# Photochemical Reaction of Excited Benzophenone in the Gas Phase

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Photochemical reactions of benzophenone with hydrogen-donating compounds have been studied in the gas phase. It has been found that the photoreduction of excited benzophenone proceeds to form benzophenone ketyl radical without contributions from surrounding solvents. The quenching rate constant measurements of benzophenone triplet have suggested that, in addition to its role in the condensed phase, the charge-transfer interaction also plays an important role in the photoreduction process of benzophenone-amine systems in the gas phase.

#### Introduction

The behavior of carbonyl compounds in the excited triplet state has been one of the most fundamental and important subjects in photochemistry.<sup>1,2</sup> In particular, the reactions of benzophenone in the excited state have been studied extensively.<sup>3-11</sup> Photoexcited benzophenone rapidly undergoes intersystem crossing and populates the lowest triplet state with a yield of unity. It is well-known that the lowest triplet state has a highly electrophilic carbonyl group, which may lead to charge transfer and hydrogen abstraction reactions. The hydrogen abstraction of the lowest triplet benzophenone from various hydrogen-donating compounds in the condensed phase has been extensively investigated and a number of results have been reported.

It is widely known that the reaction rates of benzophenone triplet with various amines are close to the diffusion-controlled reaction rate and the yields of the reaction are very high.<sup>1,4,5,7</sup> Thus much attention has been paid to the reaction mechanism. Cohen and co-workers<sup>4,5</sup> proposed that the hydrogen abstraction of benzophenone from amines proceeded by rapid formation of the charge-transfer complex or ion pair state followed by proton transfer to generate benzophenone ketyl radical (BPK). On the basis of the picosecond dynamics of benzophenone-amine systems, Peters and co-workers<sup>6</sup> concluded that the photoreduction proceeded by rapid electron transfer to form the solvent-separated ion pair. The ion pair formation was followed by diffusion to form the contact ion pair and this structural change of the relatively long-lived ion pair is the key process for the reaction to progress. On the other hand, Miyasaka et al.<sup>12</sup> recently reported the femtosecond and picosecond laser photolysis studies on the reaction of excited benzophenone with amines in the several kinds of solvents and demonstrated that the reaction mechanism strongly depended on the nature of amines and solvents.

Though the mechanism for the photoreduction of benzophenone has been extensively studied, many questions remain unanswered. If proton transfer following electron transfer between benzophenone and amine is the dominant process of the reaction, can the proton transfer directly or is it necessary to form a long-lived

(3) Beckett, A.; Porter, G. Trans. Faraday Soc. 1963, 59, 2038.

- (4) Guttenplan, J. B.; Cohen, S. G. J. Am. Chem. Soc. 1972, 94, 4040.
  (5) Cohen, S. G.; Parola, A.; Parsons, Jr., G. H. Chem. Rev. 1973, 73, 141.
  (6) (a) Shaefer, C. G.; Peters, K. S. J. Am. Chem. Soc. 1980, 102, 7566.
  (b) Simon, J. D.; Peters, K. S. Ibid. 1981, 103, 6403.
- (7) (a) Inbar, S.; Linschitz, H.; Cohen, S. G. J. Am. Chem. Soc. 1980, 102, (b) Inbar, S.; Linschitz, H.; Cohen, S. G. Ibid. 1981, 103, 1048.
   (8) Encinas, M. V.; Scaiano, J. C. J. Am. Chem. Soc. 1981, 103, 6393.

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ion pair? What is the role of surrounding solvent molecules? Is a specific orientation between benzophenone and hydrogen donor necessary for the reaction to progress?

In order to investigate these problems, we have studied the photochemical reaction of benzophenone in the gas phase in which the contributions from surrounding solvents are lacking. Whereas the photoreduction process of benzophenone in the condensed phase is one of the most important photochemical reactions and has been extensively studied for several decades, very few studies on the gas-phase reaction of triplet benzophenone have been reported. Steel and co-workers<sup>13</sup> have studied the gas and solution phase reactions of triplet carbonyls. Though they measured the quenching rate constants for triplet benzaldehyde and acetophenone in the gas phase, no rate constant for the gas phase reaction of benzophenone has been reported. In the present paper, we report the kinetic studies on the reaction of excited benzophenone with hydrogen donors in the gas phase. Generation of BPK in the gas phase is reported and the mechanism of the hydrogen abstraction without the complicating effect of solvent environment is discussed.

#### **Experimental Section**

Benzophenone obtained from Wako was purified by repeated recrystallization from ethanol. The hydrogen donors were used as received without further purifications. We confirmed that these compounds did not fluoresce following laser excitation (337.1 and 460-570 nm). The following hydrogen donors were used: 1,4cyclohexadiene, triethylamine, aniline, N,N-dimethylaniline, 2butylamine, cyclohexylamine, and 2-propanol.

A 5-cm-diameter and 40-cm-length stainless cell was used for the measurement of the phosphorescence decay profile of triplet benzophenone as well as the fluorescence excitation and dispersed emission spectra of BPK. All the measurements were carried out at 380 K  $(\pm 3 \text{ K})$  to increase the vapor pressure of benzophenone to 1 Torr. The samples were irradiated with pulses from a nitrogen laser (Molectron UV-22, 337.1 nm, 8 ns duration, 4-5 mJ) to excite benzophenone. The quenching rate of triplet benzophenone was obtained by monitoring the decay profile of benzophenone phosphorescence in the 420-550-nm region in the presence of hydrogen donors. The decay profile of the phosphorescence was recorded with a digital storage scope (Gould 4074). BPK generated by the photoreduction of triplet benzophenone with hydrogen donors was subsequently excited with pulses from a dye

<sup>(1)</sup> Scaiano, J. C. J. Photochem. 1973/4, 2, 81.

<sup>(2)</sup> Turro, N. J. Modern Molecular Photochemistry; Benjamin/Cummings: Menlo Park, 1978.

<sup>(8)</sup> Encinas, M. V.; Scalano, J. C. J. Am. Chem. Soc. 1981, 105, 6393.
(9) Manring, L. E.; Peters, K. S. J. Am. Chem. Soc. 1985, 107, 6452.
(10) Devadoss, C.; Fessenden, R. W. J. Phys. Chem. 1990, 94, 4540.
(11) Redmond, R. W.; Scalano, J. C. Chem. Phys. Lett. 1990, 166, 20.
(12) (a) Miyasaka, H.; Mataga, N. Bull. Chem. Soc. Jpn. 1990, 63, 131.
(b) Miyasaka, H.; Morita, K.; Kamada, K.; Mataga, N. Ibid. 1990, 63, 3385.
(c) Miyasaka, H.; Morita, K.; Kamada, K.; Mataga, N. Chem. Phys. Lett. 1991, 178, 504.

<sup>(13)</sup> Berger, M.; Nicholas, C.; Demetrescu, I.; Giering, L.; Steel, C. Isr. J. Chem. 1977. 16. 311.



Figure 1. Fluorescence excitation (Ex.) and dispersed emission (Em.) spectra observed 10 µs after 337.1-nm excitation for the benzophenone (1.0 Torr) and 1,4-cyclohexadiene (10.0 Torr) system in the gas phase. A 530-nm dye laser was used for the measurement of dispersed emission spectrum. The spectral response of the fluorescence was not corrected.

laser (Lumonics HyperDye-300) pumped by a XeCl laser (Lambda Physik EMG 52 MSC). The laser beams enter and exit through 17-cm-long baffle arms to reduce scattered light. The excitation and probe pulses coincided spatially in the sample cell and were synchronized with a variable time delay from 100 ns to several hundred micro seconds. In the kinetics measurements, the time delay was kept less than 50  $\mu$ s so as to neglect drift of the excited molecules from the detection region.

BPK fluorescence and benzophenone phosphorescence were observed by a photomultiplier (Hamamatsu R-928) connected to an EG&G Model-115 amplifier. The emitting light was detected through cutoff filters for the fluorescence excitation spectrum measurements. A monochromator (Nikon P-250) was used for the dispersed emission spectrum measurements. The signals were integrated with a Stanford SR-250 gated integrator before being digitized by an SR-245 A/D converter. A personal computer was used to normalize the signals for laser intensity fluctuations and to record excitation and dispersed emission spectra.

#### **Results and Discussion**

Emission Spectrum of BPK in the Gas Phase. It has been widely known that BPK is generated by photoreduction of benzophenone in a hydrogen-donating solvent (Scheme I). In the condensed phase, BPK has an absorption band in visible region with an absorption maximum at around 545 nm with a shoulder at 500-525 nm. Fluorescence from excited BPK characterized by a maximum near 575 nm is readily observable after the excitation into the  $D_1$  state.<sup>14-18</sup>

We tried to observe the hydrogen abstraction process of benzophenone in the gas phase by monitoring the fluorescence of BPK. Figure 1 shows fluorescence excitation (Ex.) and dispersed emission (Em.) spectra for the benzophenone (1.0 Torr)-1.4cyclohexadiene (10.0 Torr) system observed at 10  $\mu$ s after 337.1-nm excitation. A 530-nm dye laser was used for the measurement of the dispersed emission spectrum. They are very similar to the spectra of BPK in the liquid phase.

On the basis of the good agreement of the spectral data, it can be concluded that the chemical species generated in the gas phase is BPK. To our knowledge, this is the first observation of fluorescence excitation and dispersed emission spectra of BPK in the gas phase. In addition to 1,4-cyclohexadiene, similar spectra were observed when the following hydrogen donors were used: 2-propanol, triethylamine, and N,N-dimethylaniline. From the above results, we can clearly conclude that excited benzophenone

- (14) Topp, M. R. Chem. Phys. Lett. 1976, 39, 423. (15) Razi Naqvi, K.; Wild, U. P. Chem. Phys. Lett. 1976, 41, 570.
- (16) Obi, K.; Yamaguchi, H. Chem. Phys. Lett. 1978, 54, 448.



Figure 2. (a) Decay profile of benzophenone phosphorescence after 337.1-nm excitation. (b) Rise profile of fluorescence intensity of BPK probed with a 530-nm dye laser.

is reactive with hydrogen donors in the gas phase where contributions from surrounding solvents are lacking.

The fluorescence decay measured in the gas phase was as short as the scatter width of the dye laser pulse. Considering the time resolution of about 15 ns of the system in this study, the fluorescence lifetime of BPK was estimated to be less than 5 ns. The emission of BPK in the 550-650-nm region attributed to doublet-doublet transition was reported to have a fluorescence lifetime of approximately 2-5 ns in solution at room temperature.<sup>15,19,20</sup> The fluorescence lifetime measured in the gas phase shows good agreement with that in solution.

Kinetic Studies on the Decay Process of Triplet Benzophenone. The photophysics of benzophenone is governed by rapid  $S_1 \rightarrow T_1$ intersystem crossing and almost lack of fluorescence from the S<sub>1</sub>  $(n\pi^*)$  state. The absorption spectrum of benzophenone shows a weak  $n\pi^*$  transition centered near 350 nm and a more intense absorption starting at  $\sim$  310 nm due to  $\pi\pi^*$  transitions. Benzophenone emits long-lived phosphorescence after the excitation into the S<sub>1</sub> ( $n\pi^*$ ) state in the condensed phase.<sup>15,21</sup>

We observed long-lived emission from photoexcited benzophenone at 337.1 nm in the gas phase. The emission shows biexponential decays under typical experimental conditions. The emission lifetimes of benzophenone (1.0 Torr) at 380 K are about 5  $\mu$ s for the fast component and longer than 600  $\mu$ s for the slow component in the absence of hydrogen donors.

The time-resolved emission from excited benzophenone has served as a model to test various theories of radiationless processes in large molecules, thus many groups have studied the radiationless processes of excited benzophenone in the gas phase.<sup>22-24</sup> On the basis of these results, the fast and slow components of the emission observed in this study can be attributed to hot phosphorescence from unrelaxed triplet benzophenone and phosphorescence from the vibrationally relaxed levels of the triplet, respectively. The addition of hydrogen donors shortened both fast and slow components. In order to discuss the dynamics of relaxed triplet benzophenone, we will take into consideration only the slow component.

The quenching rates of triplet benzophenone by hydrogen donors were measured by monitoring the decay profiles of the phosphorescence for 337.1-nm excitation as a function of hydrogen donor pressure, while maintaining benzophenone at a constant pressure of 1.0 Torr. The pressure of hydrogen donors ranged from 0 to 50 Torr.

- 24, 162
- (23) Zevenhuijzen, D.; van der Werf, R. Chem. Phys. 1977, 26, 279. (24) Naaman, R.; Lubman, D. M.; Zare, R. N. Chem. Phys. 1978, 32, 17.

<sup>(17) (</sup>a) Hiratsuka, H.; Yamazaki, T.; Takahashi, M.; Hikida, T.; Mori, Y. Chem. Phys. Lett. 1983, 101, 341. (b) Hiratsuka, H.; Yamazaki, T.; Mackawa, Y.; Hikida, T.; Mori, Y. J. Phys. Chem. 1986, 90, 774.

<sup>(18)</sup> Johnston, L. J.; Lougnot, D. J.; Wintgens, V.; Scaiano, J. C. J. Am. Chem. Soc. 1988, 110, 518.

<sup>(19)</sup> Nagarajan, V.; Fessenden, R. W. Chem. Phys. Lett. 1984, 112, 207. (20) Johnston, L. J.; Lougnot, D. J.; Scaiano, J. C. Chem. Phys. Lett. 1986, 129, 205.

<sup>(21) (</sup>a) Jones, P. F.; Calloway, A. R. J. Am. Chem. Soc. 1970, 92, 4997.
(b) Jones, P. F.; Calloway, A. R. Chem. Phys. Lett. 1971, 10, 438.
(22) Hochstrasser, R. M.; Lutz, H.; Scott, G. W. Chem. Phys. Lett. 1974,



**Figure 3.** Stern-Volmer plots of reciprocal values of triplet lifetime of benzophenone,  $1/\tau_{T}$ , and rise time of fluorescence intensity of BPK,  $1/\tau_{R}$ , for the benzophenone-1,4-cyclohexadiene system. The squares and circles correspond to  $1/\tau_{T}$  (**D**) and  $1/\tau_{R}$  (O), respectively.



Figure 4. Stern-Volmer plots of quenching rate of triplet benzophenone.

The ketyl radical formed by 337.1-nm excitation was detected with the probe laser. Increasing the delay time between the excitation and probe lasers from 100 ns to 50  $\mu$ s resulted in an increase of ketyl radical fluorescence intensity. The rise time of BPK fluorescence also observed while increasing the pressure of hydrogen donors. Figure 2 shows a typical decay profile of benzophenone phosphorescence and a rise profile of BPK fluorescence intensity obtained in the benzophenone (1.0 Torr)-1,4-cyclohexadiene (4.0 Torr) system. From this figure, the decay time of the phosphorescence and the rise time of the fluorescence were determined to be 10.4 and 9.8  $\mu$ s, respectively. The triplet decay time was determined from the phosphorescence decay profiles in the time region from 0 to 50  $\mu$ s after the excitation to eliminate the effect of excited molecules drifting from the detection region. One can clearly see that the formation process of BPK corresponds very well to the decay process of triplet benzophenone. We confirmed that the rise profiles of BPK were in agreement with the decay profiles of triplet benzophenone varying the pressure of hydrogen donors. Typical plots of the reciprocal values of the phosphorescence lifetime,  $1/\tau_{\rm T}$ , and the rise time of fluorescence intensity of BPK,  $1/\tau_{\rm R}$ , vs the pressure of 1,4-cyclohexadiene are shown in Figure 3. Good agreement between  $\tau_T$  and  $\tau_R$  was also confirmed when 2-propanol and triethylamine were used as hydrogen donors. These facts demonstrate that triplet benzophenone generated by the photoexcitation directly produces BPK.

The phosphorescence quenching of benzophenone was also measured for the following compounds: aniline, triethylamine, N,N-dimethylaniline, cyclohexylamine, 1,4-cyclohexadiene, 2butylamine, and 2-propanol. Quenching rate constants were obtained from the plots of the decay rate for triplet benzophenone vs hydrogen donor pressure. Typical plots are shown in Figure 4 and the quenching rate constants obtained are summarized in Table I. Quenching rate constants in the liquid-phase reaction

TABLE I: Quenching Rate Constants of Triplet Benzophenone in the Gas Phase

	n an an an ann an Anna an Anna Anna Ann	$k_{\rm q} \times 10^6$ , ${\rm M}^{-1} {\rm s}^{-1}$		
	quencher	gas phase <sup>a</sup>	liquid phase <sup>b</sup>	vIP, <sup>c</sup> eV
1	aniline	31000		8.05
2	triethylamine	7800	2300	8.10
3	N,N-dimethylaniline	2900	2700	7.37
4	cyclohexylamine	960	320	9.16
5	1,4-cyclohexadiene	660	290	8.82
6	2-butylamine	500	240	9.30
7	2-propanol	15	1.7	10.40

<sup>*a*</sup>All measurements were carried out at 380 K. <sup>*b*</sup>Rate constants at room temperature obtained from refs 1, 4, 7, 8, and 24. <sup>*c*</sup>Vertical ionization potential obtained from ref 26.

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and vertical ionization potential of the quenchers are also listed in the table.

The rate constants in the gas phase and liquid phase show a similar trend for the hydrogen donors though the measurements in the gas and liquid phases were carried out at 380 and 298 K, respectively. The quenching rate constants for amines are 30–500 times larger than that for 2-propanol in the gas phase, which is comparable with the effective reactivity of amines in the liquid phase, that is,  $1.5 \times 10^2-10^3$  times larger than 2-propanol.

The mechanism for photoreduction of benzophenone by amines in the liquid phase has been extensively investigated. Cohen and co-workers<sup>4,5</sup> proposed the following reaction mechanism to explain the effective photoreduction of triplet benzophenone by amines leading to BPK formation. First, an electron is transferred from an amine to the triplet state of benzophenone, forming a charge transfer or ion pair complex. This complex is then quenched either by proton transfer generating BPK and amine radicals or by spin inversion followed by back electron transfer, resulting in the ground-state benzophenone and amines. In this generally accepted mechanism, the charge transfer interaction plays an important role, and the mechanism is represented in Scheme II.

As described above, the quenching rate constants of triplet benzophenone with amines are much larger than that with 2propanol, which is a typical hydrogen donor. It is mentioned that increase in the ionization potential of amines tends to decrease the quenching rate constant in the gas phase. These results lead us to conclude that the charge-transfer or ion pair state also plays an important role in the gas-phase reaction.

In order to clarify the importance of charge-transfer interactions in the gas-phase reaction, we have examined the relation between the quenching rate and the ionization potential of the hydrogen donors. It has been widely accepted that there is a linear inverse relation between the logarithm of quenching rate constant, log  $k_{q}$ , and ionization potential of quencher, IP, when charge transfer is the dominant process of the reaction:<sup>4,5</sup>

$$\log k_{a} = \alpha \cdot \mathrm{IP} + \beta$$

where  $\alpha$  and  $\beta$  are constants.

Recently Jacques<sup>25</sup> reported that an electron donor with the lowest IP was not necessary for the best quencher and its

<sup>(25) (</sup>a) Jacques, P. Chem. Phys. Lett. 1987, 142, 96. (b) Jacques, P. J. Photochem. Photobiol. A: Chem. 1991, 56, 159.



Figure 5. Correlation between the quenching rate constant of benzophenone triplet,  $k_q$ , and the vertical ionization potential of the quencher, vIP. Numbers refer to the compounds in Table I.

quenching efficiency depends on the nature of n or  $\pi$  electron involved. His plots of log  $k_q$  vs IP lie on two lines: the "n line" corresponds to compounds involving n ionization and the " $\pi$  line" corresponds to aromatic compounds involving  $\pi$  ionization.

Logarithms of the quenching rate constants,  $k_q$ , are plotted against the vertical ionization potential, vIP, in Figure 5 where 1,4-cyclohexadiene is not included due to its very weak ability to make the charge transfer or ion pair state. In general, reliable values of adiabatic ionization potential of organic compounds are less available than vertical ionization potential. Therefore, we restricted our discussion only to vertical ionization potential. The data except that of N,N-dimethylaniline lie on a line, which corresponds to the n line. Since N,N-dimethylaniline is classified to the compounds involving an electron of  $\pi$ -type ionization, it is less effective quencher and deviates from the n line. These facts evidently support that the charge-transfer-interaction mechanism also works in the gas-phase reaction of excited benzophenone.

Peters and co-workers<sup>6</sup> investigated the picosecond dynamics of the excited benzophenone-amine system and concluded that a key process for the proton transfer was the structural change of the solvent-separated ion pair formed by the electron transfer to the contact ion pair. On the other hand, Miyasaka et al.<sup>12</sup> recently proposed on the basis of femtosecond photolysis of the benzophenone-diphenylamine system that a very short-lived charge-transfer state at the encounter between triplet benzophenone and amine played a crucial role in the proton-transfer reaction, thus not requiring a structural change of the solventseparated ion pair state. Owing to their investigations, a long-lived ion pair state proposed by Peters and co-workers does not participate in the ketyl radical formation and the mutual orientation of benzophenone and amine in a very short-live charge-transfer state determines the successive processes, that is, the formation of BPK or relaxation without forming the radical.

As described above, it was clearly revealed that benzophenone and several hydrogen donors were reactive in the gas phase without contributions from surrounding solvent molecules and the charge-transfer interaction mechanism accounted for the gas-phase reaction. Though it is rather difficult to compare the gas-phase and liquid-phase reactions directly, we can conclude that the formation of a long-lived complex is not necessary for the reaction to take place. As shown by Miyasaka et al., the mutual orientation in a short-lived complex at encounter is important and determines the subsequent processes.

### Conclusion

Photochemical reaction of excited benzophenone with several kinds of hydrogen donors has been studied in the gas phase. Although the reaction has been well studied as one of the most fundamental photochemical reactions in the condensed phase, there was no report on the gas-phase reaction. It has been shown in this investigation that hydrogen abstraction also occurs in the gas phase without the contributions from surrounding solvent molecules. Fluorescence excitation and dispersed emission spectra of benzophenone ketyl radical in the gas phase have been reported for the first time.

We measured the quenching rate constants of triplet benzophenone with 2-propanol, 1,4-cyclohexadiene, and several kinds of amines. From these results, it was suggested that the charge-transfer interaction also played an important role in the gas-phase reaction of benzophenone-amine systems.

Recently much attention has been paid to the reactions in molecular clusters generated in a supersonic free jet expansion. It has been expected that molecular clusters enable us to study liquid-phase reaction at a molecular level without the complicating effects of the solvent environment. In the forthcoming paper, we will report the hydrogen abstraction reaction in molecular clusters of carbonyl compounds and hydrogen donors.

<sup>(26)</sup> Ionization Potential and Appearance Potential Measurements (1971-1981); NSRDS, US Department of Commerce, 1982.