyl ketone, $(\phi CH_2)_2CO$, leads to the bond rapture of two C–CO bonds to produce two benzyl radicals and CO with the high quantum yield.[6] The photochemistry of aromatic ketones in their lowest excited states has been reasonably established. On the contrary, there are few reports on photochemical reactions which take place on highly excited triplet surfaces in a condensed medium. The photodissociation of aromatic ketones in their higher triplet states was detected in 77 K matrices by the ESR technique.[7] Since the C–CO bond energy of benzophenone is higher than the excitation energy of the lowest triplet state, benzophenone in the T_1 state can not dissociate. It is well-known that benzophenone in the S_1 state undergoes very rapid intersystem crossing to the triplet state and the T_1 molecule abstracts a hydrogen atom from the hydrogen donating solvent to yield a diphenylketyl radical.[8] However, triplet benzophenone in the benzene solvent has considerably long lifetime because the hydrogen abstraction from benzene hardly occurs. Therefore, benzophenone in benzene has been used as an optical standard to determine the triplet quantum yield and the extinction coefficient of the transient species.[9]

When we examined the utility of benzophenone as a calorimetric reference for time-resolved thermal lensing (TRTL) spectroscopy, we encountered the occurrence of a new photochemical reaction under high intensity. Since the energy content of two photons absorbed reaches to the energy of a VUV photon, the above observation suggests that highly excited electronic states like S_n and T_n prepared by multiphoton absorption might play an important role in the primary process of the photochemical reaction.

The direct measurement of heat emitted in condensed phase after the pulse laser excitation of molecules can provide us information on kinetic (quantum yield and lifetime) and calorimetric (heat of formation or reaction) parameters of the short lived species.[10] This heat causes a temperature jump to alter the refractive index of the medium. One can probe the time evolution of heat as TRTL signals. In this paper, we have applied the TRTL spectroscopy, as well as the laser flash photolysis technique, to elucidate the photophysical and photochemical processes of benzophenone occurred under high light intensity at 308 nm.

Experimental

The TRTL experimental set-up is illustrated in Fig. 1. A XeCl excimer laser (Lambda Physik LPX105; ca. 20 ns and <130 mJ $pulse^{-1}$) was used as an excitation light source. The laser power was monitored by a silicon photodiode (Hamamatsu S1336-5BQ) calibrated by a pyroelectric detector (Gentec ED 100), after a partial fraction of laser beam was reflected by a beam splitter and attenuated through variable neutral density filters (Corion 2161). The sample solution was flowed in a cuvette (NSG T-59FL-UV-10) to eliminate the effect of photoproducts. A He–Ne laser beam (NEC GLG-5380; 1.5 mW) used as an analyzing beam of TRTL was focused in front of the sample cuvette by a 30 mm focal length lens. In pump-probe TRTL experiments, the excimer laser light was divided into two beams. One was the pump beam used for the preparation of benzophenone in the triplet state. This pump

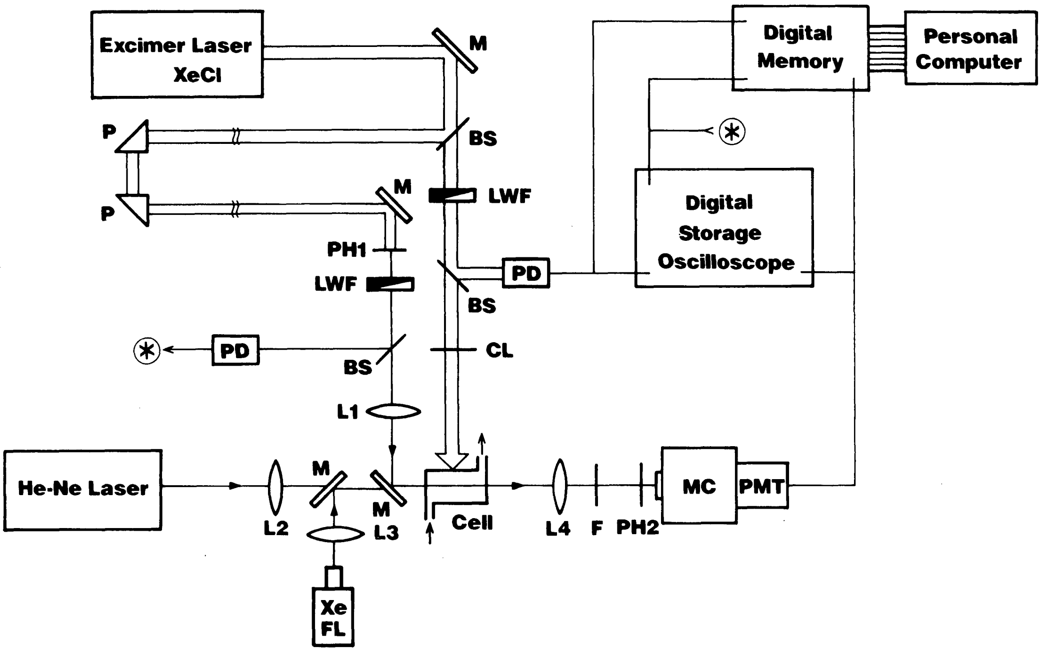

Fig. 1. Experimental arrangement: UV reflectors (M), variable linear wedge neutral density filters (LWF), rectangular prisms (P), laser energy meters (PD), pinholes 5 mm (PH1) and 300 μm (PH2), and beam splitters (BS). L1 (*f*=200 mm), L2 (*f*=30 mm), L3 (*f*=120 mm), and L4 (*f*=100 mm) lenses. L4 was removed during TRTL measurement. CL, F, MC, and PMT are cylindrical lens (*f*=130 mm), UV cutoff filter, monochromator, and photomultiplier, respectively.

beam was focused by a cylindrical lens and introduced into the cuvette from its lateral side. The other was probe pulse which was adjusted to arrive the cuvette 50 ns after the pump pulse by setting an optical delay line and traveled colinearly with the analyzing He–Ne laser beam through the cuvette. The analyzing He–Ne laser beam was sampled through a pinhole (Corion 2401; diameter 300 μm) and a monochromator (Nikon P250), and detected by a photomultiplier. The resultant output signal was converted into the voltage with a 50 or 500 Ω load resister, amplified by a preamplifier (ORTEC 574), measured by a transient memory (Iwatsu DM-901; 10 ns/word, 2 kwords memory) or a digital storage oscilloscope (GOULD 7404; 400 MHz), and transferred to a personal computer (NEC PC9801 F2). The TRTL signals were normally averaged over a hundred times to improve S/N ratios. In order to determine the absorbance of triplet benzophenone, the TRTL detection system was combined with the laser flash photolysis set-up described previously.[11]

Benzophenone (Merck) was purified by recrystallizing several times in hexane. Benzene (Uvasol), acetonitrile (Uvasol), and potassium iodide (GR grade) were used without further purification. All samples were deaerated by bubbling Ar half an hour before use. All measurements were carried out at room temperature. The liquid photoproducts were analyzed with a JASCO UVIDEC 100-IV HPLC apparatus. The CO product was detected with IR absorption. The vapor part of the products at 179 K was deposited onto a 20 K cooled CsI window and IR spectrum was averaged by 100 times in order to improve S/N ratio.

Results and Discussion

Photochemical Change in Absorption Spectrum of Benzophenone. Photoirradiation of degassed benzophenone in benzene at 308 nm under high laser power (10 mJ pulse^{-1}) yielded photo-bleaching in the region between 270 and 350 nm. This observation strongly suggests that benzophenone is consumed through some photochemical reactions. The absorption due to the reaction products seems to be in the spectral range shorter than 270 nm. The spectrum did not change any more even after the photoirradiated solutions were left over a night at room temperature. The photoproducts seem rather stable. A similar spectral change was observed even with irradiation of the aerated benzene solution. Although benzophenone in T_1 is well-known to abstract a hydrogen atom from solvent molecules yielding a ketyl radical, some other reactions seem to take place in the benzophenone–benzene system. Based on the reported rate constant[12] of the hydrogen abstraction from benzene, 1.6×10^2 dm^3 mol^{-1} s^{-1}, there is no chance for triplet benzophenone to react with benzene in the presence of oxygen during the lifetime of triplet benzophenone. Figure 2 shows the decrease in absorbance at 280 nm versus laser power where 2×10^3 shots were irradiated at 308 nm. The apparent index of the laser power dependence is 1.7, which implies that the photochemical reaction takes place through at least two

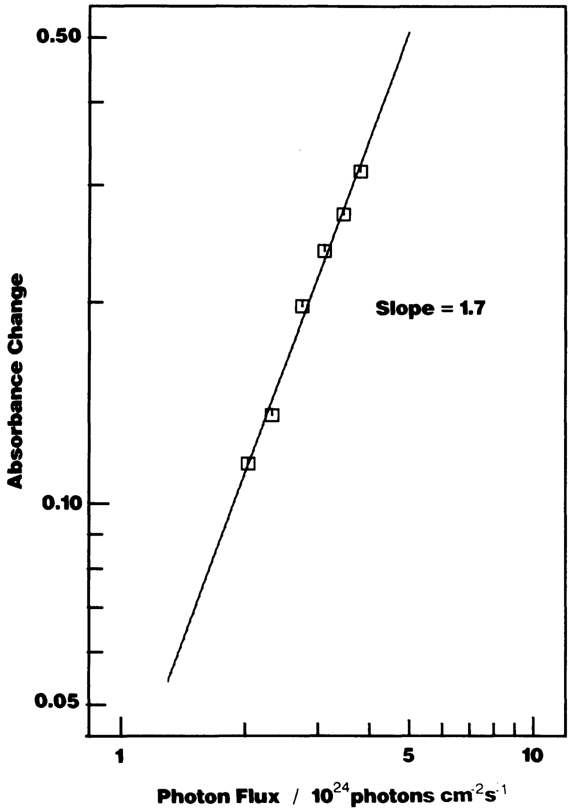

Fig. 2. Doublly logarithmic plot of the absorbance change at 280 nm versus laser power. The data were obtained after 2×10^3 shots at 308 nm.

photon process. There are two possible mechanisms explaining this quadratic laser power dependence; one is T–T annihilation and the other is two-photon absorption. The contribution of T–T annihilation could be safely neglected, because the triplet benzophenone was found to decay single-exponentially in the laser flash photolysis carried out at laser fluence lower than 5×10^{24} photons cm^{-2} s^{-1}. Therefore, the photochemical process of present interest would be induced by the two-photon absorption. There are two possible decomposition processes for highly excited benzophenone (ϕ_2CO^{**}).

$$\phi_2CO^{**} \longrightarrow 2\phi\cdot + CO \qquad (I)$$

$$\longrightarrow \phi\cdot + \phi\dot{C}O \qquad (II)$$

The products analysis by HPLC revealed that the main photoproduct was biphenyl. Benzil and benzaldehyde, the main photoproducts expected for reaction (II), were not detected. The vapor part of the photoproducts showed a clear peak of CO at 2140 cm^{-1} in the IR absorption spectrum. Therefore, these products would be formed by the decomposition reaction (I) from the highly excited benzophenone.

Time-Resoved Thermal Lensing (TRTL) Signals of Benzophenone. Figure 3 shows a typical time evolution

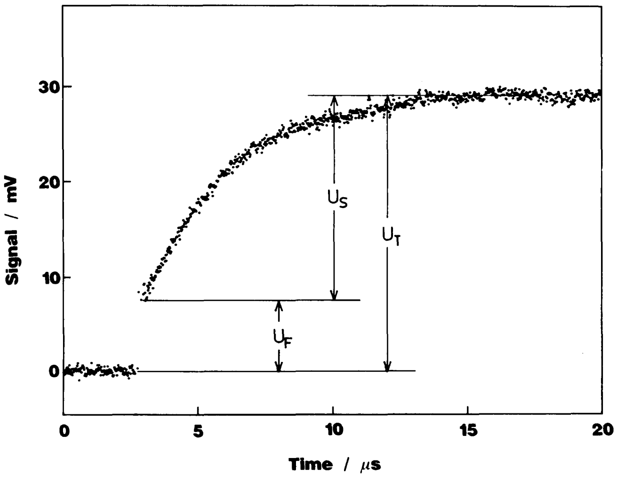

Fig. 3. Typical time evolution of a TRTL signal.

of a TRTL signal of benzophenone is degassed benzene stimulated by the 308 nm laser irradiation of 5 μJ. The time profile has apparently two components; one is of the fast rise, U_F, immediately after the laser excitation, and the other, U_S, rises slowly and becomes flat after ca. 10 μs. The U_T ($=U_F+U_S$) signal stays for several milliseconds and decays. The fast rise corresponds to the heat released by nonradiative relaxation from the photoexcited singlet state of benzophenone to the lowest triplet state (T_1), and the slow one corresponds to that by the recovery of S_0 from T_1. The slow component grew single-exponentially with a lifetime of 3.1 μs, which was consistent with the triplet lifetime (3.7 μs) measured by the laser flash photolysis. The total heat released by overall nonradiative processes, U_T, is plotted as a function of incident laser power, I_L, in Fig. 4-a. The U_T signals increase more rapidly than they do linearly with I_L. The laser power dependence of U_T was fitted well by the formula,

$$U_T = aI_L + bI_L^2, \qquad (1)$$

as the solid curve shown in the figure. Here a and b denote the coefficients of linear and quadratic terms, respectively. Alternative analysis was carried out by plotting U_T/I_L against I_L as shown in Fig. 4-b, which exhibited the linear tendency. These analyses indicate that there should be at least two different sources of the heat released, presumably single- and two-photon absorption processes.

Two-Photon Absorption Process. Benzophenone absorbs two photons at relatively low laser power of ca. 20 μJ pulse^{-1}. There are two possible states responsible for the quadratic dependence of the laser power, S_1 and T_1. Immediately after the first photon absorption, the excited singlet state decays to form the T_1 state within a few picoseconds.[13] The extinction coefficient of triplet benzophenone ε_T at 308 nm is reported[14] to be 10^4 dm^3 mol^{-1} cm^{-1}. Judging from the fast intersystem

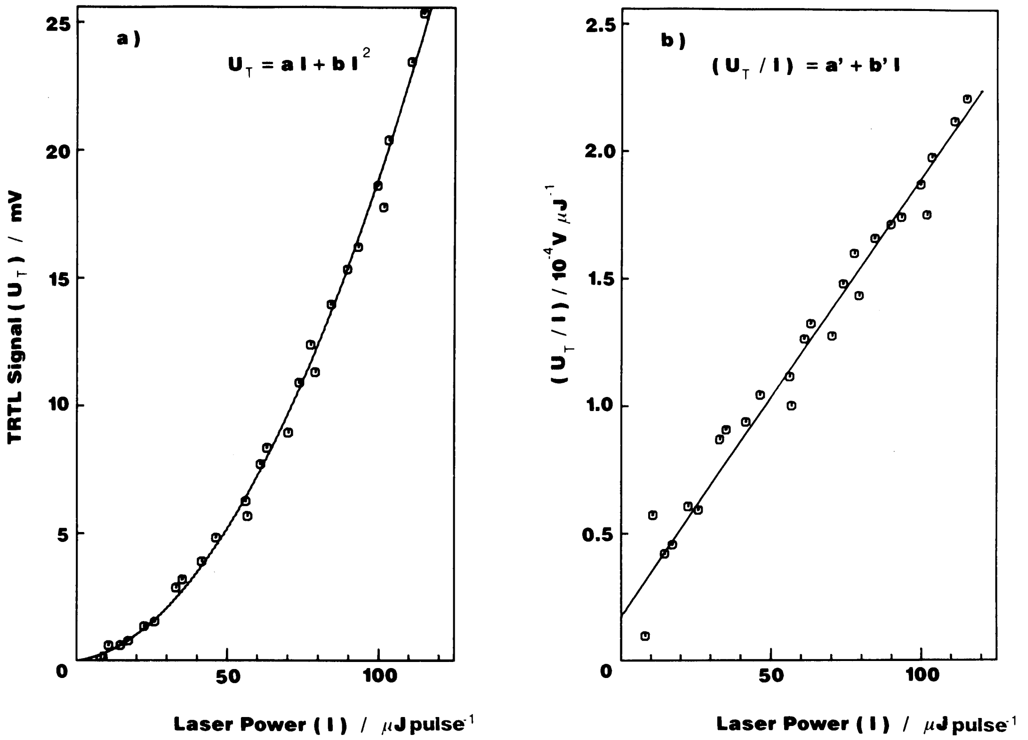

Fig. 4. a) Plot of the total heat U_T versus laser power I_L. Solid curve is the best fitting of the data by Eq. 1 under $a=(1.84\pm0.40)\times10^{-5}$V μJ^{-1} and $b=(1.70\pm0.04)\times10^{-6}$V μJ^{-2}. b) Plot of U_T/I_L versus I_L. Solid line is the best fitting by $U_T/I_L=a'+b'I_L$ under $a=(1.73\pm0.23)\times10^{-5}$V μJ^{-1} and $b=(1.72\pm0.04)\times10^{-6}$V μJ^{-2}.

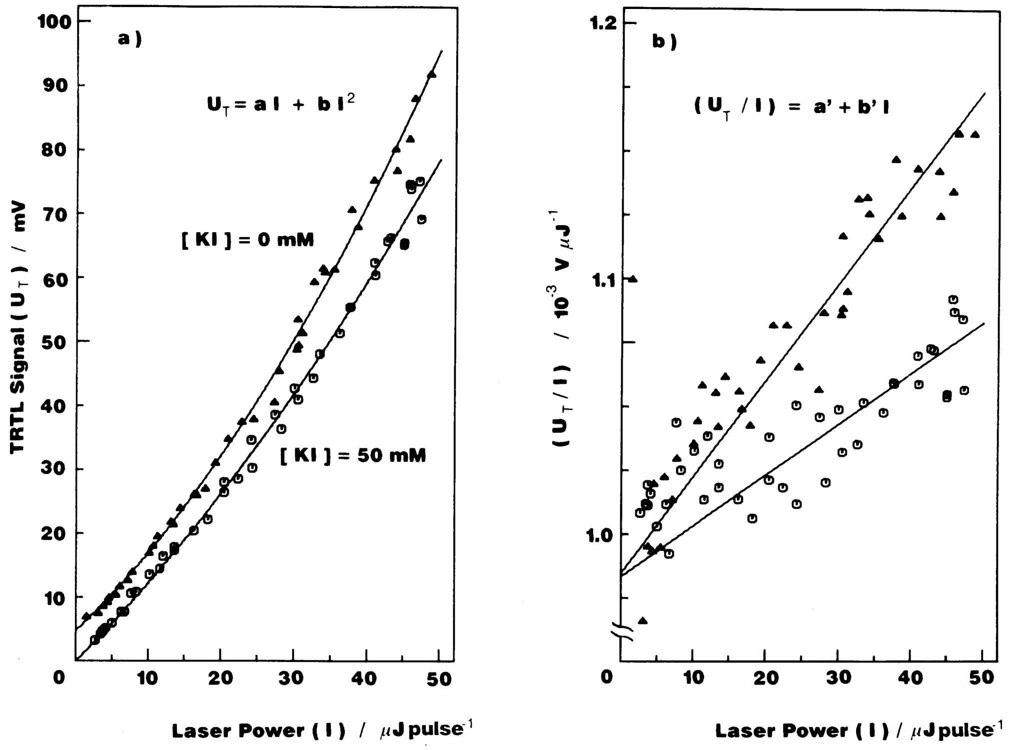

Fig. 5. a) Plots of the total heat U_T versus laser power I_L in the absence (—▲—) and in the presence (—○—) of KI (50 mM). Solid curves are the best fittings of the data by Eq. 1. b) Plots of U_T/I_L versus I_L in the absence (—▲—) and in the presence (—○—) of KI (50 mM). Solid lines are the best fittings by $U_T/I_L=a'+b'I_L$.

crossing rate and fairly large ε_T, it is reasonable that the second photon is absorbed by benzophenone in the T_1 state, that is, the T_n—T_1 absorption. To confirm this mechanism, we carried out the quenching experiment of triplet benzophenone in TRTL studies. Anions such as I^-, SCN^-, and N_3^-, are known to quench efficiently triplet aromatic ketones. Potassium iodide, KI, is reported[15] to quench triplet benzophenone in H_2O/CH_3CN (4 : 1) mixtures with the rate constant of k_q=3.5×10^9 dm^3 mol^{-1} s^{-1}. Therefore, we can easily control the lifetime of triplet state of benzophenone by changing the KI concentration. If the mechanism of two-photon absorption described above is operative, the heat released after the T_n—T_1 absorption should decrease by shortening the T_1 lifetime of benzophenone comparable to the laser pulse width (ca. 20 ns). Figure 5-a shows the laser power dependences of U_T of benzophenone in acetonitrile in the absence and in the presence of KI. The lifetime of T_1 is estimated to be 5.7 ns in the presence of KI (50 mM). The difference between these two plots apparently becomes larger in the higher laser power region, though both the plots are well fitted by Eq. 1. Figure 5-b shows the plots of U_T/I_L versus I_L, which exhibits that the coefficient b is decreased by the addition of KI. This result confirms that initially photoexcited benzophenone undergoes rapid intersystem crossing to triplet benzophenone, which in turn absorbs the second photon by the T_n—T_1 transition.

Photodissociation of Highly-Excited Triplet State, T_n. Benzophenone absorbs two photons stepwisely to yield the highly-excited triplet state, T_n. Murai and Obi reported[7] the occurrence of chemical reaction of the aromatic ketones in T_n states. They found that benzophenone in T_n abstracted a hydrogen atom from alcohol even at 77 K to form diphenylketyl and alcohol radicals. In the present case, benzene and acetonitrile were used as the solvent. The HPLC analyses did not indicate formation of benzpinacol as the final product, which suggests that ketyl radicals are not generated as transient species. Benzophenone in T_n is unlikely to react with the solvent molecules. It might reasonable to consider the photochemical initial step of T_n to be photodissociation.

Quantitative analysis of heat emitted through the disappearance of T_n by the TRTL method gives us calorimetric and kinetic information. The heat conversion efficiency, α_T, which is the ratio of the photon energy (E_{ex}) absorbed by the T_n-T_1 transition to the heat energy released to the solvent within the time window of the TRTL measurement, is written as Eq. 2.

$$\alpha_T = \frac{E_{ex} - \Phi_r \Delta E_r}{E_{ex}}. \qquad (2)$$

The term $\Phi_r \Delta E_r$ is the energy consumed for chemical reactions within the time window; the chemical energy stored in the system. Here Φ_r and ΔE_r are the reaction quantum yield and the reaction energy relative to the T_1 state of benzophenone, respectively. To determine α_T, we employed the pump-probe method in the TRTL experiment. The pump laser pulse (the intensity of I_{pump}) was introduced into the sample cell to excite benzophenone in S_0. The probe laser pulse (the intensity of I_{probe}), experiencing an optical delay of 50 ns to avoid the simultaneous absorption by pump and probe laser pulses, was focused in the sample cell colinearly with the analyzing continuous wave He-Ne laser beam for TRTL. Since the probe laser light is absorbed by benzophenone in both the S_0 and T_1 states, the heat of U_T delivered to the solvent by nonradiative relaxation is given as follows,

$$U_T = k\{\alpha_G(1 - 10^{-A_G}) + \alpha_T(1 - 10^{-A_T})\} I_{probe} \qquad (3)$$

where α_G and α_T are the heat conversion efficiencies after the S-S excitation of benzophenone in S_0 with the absorbance of A_G at 308 nm and the T-T excitation of T_1 with A_T, respectively. The transient absorption technique was employed to determine the triplet state absorbance, A_T, at 308 nm. The T-T absorption signal rises within ca. 30 ns and then becomes plateau beyond 50 ns after the pump pulse. The A_T values obtained are plotted against I_{pump} in Fig. 6, which shows a good linear relation. Thus the concentrations of triplet benzophenone can be controlled by varying the pump laser

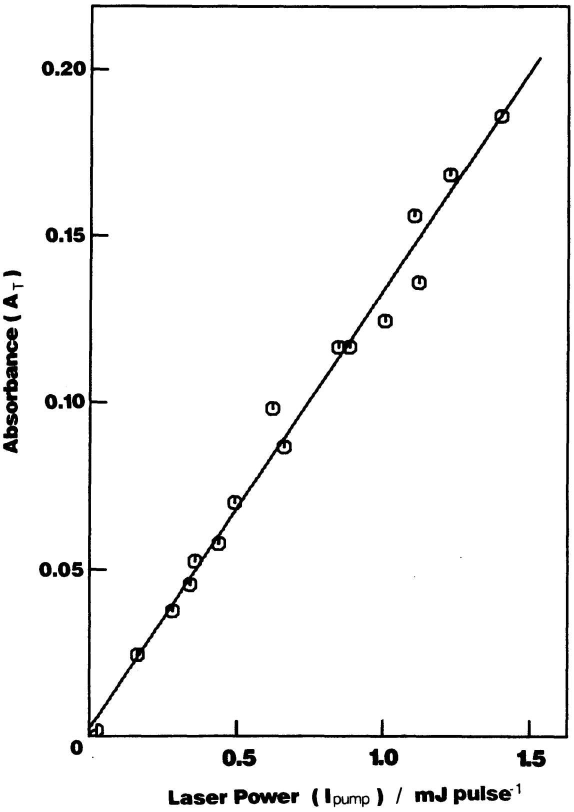

Fig. 6. Plot of the absorbance of triplet benzophenone versus pump laser intensity, I_{pump}.

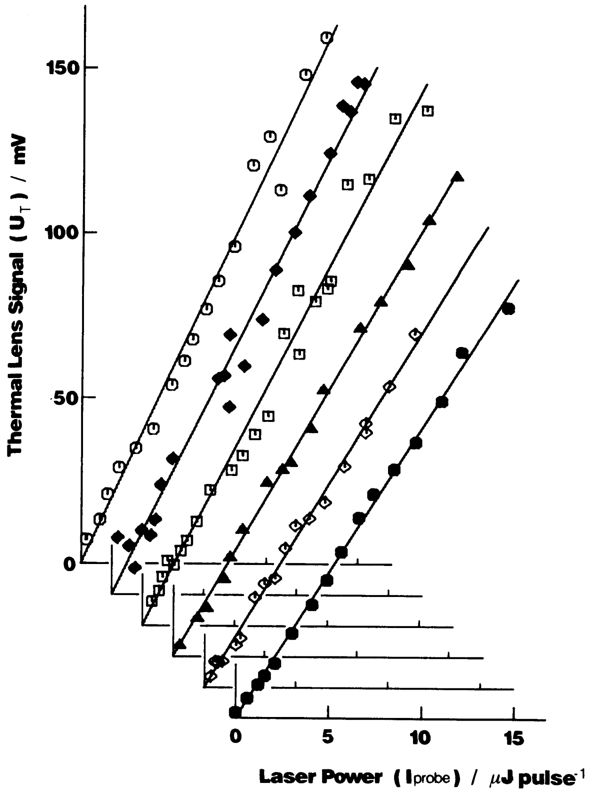

Fig. 7. Plots of TRTL signals versus probe laser intensity, I_{probe} for various triplet absorbance A_T. (—●—), A_T=0; (—◇—), A_T=0.042; (—▲—), A_T=0.068; (—□—), A_T=0.116; (—◆—), A_T=0.144; (—○—), A_T=0.175.

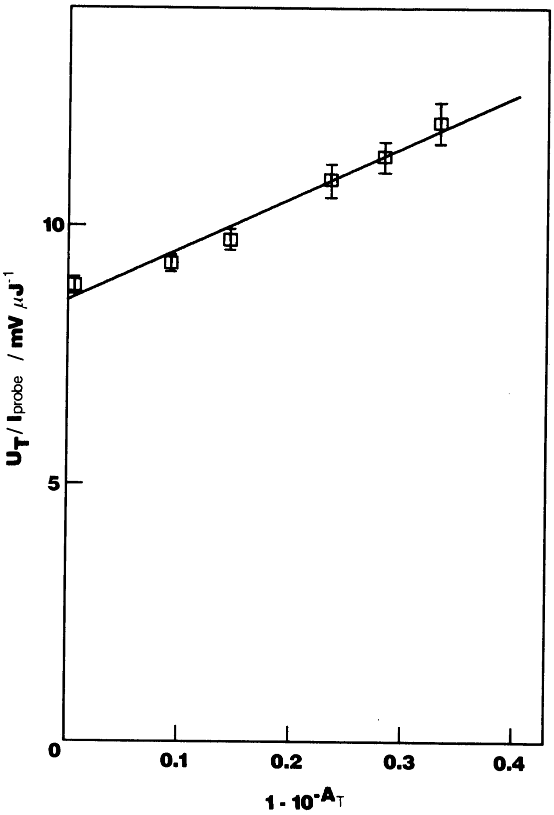

Fig. 8. Plot of U_T/I_{probe} versus (1-10^{-A_T}).

intensities. The plots of U_T versus I_{probe} give good linear relations for constant values of A_T as seen in Fig. 7. Therefore, the TRTL signals reflect the single photon process for the probe laser up to the power of 15 μJ pulse^{-1}. The slopes, U_T/I_{probe}, of these 6 straight lines are plotted against (1—10^{-A_T}) in Fig. 8. The heat conversion efficiency of α_T is determined to be 0.51±0.06, from the slope-to-intercept ratio of this straight line, using α_G=1.

McGimpsey and Scaiano[16] reported the T-T energy transfer from benzophenone in higher triplet state (T_n') excited by green light to benzene. If T-T energy transfer is mainly operative in our system, α_T is estimated to be equal to or greater than 0.84 from Eq. 2 using the T-T energy transfer quantum yield of unity and the triplet energy of 84 kcal mol^{-1} for benzene. This calculated value is inconsistent with the experimental (α_T=0.51) and the T-T energy transfer can be neglected as the decay channel of benzophenone in T_n excited at 308 nm. Benzophenone in T_n' pumped by green light does not undergo bond scission and transfers its energy to benzene, while benzophenone in highly excited triplet T_n generated with UV light would strongly interact with a repulsive potential surface and hence bond fissions will take place very rapidly from T_n rather internal conversion

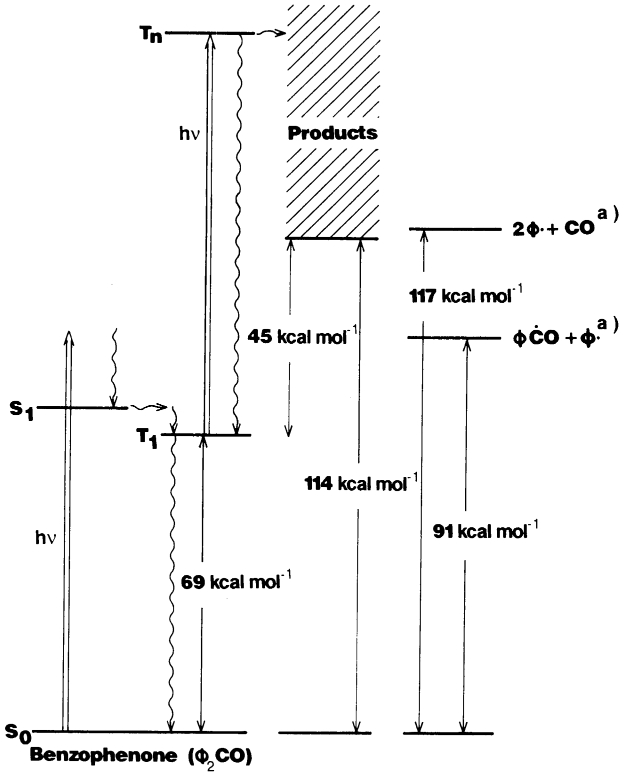

Fig. 9. Energy diagram of benzophenone. a) The literature values in the gas phase taken from Ref. 17.

or T–T energy transfer.

From Eq. 2, $\Phi_r \Delta E_r$ is obtained to be 45 kcal mol^{-1}. The energy stored in the system, ΔE_r, is equivalent to the difference between the heat of reaction and the T_1 energy of benzophenone (E_T); $\Delta E_r = \Delta H_r - E_T$. The condition of $\Phi_r \leqslant 1$ leads to $H_r \geqslant 115$ kcal mol^{-1}. According to available thermochemical data,[17] the heat of reaction for $\phi_2CO \rightarrow 2\phi\cdot + CO$ is calculated to be 117 kcal mol^{-1} in the gas phase, which coincides with the lower limit of ΔH_r obtained here. The energy levels relating to this study are illustrated in Fig. 9. Provided that the energy shift due to the solvent effect is negligible, the photodissociation into $2\phi\cdot + CO$ seems to take place very efficiently. The final T_n state of benzophenone in benzene after two-step absorption process lies at 7.0 eV above the ground state. Although the ionization threshold, I_{Th}, of benzophenone in benzene is not available in the literature, it is supposed to lie above 7 eV referred to I_{Th} of benzene in nonpolar solvents.[18] In the present experiment, no photocurrent was detected in the benzophenone–benzene system under the present laser power conditions. The ionization might not be induced in the present two step absorption at 308 nm. Thus, we concluded that the reaction (I) is the major decay process of the T_n state.

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