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Effect of Pressure on the Primary Process of Benzophenone Photoreduction

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Abstract: The triplet lifetime of benzophenone was measured in alcohols and hydrocarbons by means of laser photolysis at high pressure. It was found that the lifetimes in the solvents used decreased monotonically with increasing pressure. The activation volume for the photoreduction at 25 °C, determined from the pressure dependence of the lifetimes, was from −6.9 cm^3/mol in methanol-d_4 to −13.1 cm^3/mol in methylcyclohexane. From the activation volume, the reactivity of triplet benzophenone for the hydrogen abstraction reactions was discussed.

The photochemistry of aromatic ketones has been studied extensively, and now it is well understood. The primary processes for the benzophenone photoreduction are characterized by the hydrogen abstraction reactions of the triplet from solvent molecules, which lead to the formation of a ketyl radical in virtually unit quantum yield in solvents such as parafins and alcohols.[1]

$$\begin{aligned} &\mathrm{Ph_2CO} \xrightarrow{h\nu} \mathrm{Ph_2CO^*} \rightarrow \mathrm{^3Ph_2CO^*} \\ &\mathrm{^3Ph_2CO^*} + \mathrm{RH} \xrightarrow{k_r} \mathrm{Ph_2\dot{C}OH} + \mathrm{\dot{R}} \end{aligned} \tag{1}$$

High-pressure study gives important information about the reaction mechanism through the activation volume.[2] Although the attempts have been mainly limited to the thermal reactions, a few works in the field of photochemistry have also proved the usefulness of high pressure from the fluorescence quantum yield and lifetime measurements.[3] However, to the authors' knowledge the pressure effect on the photoreduction has not been reported in spite of a fundamental photochemical reaction, whose reasons may be attributed to the short lifetime of the triplet (less than 1 μs).

The present work was carried out to study the volume profile for the primary process of the benzophenone photoreduction from measurements of the transient absorptions of the triplet in various solvents by means of laser photolysis under high pressure. From the activation volume for the primary process, we will discuss the reaction mechanism.

Experimental Section

Benzophenone of guaranteed grade was recrystallized twice from benzene. Solvents of spectroscopic grade were used without further purification. Toluene-d_8, 2-propanol-d_8, and methanol-d_4 were purchased from Aldrich and were used without further purification.

The block diagram of the laser photolysis system at high pressure is shown in Figure 1. A high-pressure vessel has four windows made of sapphire with an effective diameter of 8 mm. A nitrogen laser provides a pulse of 8 ns and energy of about 3 mJ/pulse. A flash lamp was used as a monitoring light source. A transient absorption was detected by a Hamamatsu R 928 or R 666 photomultiplier through a monochromator and lenses. A timing circuit adjusted a timing to turn on the laser and the flash lamp by a relay time between them. The output signal was digitized by an Iwatsu TS 8123 Stragescope (resolution: *x*, 512; *y*, 256) which was triggered with the output of a pin-photodiode (P) and transferred into a Sharp MZ 80 microcomputer through an appropriate interface. The time-resolution for this system was less than 10 ns when the signal line was terminated with 50 Ω. A sample cell with four windows (6 × 4 mm for the exciting light side; 1.3 mm ϕ for the monitoring light side) was used as an inner cell placed in the high-pressure vessel. The sample solution was separated from a pressure transmitting medium (silicon oil) by a piston with an O-ring. The angle between the monitoring light and the exciting light was 90°. The inner cell was placed so that two beams overlapped strictly by using a He-Ne laser.

Table I. Triplet Decay Constants k_T and Photoreduction Rate Constants k_r for Benzophenone at 0.1 MPa and 25 °C

substrate	solvent	$k_T/10^6$ s^{-1}	$k_r/10^5$ M$^{-1}\cdot$s^{-1}
2-propanol	neat	25.1 ± 0.4	19.2
	neat[a]	22	17
	neat[b]	14	11
	benzene[c]		18
	benzene[d]		12.8
2-propanol-d_8	neat	9.63 ± 0.11	7.35
methanol	neat	5.22 ± 0.02	2.12
methanol-d_4	neat	1.95 ± 0.01	0.789
toluene	neat	3.87 ± 0.07	4.13
	neat[e]		6.3
	benzene[f]		3.8
toluene-d_8	neat	2.15 ± 0.02	2.30
hexane	neat	3.12 ± 0.02	4.11
methylcyclohexane	neat	8.44 ± 0.11	10.8

[a] Reference 5. [b] Reference 6. [c] Reference 7. [d] Reference 8. [e] Reference 9. [f] Reference 10.

In order to check this system, we observed the singlet lifetime of phenanthrene in heptane independently by the decay measurements of fluorescence and the transient absorption due to $S_1 \rightarrow S_n$ transition up to 343 MPa. Both lifetimes obtained were equal within 5%.

The concentration of benzophenone was between 7 × 10^{-3} and 9 × 10^{-3} M. The solution was deoxygenated by bubbling nitrogen gas under nitrogen atmosphere. Temperature was controlled at 25 ± 0.1 °C. Pressure was measured by a manganin wire.

Results and Discussion

The time dependence of the observed absorbance $A(t)$ is expressed by eq 2, based on the reaction scheme of eq 1.[4]

$$A(t) = A(\infty) + [A(0) - A(\infty)]e^{-k_T t} \tag{2}$$

where

$$k_T = k_r[\mathrm{RH}]$$

In eq 2, k_T is the triplet decay constant of benzophenone, $A(0)$ is the initial absorbance of the triplet benzophenone, $A(\infty)$ is the final absorbance of the ketyl radical, and [RH] is the concentration of RH. A typical example of the decay at 530 nm is shown in Figure 2. The values of k_T were determined from the time

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(4) In general, a unimolecular decay of benzophenone triplet should be considered; however, because of the unit quantum yield for bimolecular reaction with the solvents used in this experiment, contributions from this term were assumed to be negligible.

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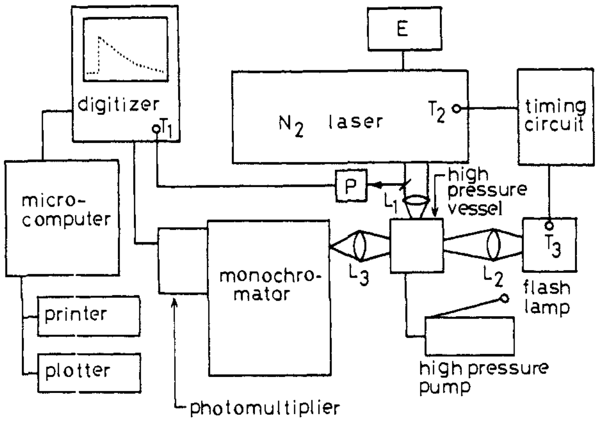

Figure 1. Block diagram for transient absorption measurements at high pressure: E, high-voltage power supply for nitrogen laser; P, pin-photodiode; L_1, L_2, and L_3, lenses; T_1, T_2 and T_3, triggers.

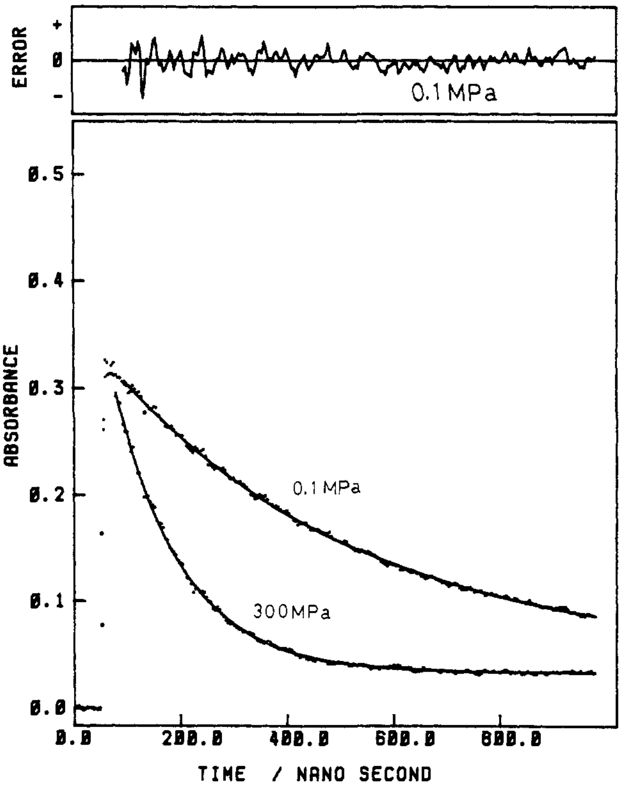

Figure 2. Time-course of absorbance (530 nm) in toluene-d_8 at two pressures.

dependence of absorption by a nonlinear least-squares method based on eq 2 (the solid lines in Figure 2). The values of k_T and k_r thus obtained at 0.1 MPa are listed in Table I and compared with those in the literature. As predicted in Table I, the present results are in good agreement with those reported previously.

As seen in Figure 2, the pressure effect on k_T is significant (the uncertainty in determinations of k_T at high pressures was found to be less than 5%). Figure 3 shows the pressure dependence on k_T. As shown in Figure 3, k_T increases monotonically with increasing pressure in the solvents used.

The pressure effect on the rate constant k_r (in molarity unit) is generally expressed in terms of the volume of activation $\Delta V_r^\ddagger$.

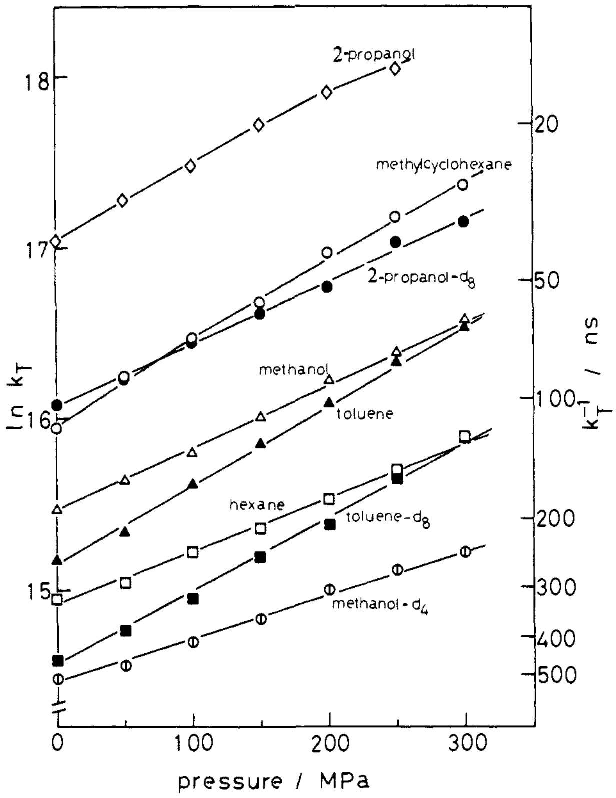

Figure 3. Pressure dependence on k_T in various solvents at 25 °C (k_T uncertainties are within 5%).

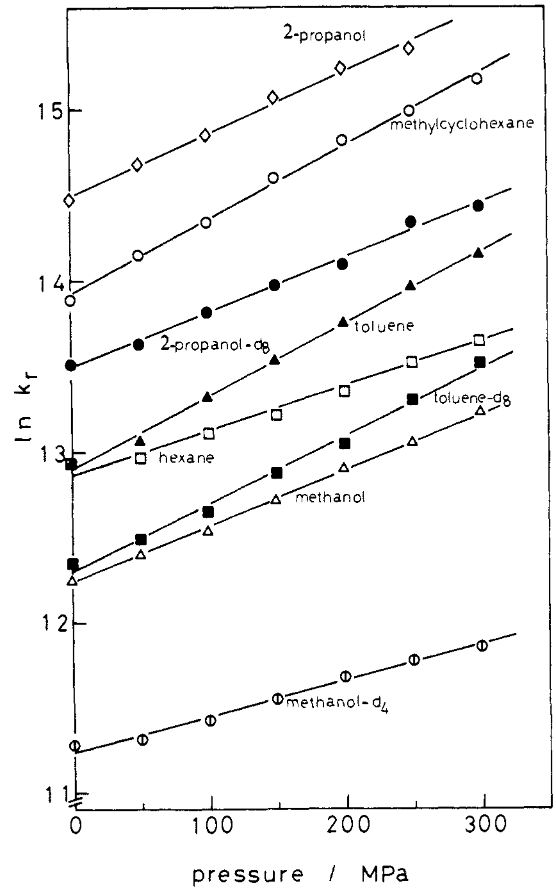

Figure 4. Pressure dependence of k_r in various solvents at 25 °C (k_r uncertainties are within 5%).

$$RT\left(\frac{\partial \ln k_r}{\partial P}\right)_T = -\Delta V_r^\ddagger + RT\kappa\Delta\beta^\ddagger \qquad (3)$$

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Table II. Activation Volumes $\Delta V_r^\ddagger$ for Photoreduction of Benzophenone at 0.1 MPa and 25 °C

substrate	$\Delta V_r^\ddagger$/cm^3·mol^{-1}
2-propanol	-10.6 ± 0.3
2-propanol-d_8	-9.6 ± 0.2
methanol	-9.7 ± 0.1
methanol-d_4	-6.9 ± 0.2
toluene	-12.6 ± 0.2
toluene-d_8	-11.8 ± 0.3
hexane	-9.7 ± 0.3
methylcyclohexane	-13.1 ± 0.3

In eq 3, κ is the compressibility of the solvent and $\Delta\beta^\ddagger$ is the difference in the number of molecules between the initial and the transition states. In the present work, $\Delta\beta^\ddagger = -1$. The term $RT\kappa$ at 25 °C and 0.1 MPa was calculated from the available data.[11] The plots of ln k_r against pressure were almost linear (Figure 4). From the plots, $\Delta V_r^\ddagger$ was determined by a least-squares method. The results are summarized in Table II.

The volume of activation consists of two major contributions, one due to structure change of activation $\Delta V^\ddagger_{(str)}$ and the other due to solvation change $\Delta V^\ddagger_{(solv)}$. In the case of the bond-forming process, $\Delta V^\ddagger_{(str)}$ would be negative. When electronic charge is generated during activation, $\Delta V^\ddagger_{(solv)}$ will also be negative, the magnitude of which depends on the solvent polarity. As indicated in Table II, the values of $\Delta V_r^\ddagger$ are almost constant in alcohols and nonpolar solvents. Therefore, the present results may mean that the transition state is not polar and that the negative activation volume is mainly attributed to the structural change, leading to an estimation of $\Delta V_r^\ddagger$ by a cylindrical model.

Previtali and Scaiano[12] have successfully applied the bond energy-bond order (BEBO) method to the hydrogen abstraction reactions of the triplet state of carbonyl compounds and calculated the activation energies and preexponential factors for radical-like atom abstractions. According to their calculation, the fractional bond orders of $n^\ddagger$ in the transition state are 0.77 and 0.57 for toluene and methanol, respectively, where $m^\ddagger + n^\ddagger = 1$.

$$\mathrm{C{=\!=}O}\overset{m^\ddagger}{\cdots}\mathrm{H}\overset{n^\ddagger}{\cdots}\mathrm{C_\alpha H_2R'}\ (\mathrm{R'} = \mathrm{Ph, OH}) \qquad (4)$$

From the fractional bond orders, the bond length in the transition state was determined to be 0.135 nm (O- - -H bond) and 0.116 nm (C_α- - -H bond) for toluene and 0.119 nm (O- - -H bond) and 0.124 nm (C_α- - -H bond) for methanol. Assuming that the O, H, and C_α atoms are collinear in the transition state, the distances between O and C_α atoms are 0.251 and 0.243 nm for toluene and methanol, respectively. The initial O- - -C_α distance is the sum of the C_α—H bond length (0.109 nm) and van der Waals radii of H (0.120 nm) and O (0.152 nm), i.e., 0.381 nm, so that the shortening of the distances between O and C_α atoms on forming the transition state is thus 0.130 nm for toluene and 0.138 nm for methanol. If the cross section is taken to be the van der Waals radius of CH_3 (0.200 nm), the values of $\Delta V_r^\ddagger$ are estimated to be −9.8 and −10.4 cm^3/mol for toluene and methanol, respectively. The agreement with the experimental values (Table II) is satisfactory.

There is no comparable information about the pressure effect on the chemical reactivity of the excited molecules. However, the reactivity for the hydrogen abstraction reactions of triplet aromatic ketones has been compared to that of alkoxy radicals.[13] In fact, the magnitude of $\Delta V_r^\ddagger$ (Table II) is nearly equal to that of hydrogen abstraction reactions between DPPH and phenol derivatives (−11.4 to −13.5 cm^3/mol)[14] and that for the reactions between hydrogen donors and various radical sources.[15] From the facts mentioned above, we may conclude that triplet benzophenone is radical-like in reactivity.

Finally, the deuterium isotope effects k_r^H/k_r^D were 2.61, 2.69, and 1.80 at 0.1 MPa for 2-propanol, methanol, and toluene, respectively. The values of k_r^H/k_r^D in alcohols are nearly equal to that reported for benzohydrol (2.7).[16] Furthermore, it is of worth to note that k_r^H/k_r^D was almost independent of pressure for 2-propanol and toluene, while it increased slightly with increasing pressure for methanol (Table II). Isaacs et al.[17] and Sugimoto et al.[18] have independently suggested that for the proton transfer and hydride transfer reactions associated with tunneling the kinetic isotope rate ratio k^H/k^D is changed with pressure. Formosinho[19] has tried to interpret theoretically the hydrogen abstraction reactions of triplet ketones in terms of tunneling. Therefore, experiments along these lines for the methanol system are continuing in our laboratory.

Registry No. Ph_2CO, 119-61-9; D_2, 7782-39-0.

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