



Reaction volume and enthalpy changes in photochemical reaction detected by the transient grating method; photodissociation of diphenylcyclopropenone

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Abstract

A method for the measurement of reaction volume (ΔV) and enthalpy (ΔH) changes of a photochemical reaction is presented based on the transient grating technique. Since ΔV and ΔH contributions are detected separately by the time-resolved manner, this new method does not require changing the temperature or the solvent. If the diffusion constants of the species are very different, the partial molar volume of each chemical species can be determined. This method is applied to the photodissociation reaction of diphenylcyclopropenone. This method also provides a very accurate and convenient way to measure the diffusion constant of gaseous molecules in liquids.

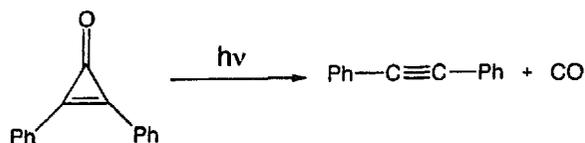
1. Introduction

Since molecular volume (ΔV) and enthalpy (ΔH) changes during a photochemical reaction are important and fundamental quantities which characterize the reaction, many attempts have been made to develop a methodology for the measurement.

Photothermal techniques such as the photoacoustic (PA), thermal lens (TL), and transient grating (TG) methods can detect the (thermal) volume change of the medium, and they provide very useful ways for detecting the volume change as well as the enthalpy change, in particular, for irreversible chemical reactions. Indeed, Westrick et al. have shown a ΔV and ΔH measurement in 1987 using the PA method [1]. Various extensions of this method have been reported since then [2-8]. Morais et al. showed

that the TG method is also useful for these measurements [9]. Genberg et al. used the TG method for evaluating the volume change of a protein after photoexcitation [10,11]. Recently, Schulenberg et al. used the photothermal beam defraction (similar to TL) to measure ΔV and ΔH in some chemical reactions [12].

Although they are useful and elegant spectroscopic methods for evaluating ΔV and ΔH , they still suffer from some limitations. The most serious limitation is that we have to detect the photothermal signals separately due to the volume change from that due to the thermal effect. Unfortunately, this separation is not trivial in many cases (except a special case where the volume effect is much larger than the thermal effect) [10,11]. For the separation, in most of the previous studies, they changed the



Scheme 1.

efficiency of the signal creation from the thermal effect by changing the temperature in aqueous solution cases [1–5,7,8,12], or by changing the matrix (a series of alkanes or binary solution) [3,6,8,9]. However, in both cases, one has to assume that ΔV and ΔH are independent of the temperature or the solvent, and sometimes this assumption cannot be correct.

In this Letter, we show a new method to measure ΔV and ΔH by using the TG method but without changing the temperature or the solvent. This method is based on the separation of the ΔV effect from the thermal effect by a time-resolved manner. Furthermore there are more merits in this method. If the diffusion constants of the species involved in the reaction are different, the partial molar volume of each species in the solution can be determined. Here we studied the photodissociation of diphenylcyclopropenone (DPCP), an extensively studied reaction systems [3,6,13,14] as an example (Scheme 1). The reaction takes place within a few picoseconds after the photoexcitation with a quantum yield of unity [13,14].

From the TG signal, we can measure not only the total ΔV in the reaction, but also the partial molecular volume of CO as well as ΔH in one solvent at one temperature. We would also like to stress that this method provides a very convenient and accurate way for measuring the diffusion constant of a gaseous molecule (CO in this case) in liquid.

2. Experiment

The experimental setup for the TG measurement is similar to the one reported previously [15–17]. Briefly, the third harmonics of a Nd:YAG laser (Spectra Physics, GCR 170-10) with a 10 ns pulse width was used as an excitation beam. The pulse was split with a beam splitter and then crossed inside a quartz square sample cell. A He–Ne laser beam (a

probe beam) was brought into the sample at the Bragg condition. The diffracted probe beam by the grating was detected by a photomultiplier tube (Hamamatsu R-928), fed into a digital oscilloscope and then the data were transferred to a microcomputer for averaging and signal processing.

The sample solution was gently stirred with a micromagnetic stirrer to dissipate products away from the excitation region. The irradiated volume is so small (typically $\approx 0.03 \text{ cm}^3$) compared with the entire volume of the sample ($\approx 4 \text{ cm}^3$) that the interference due to the products in the signal should not be serious during the measurement. We checked that the stirring did not distort the time profile of the signal. For a reference sample, nitrobenzene was used. Since the lifetimes of the photoexcited states of nitrobenzene are less than 1 ns, and the radiative transition (luminescence) and a photochemical reaction are negligible [18], all of the photon energy absorbed by nitrobenzene should be released as heat promptly in a time scale longer than 10 ns. Furthermore, the short lifetimes of the excited states ensure that the molecular volume or solvent re-organization around it will be restored quickly. DPCP, a solvent (heptane), and nitrobenzene were purchased from Nakarai Chem. Co. and used without purification. The absorbance of all samples is adjusted to 0.2 at the excitation wavelength.

3. Results and discussion

3.1. ΔH and molecular volume of CO

After the photoexcitation of nitrobenzene in heptane, a strong thermal grating signal, which comes from the thermal energy released by the nonradiative transition is observed (Fig. 1). The signal decays to the baseline completely with a time constant of $D_{\text{th}}q^2$, where D_{th} is the thermal diffusion constant and q is the wave vector of the grating. Since all of the photon energy absorbed by nitrobenzene is released as heat, the signal intensity should be expressed by

$$I_{\text{ref}}^{1/2}(t) = A \frac{dn}{dT} h\nu \Delta N / C_p \rho \exp(-D_{\text{th}}q^2t), \quad (1)$$

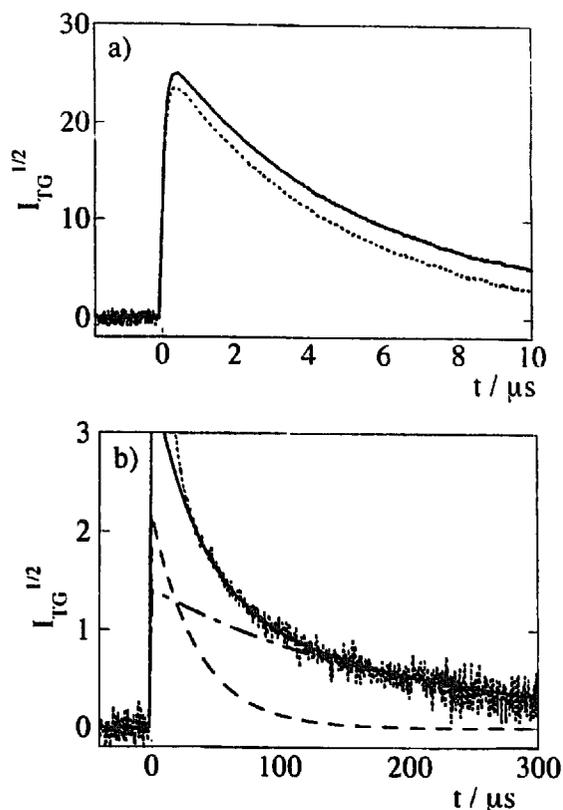


Fig. 1. (a) The thermal grating signal after the photoexcitation of the reference (nitrobenzene) sample (dotted line) and that of DPCP in heptane (solid line). (b) The grating signal of the species component of DPCP sample (solid line) and the best fitted curve with Eqs. (4b) and (4c) (dotted line). The deviation of the calculated line from the observed one in $t < 20 \mu\text{s}$ is due to the contribution of the thermal grating. Contributions from CO (Eq. (4b)) and DPA + DPCP (Eq. (4c)) are separately shown by the broken lines.

where A is a proportional constant (instrumental factor), $h\nu$ the photon energy for the excitation, C_p the heat capacity of the solution, ρ the density, dn/dT the temperature coefficient of the refractive index at the temperature, and ΔN is the number of the photoexcited molecules in unit volume.

The TG signal after the photoexcitation of DPCP in heptane is shown in Fig. 1. First, a strong thermal grating signal is observed. After this signal, another weaker signal becomes apparent in a longer time scale. Apparently the slower decay is a consequence of the mass diffusion of the reactant and the products in the solution (vide infra). Since there is no absorption around the probe wavelength from any species involved in this reaction, the signal should be due to

the pure phase grating. Hereafter this component due to the chemical species is called the species component. Theoretically the temporal profile in this system should be expressed by [16,17]

$$I_{\text{TG}}^{1/2}(t) = A \left[\delta n_{\text{th}} \exp(-D_{\text{th}} q^2 t) + \delta n_{\text{CO}} \exp(-D_{\text{CO}} q^2 t) + \delta n_{\text{DPA}} \exp(-D_{\text{DPA}} q^2 t) - \delta n_{\text{DPCP}} \exp(-D_{\text{DPCP}} q^2 t) \right], \quad (2)$$

where the subscripts CO and DPA stand for carbon monoxide and diphenylacetylene, respectively, δn is the refractive index change due to the creation (or depletion) of the species, and D the diffusion constant. The refractive index changes of the species components can originate from the refractive indexes of these species (the so-called population grating component) and from the volume change (we may call this TG signal the volume grating component). Essentially, the origin of the volume grating comes from the refractive index difference between the presence and absence of the 'solvent' molecules in the volume of the 'solute' as shown later.

We find that the temporal profile of the TG signal after the photoexcitation of DPCP (Fig. 1) can be fitted reasonably well with a sum of three exponentials,

$$I_{\text{TG}}^{1/2}(t) = a_1 \exp(-D_1 q^2 t) + a_2 \exp(-D_2 q^2 t) + a_3 \exp(-D_3 q^2 t), \quad (3)$$

where the decay rate constants are ordered as $D_1 q^2 > D_2 q^2 > D_3 q^2$. Since, apparently, the thermal diffusion should be faster than any mass diffusion, we can safely attribute a_1 and D_1 to $A\delta n_{\text{th}}$ and D_{th} , respectively. The second and third terms in Eq. (3) should be assigned to the chemical species of CO, DPA and DPCP. According to the studies on diffusion constants, D of CO should be an order of magnitude larger than that of DPA or DPCP (Section 3.4) [19]. Therefore, it is reasonable that D_2 is attributed to D_{CO} . The remaining component, D_3 is now assigned to D_{DPA} or D_{DPCP} . Probably the diffusion constants of DA and DPCP are similar to each other and the observed D_3 may be an average of D_{DPA} and D_{DPCP} .

It is important to note that the total phase grating signal can be now separated into the thermal grating, the species grating due to CO and that due to DPA and DPCP. The magnitudes of these signals at $t = 0$ should be proportional to the refractive index change and are given by

$$I_{\text{th}}^{1/2}(t=0) = A\delta n_{\text{th}} = A \frac{dn}{dT} h\nu \Delta N \phi / C_p \rho, \quad (4a)$$

$$I_{\text{CO}}^{1/2}(t=0) = A\delta n_2 = A\delta n_{\text{CO}}^0 + B\bar{V}_{\text{CO}}, \quad (4b)$$

$$I_3^{1/2}(t=0) = A\delta n_3 = A(\delta n_{\text{DPA}}^0 - \delta n_{\text{DPCP}}^0) + B(\bar{V}_{\text{DPA}} - \bar{V}_{\text{DPCP}}), \quad (4c)$$

where ϕ is the efficiency of the heat releasing process ($\phi = (h\nu - \Delta H)/h\nu$), \bar{V} represents the partial molar volume of each species in the solution, and δn^0 is the refractive index change which is concomitant with the absorption change of each species. B is a conversion factor from the volume of the species to the refractive index of the 'solvent'. If we evaluate the refractive index with the Lorentz–Lorenz relation, the δn^0 terms and B can be written as [20]

$$\delta n_{\text{CO}}^0 = \left[(n_0^2 + 2)^2 / 18n_0 \epsilon_0 \right] \alpha_{\text{CO}} \Delta N, \quad (5a)$$

$$B = -A \left[(n_0^2 + 2)^2 / 18n_0 \epsilon_0 \bar{V}_{\text{solvent}} \right] \alpha_{\text{solvent}} \Delta N, \quad (5b)$$

by using n_0 , the refractive index of the solvent, ϵ_0 , the permittivity of vacuum, and α , the polarizability of the species.

After these notations, the species component at $t = 0$ is written by the sum of the population grating and volume grating as $A(\delta n_{\text{CO}}^0 + \delta n_{\text{DPA}}^0 - \delta n_{\text{DPCP}}^0) + B\Delta V$, where the total reaction volume change in this reaction is given by

$$\Delta V = \bar{V}_{\text{CO}} + \bar{V}_{\text{DPA}} - \bar{V}_{\text{DPCP}}.$$

Based on the separation of the species grating from the thermal grating, the enthalpy change of this reaction can be directly obtained by comparing the thermal signal intensity ($I_{\text{th}}^{1/2}(t=0)$) with the reference sample ($I_{\text{ref}}^{1/2}(t=0)$) and the quantity is found $\Delta H = 0.9 \pm 1.0$ kcal/mol. This value is discussed in a later section.

From the observed signal (no interference dip between the thermal component and the species

components), we can immediately find that the signs of the a_2 and a_3 in Eq. (3) should be negative. According to the Kramers–Kronig relation, an absorption band located at a shorter wavelength than the probe wavelength gives positive phase grating. Therefore the negative sign of δn_{CO} should be mainly caused by the presence of \bar{V}_{CO} in Eq. (4b). We estimate δn_{CO}^0 from Eq. (5) and the partial molar volume of CO in heptane (\bar{V}_{CO}) is obtained ($\bar{V}_{\text{CO}} = 39 \pm 3$ cm³/mol). To our knowledge, this is the first measurement of \bar{V}_{CO} in heptane. For checking the adequacy of this method, we compared this value with that of a similar gaseous molecule measured by a traditional method. For example, the molar volume of nitrogen, \bar{V}_{N_2} , in CCl₄ has been measured to be 58.1 cm³/mol by a pressure dependence of the solubility [21]. \bar{V}_{CO} in heptane is somewhat smaller than \bar{V}_{N_2} in CCl₄. However, the value is close to the molar volume of CO at the boiling point (34.9 cm³/mol) [21]. Considering that the partial molar volume depends on the properties of the solute (such as the dipole moment) as well as the solvent, we think the measured value is not unreasonable.

3.2. Total volume change

In Section 3.1, we determined ΔH and \bar{V}_{CO} from the thermal and species grating signals. Next, using these data, we measure the total volume change ΔV in this reaction from the TG acoustic signal. In the initial part of the TG signal, an acoustic oscillation is observable when the oscillation period is not shorter than the pulse width of the excitation beam or the relaxation rate of the excited states. This acoustic oscillation is the consequence of the heating effect of the matrix and the volume change effect (but not of the population grating). Therefore, for the DPCP sample, the square root of the maximum intensity of the acoustic signal before the acoustic damping ($I_{\text{ac}}^{1/2}$) (Fig. 2) is given by

$$I_{\text{ac}}^{1/2} = 2A \frac{dn}{dT} \Delta N (h\nu \phi / C_p \rho + \Delta V / \alpha), \quad (6)$$

where α is the thermal expansion coefficient ($\alpha = (1/V) \partial V / \partial T$). The acoustic signal intensity of the reference sample is given by the same equation with $\Delta H = \Delta V = 0$.

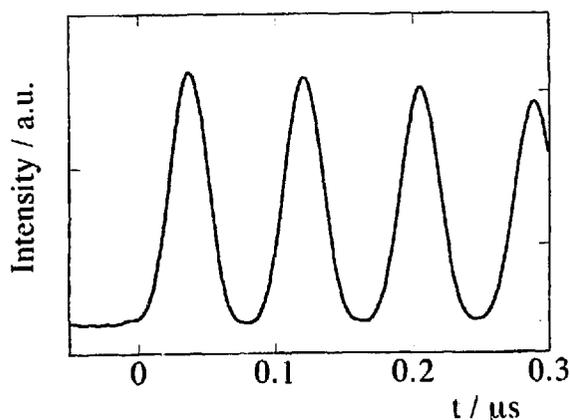


Fig. 2. Typical example of the acoustic signal of DPCP sample in heptane.

We measured the TG acoustic signal with a small Λ using the same experimental setup ($\Lambda \sim 80 \mu\text{m}$). By comparing with the signal intensity of the reference sample and using ΔH , ΔV can be determined to be $24 \pm 5 \text{ cm}^3/\text{mol}$. From $\bar{V}_{\text{CO}} = 38.5 \text{ cm}^3/\text{mol}$; $(\bar{V}_{\text{DPA}} - \bar{V}_{\text{DPCP}})$ is calculated to be $-14.9 \text{ cm}^3/\text{mol}$. Therefore, we find that the total reaction volume is similar to the molecular volume of CO, which means that ΔV mainly comes from the creation of CO.

Previously, ΔH and ΔV in this photodecomposition reaction are determined to be $2.5 \pm 2.5 \text{ kcal/mol}$ and $60.1 \pm 4.5 \text{ cm}^3/\text{mol}$ in water (from the temperature dependence method) [2] and $-6.7 \pm 1.2 \text{ kcal/mol}$ and $23 \pm 4 \text{ cm}^3/\text{mol}$ in a series of alkanes from the PA signal intensity [6]. Our determined value of $\Delta V (= 23.6 \text{ cm}^3/\text{mol})$ is close to that in alkanes, but the enthalpy change ($\Delta H = 0.9 \text{ kcal/mol}$) is rather larger than the previously reported one in alkanes by Hung and Grabowski. In their studies, they measured the PA intensity in a series of alkanes, plotted against a parameter that includes the thermal expansion coefficient, extrapolated to infinitely small thermal expansion condition for ΔV , and calculated the slope for ΔH . In these methods, it was assumed that ΔH and ΔV do not depend on the nature of the alkanes and some errors might be introduced by the extrapolation. In our measurement, the quantities are free from such errors. Now we are underway for obtaining these properties in various solvents and water to compare them to the previous ones.

3.3. Diffusion constant of gaseous molecule in liquids

In the previous sections, we have shown how ΔV and ΔH can be determined in one solvent at one temperature. Another interesting prospect from this study is the measurement of diffusion constant of a gaseous molecule in solution. Fig. 3 shows the k versus q^2 plot of the δn_2 and δn_3 components of the TG signal. Both decay rates show linear relations to q^2 , which support the prediction that the decay of the signal is determined by the diffusion process among the fringes (Eq. (2)). From the slopes, D_{CO} and D_3 are determined as 1.2×10^{-8} and $2.4 \times 10^{-9} \text{ m}^2/\text{s}$, respectively.

This method provides a very accurate, convenient and less time consuming way for the measurement of the diffusion constant of gaseous molecule in liquids, which usually requires rather complicated special setups by traditional methods [19]. Of course, this method is applicable only for the gases that can be produced by photochemical reactions. However once one has a photochemical reaction to produce a gaseous molecule, it is applicable at any temperature in any solvent under any conditions. Indeed, we recently found that D_{CO} can be measured also by the photodecomposition reaction of dibenzyl ketone and D_{N_2} by using the photodecomposition of diazo-compounds.

In summary, we present a new photothermal (TG) method for a measurement of reaction volume (ΔV)

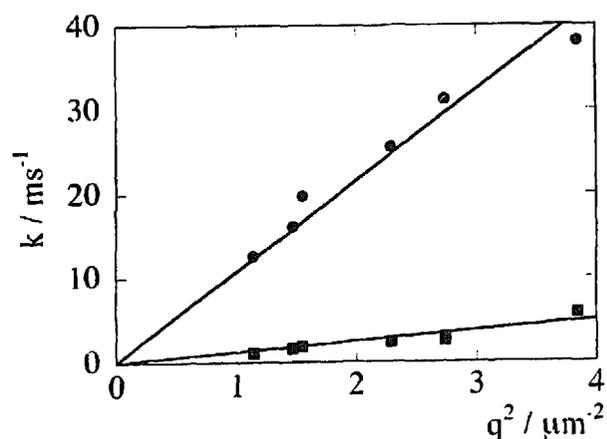


Fig. 3. Plot of the decay rate constants of the species component k versus q^2 .

and enthalpy (ΔH) changes by a photochemical reaction without using the temperature dependence nor the solvent dependence. This method is based on the separation of the ΔV effect from the ΔH effect by the time-resolved manner. We applied this method to the photodissociation reaction of DPCP and determined $\Delta V = 23.6 \text{ cm}^3/\text{mol}$ and $\Delta H = 0.9 \text{ kcal/mol}$. Not only the total ΔV but also a partial molecular volume of each species can be determined if the diffusion constants of these species are different (for example, $\bar{V}_{\text{CO}} = 38.5 \text{ cm}^3/\text{mol}$ which gives $\bar{V}_{\text{DPA}} - \bar{V}_{\text{DPCP}} = -14.9 \text{ cm}^3/\text{mol}$). Since this method does not require the solvent or temperature dependence nor any extrapolation procedure which is essential in the previous methods, it will give more accurate data and has a merit to study the effect of solvent or temperature on these properties.

References

- [1] J.A. Westrick, J.L. Goodman and K.S. Peters, *Biochem.* 26 (1987) 8313.
- [2] K.S. Peters and G.J. Snyder, *Science* 241 (1988) 1053.
- [3] M.S. Herman and J.L. Goodman, *J. Am. Chem. Soc.* 111 (1989) 1849.
- [4] M.S. Herman and J.L. Goodman, *J. Am. Chem. Soc.* 111 (1989) 9105.
- [5] K. Marr and K.S. Peters, *Biochem.* 30 (1991) 1254.
- [6] R.R. Hung and J.J. Grabowski, *J. Am. Chem. Soc.* 114 (1992) 351.
- [7] S. Malkin, M.S. Churio, S. Shochat and S.E. Braslavsky, *J. Photochem. Photobiol.* 23B (1994) 79.
- [8] M.S. Churio, K.P. Angermund and S.E. Braslavsky, *J. Phys. Chem.* 98 (1994) 1776.
- [9] J. Morais, J. Ma and M.B. Zimmt, *J. Phys. Chem.* 95 (1991) 3885.
- [10] L. Genberg, Q. Bao, S. Gracewski and R.J.D. Miller, *Chem. Phys.* 131 (1989) 81.
- [11] L. Richard, L. Genberg, J. Deak, H-L. Chiu and R.J.D. Miller, *Biochemistry* 31 (1992) 10703.
- [12] P.J. Schulenberg, W. Gartner and S.E. Braslavsky, *J. Phys. Chem.* 99 (1995) 9617.
- [13] R.W. Fessenden, P.M. Carton, H. Shimamori and J.C. Scaiano, *J. Phys. Chem.* 86 (1982) 3803.
- [14] Y. Hirata and N. Mataga, *Chem. Phys. Letters* 193 (1992) 287.
- [15] M. Terazima and N. Hirota, *J. Chem. Phys.* 95 (1991) 6490.
- [16] M. Terazima and N. Hirota, *J. Chem. Phys.* 98 (1993) 6257.
- [17] M. Terazima, K. Okamoto and N. Hirota, *J. Phys. Chem.* 97 (1993) 13387.
- [18] M. Takezaki, M. Terazima and N. Hirota, to be published.
- [19] R.J. Combs and P.E. Field, *J. Phys. Chem.* 91 (1987) 1663.
- [20] T. Hara, M. Terazima and N. Hirota, to be published.
- [21] J.H. Hildebrand, J.M. Prausnitz and R.L. Scott, in: *Regular and related solutions* (Van Nostrand Reinhold, New York, 1970).