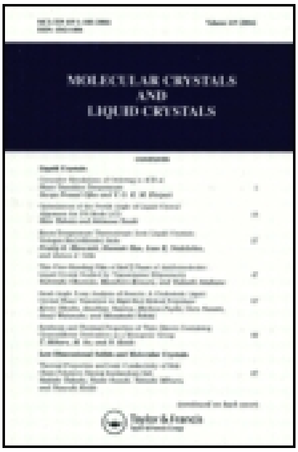

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Photochemical Hydrogen Abstraction in Benzophenone Single Crystal

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PHOTOCHEMICAL HYDROGEN ABSTRACTION IN BENZOPHENONE SINGLE CRYSTAL

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Abstract We found that photochemical hydrogen abstraction occurs in a benzophenone crystal doped with hydrogen donors such as diphenylmethane and benzhydrol. In diphenylmethane-doped benzophenone, the reaction is thermally activated. The magnitude of the activataion energy (1400cm $^{-1}$) indicates that an intramolecular vibration is involved in the reaction.

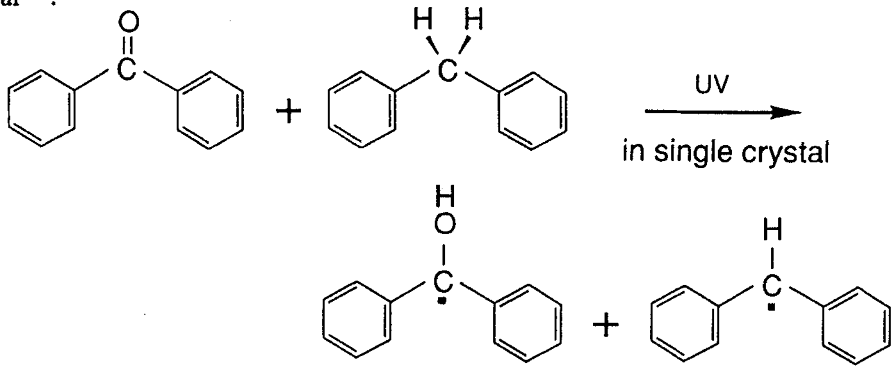
INTRODUCTION

In a solid state reaction the reaction partners are fixed in space. As a result, it is considered possible to study the temperature dependence of the reaction itself, without being disturbed, as in a liquid phase reaction, by diffusion of the solute, or the solvent which is also temperature dependent. However, the choice of the reaction partners is very often limited by the mutual solubiity in the solid. Since solid state solubility for foreign compounds is generally quite low, doped molecules tend to be expelled to surfaces and grain boundaries. As a result, many of the intermolecular reactions in the solid state occur at these sites, and not in the crystal. Hence there are only a few examples known of intermolecular hydrogen abstraction which occurs in a crystal [1, 2]. D. Stehlik and co-workers have studied photoinduced hydrogen abstraction of phenazine and acridine in fluorene single crystal. By studying temperature dependence of the reaction, they have found that paticular molecular vibration and phonon modes which play a role in shortenning intermolecular distance promote hydrogen abstraction reaction [1].

Hydrogen abstraction by benzophenone in its triplet excited state is well known. There are quite a number of reports on this photochemical reaction in solution [3-6]. On the other hand, the compound does not show any photochemical reactivity in the crystal. Benzophenone has only hydrogens attached to benzene rings which are more resistant against abstraction, compared to aliphatic hydrogens.

Also, in single crystal, molecules are fixed in mutual configuration which is not favorable for the reaction. As a result, in neat benzophenone crystal no hydrogen abstraction reaction occures. However, by introducing dopants, it becomes possible to study hydrogen abstraction reaction in benzophenone single crystal.

In a previous publication we reported that a triplet exciton in a benzophenone crystal abstracts hydrogen from diphenylmethane (DH) doped in the crystal [7].



The resulting radical, diphenylmethyl (D), acts as an efficient energy trap for triplet excitons. The green emission from a crystal which has been irradiated with UV light is a combined result of hydrogen abstraction,

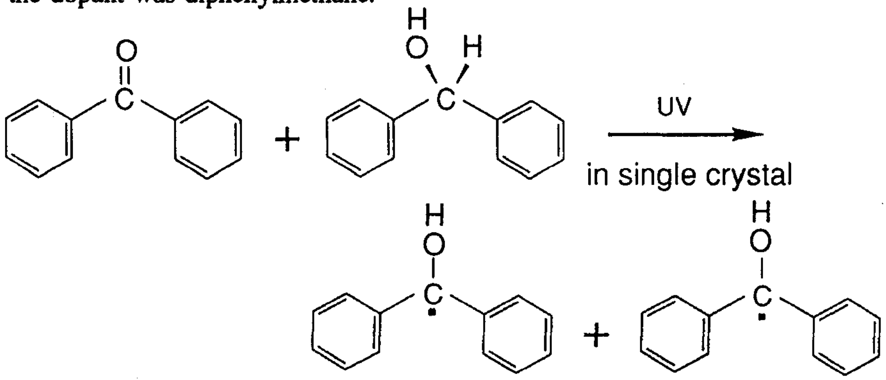
$$T^* + DH \rightarrow D \qquad \text{(step 1)}$$

and energy transfer

$$T^* + D \rightarrow D^*. \qquad \text{(step 2)}$$

We found that the green emission is strongly suppressed at lower temperatures. It has become clear that energy transfer (step 2) is insensitive to temperature change whereas the photochemical reaction (step 1) is thermally activated.

Another system which undergoes photochemical hydrogen abstraction is benzophenone doped with benzhydrol. What is unique with this system is that the reaction results in a pair of identical benzophenone ketyl radicals. We could detect fluorescence from the ketyl radical which could not be detected in the system in which the dopant was diphenylmethane.



EXPERIMENTAL

Benzophenone, benzhydrol (BH), and diphenylmethane (DH) were used as obtained (Tokyo Kasei Co.). Crystals, typically 5 cm in length and 1.5 cm in diameter, were grown by Czochralski method from benzophenone melt containing 10 % dopant. Concentration of the dopant in the crystals grown was analyzed by HPLC. Sample specimen was cut from an ingot with a thread saw and polished with a fine membrane filter wetted with methanol. Details have been described elsewhere [7]. Using these specimens, emission spectrum was recorded with a spectrofluorimeter (Hitachi, MPF-3)

Fluorescence from ketyl radical was observed with a small double monochromator (Jovin. Yvon, H10D) and a photomultiplier (Hamamatsu, R269). Excitation was made with a dye laser (Lambda Physik, FL3002), pumped with an excimer laser. Measurements were made at room temperature.

The decay of T-T absorption was measured with the same arrangement as described in the previous publication [7]. Temperature was controlled with a cryostat constructed in the laboratory in which a sample specimen could be cooled with flowing cold nitrogen gas. For photochemical reaction the light source was a dye laser (Lambda Physik, FL 3002) operated at λ =380nm (Laser dye BBQ). This wavelength was selected since excitation at this wavelength generates a spatially homogeneous distribution of triplet excitons. T-T absorption of benzophenone was probed at 540nm, using a Xe flash lamp.

RESULTS AND DISCUSSION

A benzophenone crystal containing 1 % of DH was irradiated for 2 hours at room temperature with UV light from a pulsed laser (380nm, 25Hz). Subsequently emission spectrum was measured at the same temperature. The result is shown in Fig. 1(a). A strong emission band is seen in the green region of the spectrum on top of the blue emission which is phosphorescence of benzophenone. This part of the spectrum coincides with that of diphenylmethyl radical in a matrix [8-10], which indicates that hydrogen has been abstracted from DH by an excited benzophenone. This strong fluorescence of diphenylmethyl radical is mainly due to energy transfer by triplet excitons [7].

We tried to detect fluorescence from benzophenone ketyl (BH) , which is expected to form in the reaction, but so far without success. When another system, benzophenone crystal doped with benzhydrol, was irradiated with UV light, we could observe that the intensity of the phosphorescence from benzophenone decreased, which indicated that triplet energy acceptors, most probably diphenyl ketyl, were being formed by the photoreaction. Fluorescence due to ketyl radicals peaking at 560nm [11, 12] could be observed, when the ketyl radical was excited directly at 500nm. The absence of intense green emission from diphenymethyl made it possible to detect weak emission from the ketyl radical.

When the system benzophenone / diphenylmethane was irradiated at 77K, the emission spectrum measured at the same temperature showed no radical fluorescence (Fig. 1(b)). It is possible that the chemical reaction slowed down at

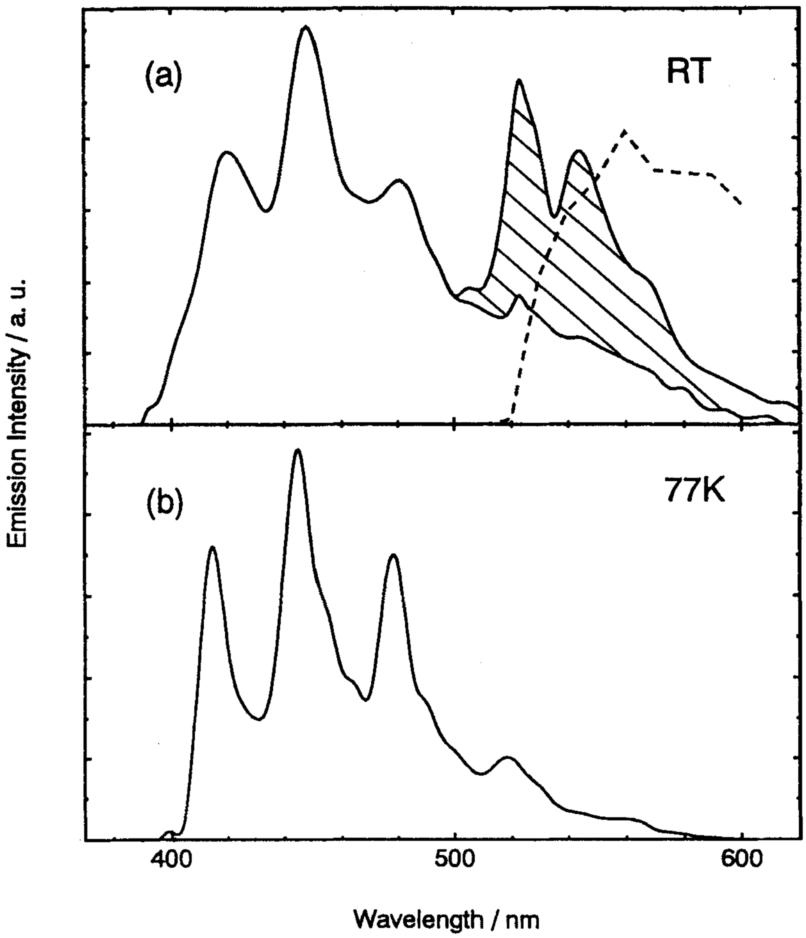


FIGURE 1 Emission spectrum of doped benzophenone crystal. (a) Before and after UV irradiation. UV irradiation and measurement of the spectrum were made at room temperature. The shaded region indicates the fluorescence of photochemically generated diphenymethyl radical in benzophenone crystal doped with diphenylmethyl radical. The broken line indicates the fluorescence of photochemically generated diphenylketyl radical in benzophenone crystal doped with benzhydrol. (b) UV irradiation and measurement made at liquid nitrogen temperature. Sample specimen is benzophenone crystal doped with diphenymethane.

lower temperatures and at 77K only a very small amount of the dopant was converted into the radical. Another possibility is that energy transfer is slow at liquid nitrogen temperature, so that the fluorescence from the radical is undetectabily weak, although radicals are formed.

In order to see whether the low fluorescence intensity is due to a low energy transfer rate or to a low reaction rate, temperature dependence of T–T absorption was measured with different samples. First, energy transfer rate was measured at various temperatures. A doped crystal was irradiated at room temperature and subsequently the triplet lifetime was measured at various temperatures. The lifetime of the triplet exciton decreased with increasing irradiation time and attained a saturation, a fact which indicates that the dopant was converted quantitatively to radicals within the penetration depth of the light.

The rate equation which governs the decay of the triplet exciton is

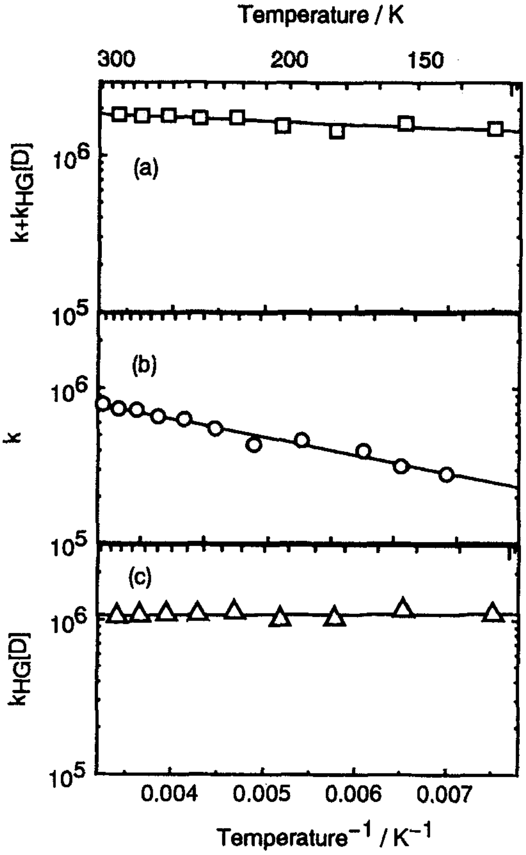


FIGURE 2 Arrhenius plots of decay constants of the T–T absorption (pump wavelength is 380nm, probe wavelength is 540nm). (a) A doped crystal thoroughly irradiated with UV at room temperature. (b) A neat benzophenone crystal. (c) Rate constant of the energy transfer from benzophenone triplet excitons to diphenylmethyl radicals, obtained by subtracting k's in Fig. 3(b) from the decay constants in Fig. 3 (a).

$$-\frac{d[T]}{dt} = k[T] + k_{HG}[D][T] + \gamma_{TT}[T]^2 , \qquad (1)$$

where [T] is the concentration of the triplet exciton, [D] is that of the radical, k is the first order decay constant of the triplet, k_{HG} is the rate constant for energy transfer and γ_{TT} is the second order rate constant for triplet-triplet (TT) annihilation. Care was taken to keep the intensity of the exciting light low, so that the decay was exponential. Figure 2 (a) shows the results. It may be seen that the decay constant, $k+k_{HG}$ [D], decreases as temperature is lowered.

Secondly, it was confirmed at various temperatures that the decay was single exponetial in a neat (i. e. , undoped) crystal. The temperature dependence of k is shown in Fig. 2(b). Fig. 2(c) shows the Arrhenius plot of the rate constant k_{HG} [D], obtained from the observed decay rate constant, $k + k_{HG}$ [D], by subtracting the temperature dependent k. It is clear from the figure that k_{HG} does not change appreciably in the temperature range studied,

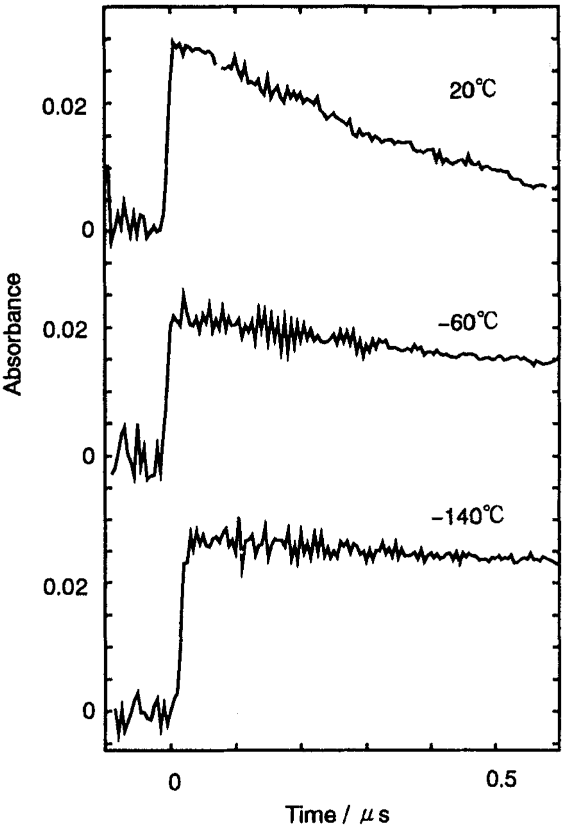


FIGURE 3 Decay of the T–T absorption at three different temperatures (pump wavelength is 380nm, probe wavelength is 540nm). Each sample specimen has been given a constant dose of UV radiation (3 × 10^4 shots of 1mJ at 380nm).

since [D] remains constant in this experiment.

Having established that temperature does not influence the rate constant of energy transfer, we examined the temperature dependence of the photochemical hydrogen abstraction reaction. Sample specimens containing 1% of DH was cooled to a temperature and irradiated with 380nm pulse from a dye laser (1mJ/shot). After 3×10^4 shots the pulse energy was reduced to 0.3mJ/shot and the decay of T–T absorption was measured at the same temperature. With this pulse energy the decay of T–T absorption was exponential, indicating that $\gamma_{TT}[T]^2$ term in the equation was not important. The results are shown in Fig. 3 for three different temperatures. It may be clear that the decay is slower at lower temperatures.

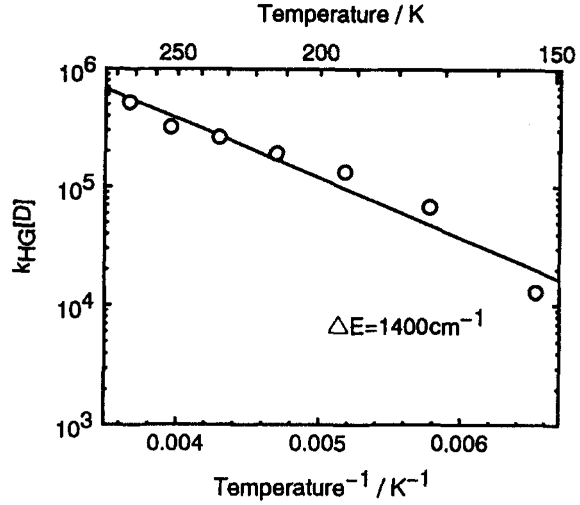


FIGURE 4 Arrhenius plot of reaction rate constant of the photochemical hydrogen abstraction in a benzophenone crystal doped with diphenylmethane. The activation energy is 1400cm^{-1}. This value is close to a molecular vibrational energy (for example, C=O stretching of triplet benzophenone is 1222cm^{-1}) [13].

The results in Fig. 3 includes parameters k_{HG} and k which also depend on the temperature.To pick out the temperaturedependence of the reaction itself, those of k_{HG} and k has to be subtracted. Using the data shown in Fig. 2, we could obtain the temperature dependence of the hydrogen abstraction reaction. Figure 4 shows k_{HG} [D] as a function of the temperature. Since k_{HG} does not change appreciably with temperature, the change in Fig. 4 is due to that of [D] and we can conclude that the hydrogen abstraction slows down with decreasing temperature. The activation energy is 1400cm^{-1}.

The activation energy of hydrogen abstraction by photoexcited benzophenone in various solvents has been obtained from the observed activation energy after it is corrected for diffusion which is temperature dependent. It has been reported to be 2–5 kcal / mol (700–1500cm^{-1}) [4] .These values are close to that we found.

In a crystal molecules are fixed in terms of translation. The fact that the activation energy observed is in the same order of magnitude with a molecular vibration, and not of a lattice vibration, seems to indicate that a molecular vibration promotes the hydrogen abstraction. Actually, in gasphase reactions there is evidence that molecular vibration enhances the rate of photodissociation[14-16]. Theoretically Sumi and Marcus introduced vibrational coordinate in potential energy surface[17,18], and their theory has been used to explain some photochemical reactions[19-20] in condenced phase. Also, it has been reported that a particular vibrational mode enhances the reactivity of photoinduced proton transfer in a condenced phase[21-23]. In single crystal, D. Stehlik and co-workers have reported that paticular vibration and phonon modes which play a role in shortenning intermolecular distance promote hydrogen abstraction reaction[1].

CONCLUSION

It has been found that photochemical hydrogen abstraction occurs in benzophenone single crystal doped with diphenylmethane or with benzhydrol. With diphenylmethane as dopant, the activation energy of the reaction is 1400cm^{-1}. The products, diphenylmethyl and diphenylketyl, could be identified by fluorescence.

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