

# Heat of reaction and reaction volume for the formation of ethers from diazo compounds in methanol

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## Abstract

The heat of reaction and reaction volume for formation of ethers from several diazo compounds with two phenyl groups in methanol were determined by the transient grating and photoacoustic methods. It was found that the reaction volume significantly contributes to the photothermal signal and that the reaction volume is sensitive to the molecular structure of the diphenyl groups. The reaction volume is as large as 51 ml/mol for the creation of diphenylmethyl methyl ether. This large volume change is interpreted in terms of the rearrangement of phenyl groups by the reaction. The partial molar volume of  $N_2$  and diffusion constants of  $N_2$  and diazo compounds are determined simultaneously. © 1998 Elsevier Science B.V.

## 1. Introduction

During photochemical reactions, atomic rearrangements occur and result in changes in molecular energy and molecular volume. To characterize the photochemical reaction, changes in volume ( $\Delta V$ ) and enthalpy ( $\Delta H$ ) are certainly fundamental quantities which have been measured mainly by the pressure and temperature dependencies of the equilibrium constant (for reversible reaction) and/or the reaction rate [1,2]. However, these methods cannot always be applied.

In one pioneering work, Simon and Peters applied photoacoustic (PA) spectroscopy to measurement of the heat of reaction for the formation of diphenylcarbene and diphenylmethyl ethyl ether from diphenyldiazomethane (DPDM) [3]. However, although the reaction volume change could contribute to the PA

signal besides the thermal energy, only the thermal energy was considered as the source of the pressure wave in their analysis. Based on recently accumulated data [4–11], it is plausible that the volume change could significantly contribute to the PA intensity. Any data in which the volume effect was not considered should be re-examined. However, separation of the thermal from the volume contribution in the PA signal is not simple. In principle, each contribution can be separated by measuring the PA intensity with varying the thermal expansion coefficient of the matrix. For aqueous solution, this can be achieved by varying the temperature. For organic solvents, the thermal expansion coefficient is less temperature dependent, and the binary-solvents method was sometimes used. Changing the solvent, however, will change the reaction mechanism or reaction rate considerably in some cases, such as the chemistry of carbenes. Therefore, it should be rather difficult to determine  $\Delta V$  and  $\Delta H$  in general by the PA method for the above-mentioned reaction system.

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Recently we presented a new method for  $\Delta V$  and  $\Delta H$  measurements using the transient grating (TG) technique [12–14]. Contributions of  $\Delta V$  and  $\Delta H$  can be separated in a time-resolved manner and do not require any temperature or solvent variations. In this Letter, we report on the application of TG to the reaction of ether formation from carbenes. The result indicates a non-negligible involvement of the volume effect in the pressure wave and grating signal. We measure accurate values of  $\Delta H$  and  $\Delta V$  for ether formation from DPDM in methanol. Furthermore,  $\Delta H$  and  $\Delta V$  for other diazo compounds were studied by the same method. The results obtained are discussed in terms of the molecular structure.

## 2. Method

### 2.1. Apparatus

The TG setup has been described previously [12–14]. Briefly, laser light from an excimer laser (Lumonics Hyper-400) was split by a beam splitter and crossed inside a quartz sample cell. Typically, the excitation laser power was in the 2–10  $\mu\text{J}$ /pulse range. The created interference pattern (transient grating) in the sample was probed by an He–Ne laser as a Bragg diffracted signal (TG signal). The TG signal was detected by a photomultiplier (Hamamatsu R928) and averaged by a digital oscilloscope.

Photoacoustic signal was detected by a piezoelectric transducer (PZT) as described previously [15]. The signal was directly detected by the digital oscilloscope and averaged about 100 times. The repetition rate of the excitation laser was about 3 Hz and the sample was gently stirred during measurement to prevent possible bleaching of the reactant. Concentrations of the samples were adjusted so that the absorbance in a cell of 1 cm optical path length became 1.0. Typically the concentration was about  $10^{-4}$  M. The quantum yields of the ether formation were measured from the ground-state absorption change after photoradiation with a certain number of photons. The photodissociation quantum yield of diphenyldiazomethane ( $\phi = 0.76$ ) was used as a reference sample [16]. All measurements were carried out at room temperature.

### 2.2. Analysis

The procedure for determination of  $\Delta V$  and  $\Delta H$  from the TG signal was reported previously [12–14]. Briefly, if the absorptive contribution is negligible and the diffraction efficiency of the probe light is small, the TG signal intensity is proportional to the square of the peak – null difference of the refractive index in the grating pattern and given by

$$I_{\text{TG}}(t)^{1/2} = A|\delta n_{\text{Q}}(t) + \delta n_{\text{H}}(t) + \delta n_{\text{p}}(t) + \delta n_{\text{v}}(t)| \quad (1)$$

where  $A$  is a constant representing the sensitivity of the system,  $\delta n_{\text{Q}}$  is thermal grating due to the non-radiative transition from the initially created excited state,  $\delta n_{\text{H}}$  originates from the thermal contribution of the reaction heat, and  $\delta n_{\text{p}}$  and  $\delta n_{\text{v}}$  are refractive index changes induced by changes of the absorption spectrum and molecular volume by the reaction, respectively. The terms  $\delta n_{\text{p}}$  and  $\delta n_{\text{v}}$  are called the ‘population grating’ and ‘volume grating’, respectively, and the sum of these terms ( $\delta n_{\text{p}} + \delta n_{\text{v}}$ ) is called ‘species grating’.

In the reaction system under consideration, the reaction completes in the initial stage of the TG signal and forms a final product (Scheme 1). The time dependence of the thermal contribution is given by

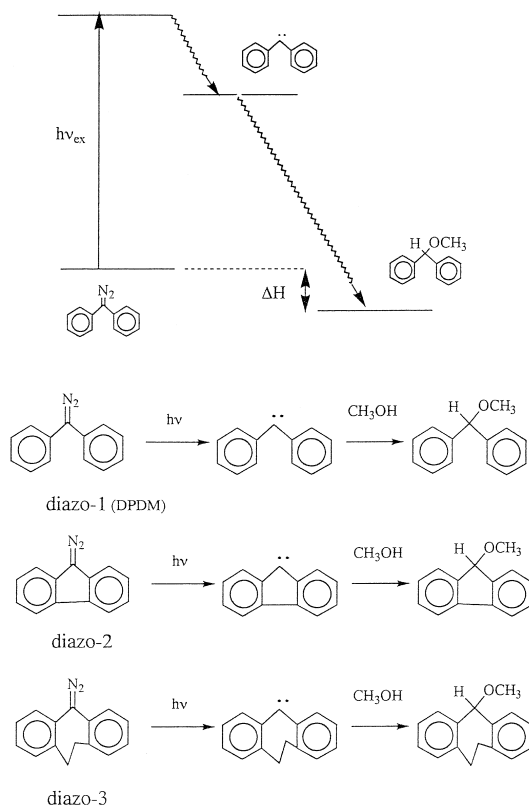
$$\delta n_{\text{Q}}(t) = \left( \frac{dn}{dT} N h \nu_{\text{ex}} \frac{W}{\rho C_p} \right) \exp(-D_{\text{th}} q^2 t) \quad (2)$$

$$\delta n_{\text{H}}(t) = \left( \frac{dn}{dT} N \phi \Delta H \frac{W}{\rho C_p} \right) \exp(-D_{\text{th}} q^2 t) \quad (3)$$

where  $dn/dT$  is the refractive index change by the temperature change,  $N$  is number density of the excited molecule,  $h\nu_{\text{ex}}$  is photon energy for the excitation light,  $W$  is molecular weight,  $\rho$  is density,  $C_p$  is heat capacity,  $\phi$  is quantum yield of the reaction,  $D_{\text{th}}$  is thermal diffusivity, and  $q$  is magnitude of the grating vector. The temporal profile of the species grating can be expressed by

$$\delta n(q, t) = -\delta n_{\text{r}} \exp(-D_{\text{r}} q^2 t) + \Sigma \delta n_{\text{p}} \exp(-(D_{\text{p}} q^2) t) \quad (4)$$

where  $\delta n_{\text{r}}$  and  $\delta n_{\text{p}}$  represent refractive index changes



Scheme 1.

by the presence of the product and reactant, respectively.  $D_p$  and  $D_r$  are the diffusion constants of the product and reactant, respectively.  $\delta n_r$  and  $\delta n_p$  contain both the population contribution and volume effect.

Since the decay rate due to thermal diffusion ( $D_{\text{th}}q^2$ ) is normally one or two orders of magnitude faster than that of the species grating ( $D_pq^2$  or  $D_rq^2$ ), these contributions can be easily separated. Hence,  $\phi\Delta H$  can be determined by comparison with the signal intensity of a reference sample, which converts the photon energy ( $h\nu_{\text{ex}}$ ) to the thermal energy with a known efficiency. The intensity,  $I_{\text{TG}}^{\text{ref}}$ , is given by

$$I_{\text{TG}}^{\text{ref}}(t)^{1/2} = A \left| \frac{dn}{dT} N \left( h\nu_{\text{ex}} \frac{W}{\rho C_p} \right) \exp(-D_{\text{th}}q^2t) \right|$$

for the unit quantum yield of the non-radiative transition.

$\Delta V\phi$  is determined from the intensity of the pressure wave after the reaction. Previously, we used the TG method for pressure detection [12,13]. In this Letter, the PA method is used because of a simple experimental setup. The PA intensity ( $I_{\text{PA}}$ ) is given by

$$I_{\text{PA}} = A'N \left| \left( h\nu_{\text{ex}} + \phi\Delta H \right) \frac{W\alpha_{\text{th}}}{\rho C_p} + \Delta V\phi \right| \quad (5)$$

where  $A'$  is a proportional constant which includes the sensitivity of the apparatus, and  $\alpha_{\text{th}}$  is the thermal expansion coefficient. From the acoustic signal intensity of the sample and that of the reference sample,  $\Delta V\phi$  can be determined.

### 3. Results and discussion

#### 3.1. Ether formation from DPDM

Upon photoexcitation of diazo compounds, nitrogen is dissociated to yield the singlet carbenes (Scheme 1) [17]. In alcoholic solvents such as methanol, O—H bond is inserted into the carbene part quickly (within 40 ps for diphenylcarbene), and an ether is formed [18–20]. Fig. 1 depicts the TG signal after excitation of DPDM in methanol. The signal rises within 20 ns after excitation and decays continuously. The time profile of the signal can be well expressed with a tri-exponential function

$$I_{\text{TG}}(t)^{1/2} = |a_f \exp(-k_f t) + a_i \exp(-k_i t) + a_s \exp(-k_s t)| \quad (6)$$

where  $k_f > k_i > k_s$ . This feature is the same as that previously reported [21]. The decay rate constant of the fastest component,  $k_f$ , agrees well with the thermal diffusion rate,  $D_{\text{th}}q^2$ , and it should be attributed to the thermal grating signal. (Hence,  $a_f (= \delta n_Q + \delta n_H)$  should be negative.) The other, intermediate and slow, components are originated by the chemical species. Considering the chemical species involved in the reaction, one may expect that the time profile of the species grating is expressed by

$$I_{\text{TG}}(t)^{1/2} = A \left| -\delta n_{\text{DPDM}} \exp(-D_{\text{DPDM}}q^2t) + \delta n_N \exp(-D_Nq^2t) + \delta n_{\text{ether}} \times \exp(-D_{\text{ether}}q^2t) \right| \quad (7)$$

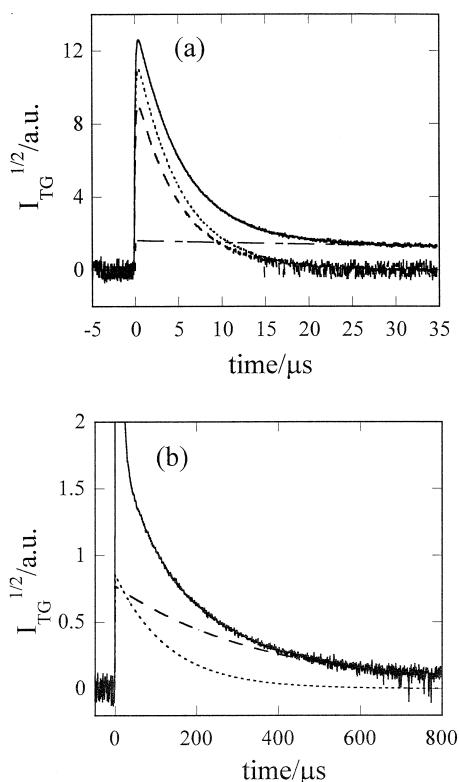


Fig. 1. Time profiles of the TG signal after photoexcitation of DPDM in methanol in different time scales. (a) —, observed total TG signal from DPDM, — · —, species grating signal from DPDM, · · · ·, thermal grating signal from DPDM, and ---, TG signal from reference (nitrobenzene). (b) —, observed TG signal; · · · ·, species grating signal due to nitrogen molecule; ---, species grating signal due to DPDM and diphenylmethyl methyl ether.

where  $\delta n$  is the refractive index change,  $D$  is the diffusion constant, and subscripts of DPDM, N and ether stand for DPDM, nitrogen molecule ( $N_2$ ) and ether, respectively. From the magnitude of  $D$  and the size of the molecules, we assign the intermediate component to the contribution of  $N_2$ , and the slow one to the ether and the parent molecule. The diffusion constants of ether and DPDM should be similar and they cannot be separated under this condition. Since the sign of  $a_i$  and  $a_s$  is the same as  $a_f$ , both contributions should be negative in sign. As discussed in the previous papers [12,13], we already know that the negative sign of  $\delta n_N$  comes from the molecular volume effect. The negative sign of  $a_s$  indicates that the contribution from the consumption

of DPDM is larger than that from the creation of ether ( $\delta n_{\text{ether}} > 0 > \delta n_{\text{DPDM}}$ , and  $|\delta n_{\text{ether}}| < |\delta n_{\text{DPDM}}|$ ), which is reasonably expected from the large blue shift of the absorption bands on transforming from DPDM to ether.

The decay rates of  $k_i$  and  $k_s$  are plotted against  $q^2$  in Fig. 2. Both plots intercept with the ordinate at  $k = 0$ .  $D_N$  and ( $D_{\text{DPDM}}$  or  $D_{\text{ether}}$ ) are determined from the slopes as  $5.3 \times 10^{-9}$  and  $1.9 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ .

The thermal grating intensity of DPDM is compared with that of a reference sample, nitrobenzene in methanol, which gives rise to only the thermal grating signal with a unit quantum yield of the non-radiative transition within the pulse width of the excitation laser [22]. The fact that the thermal grating intensity of DPDM is larger than that of the reference sample indicates that the reaction is exothermic. We confirmed that the consumption of the reactant with a prolonged photoirradiation (up to  $\approx 1000$  shots) is negligible and the relative intensity  $I_{\text{TG}}/I_{\text{TG}}^{\text{ref}}$  does not depend on the excitation laser power that we have examined (2–10  $\mu\text{J}/\text{pulse}$ ). (If we increase the excitation laser power further,  $I_{\text{TG}}/I_{\text{TG}}^{\text{ref}}$  decreases gradually because of the bleaching of DPDM.) From the thermal grating intensity,  $\phi\Delta H$  is determined as  $-99 \text{ kJ/mol}$ .

The species grating intensity due to  $N_2$  can be decomposed into population grating, which is due to the change of the absorption spectrum, and the vol-

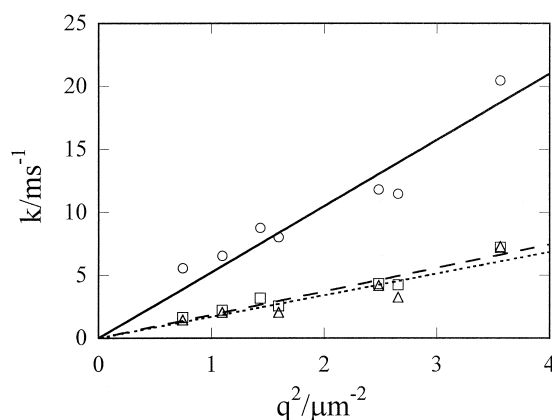


Fig. 2. The  $q^2$  plot of the decay rate constants of  $k_i$  and  $k_s$  (Eq. (6)) and the least-square fit.  $\circ$ , —:  $N_2$ ;  $\square$ , ---: DPDM;  $\triangle$ , ···: diazo-2.

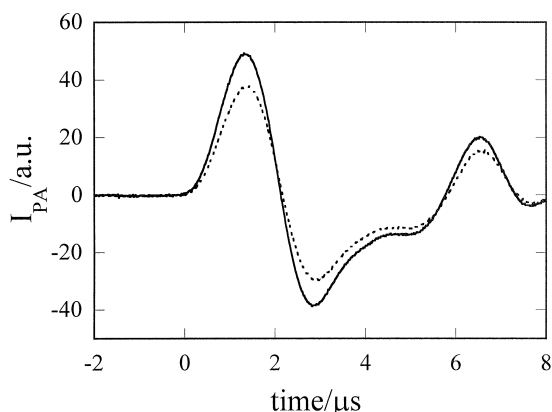


Fig. 3. PA signal after the photoexcitation of DPDM (—) and of nitrobenzene (---).

ume grating term. The former contribution can be estimated from data of the refractive index of the solvent and  $N_2$ . Hence, the partial molar volume of  $N_2$  ( $V_N$ ) in methanol can be calculated by a procedure similar to that described in Refs. [12] and [13]. The  $V_N$  determined in methanol is 50 ml/mol.

The PA signal is recorded for the same samples (Fig. 3). From a comparison of the intensity with that of the reference sample,  $\phi\Delta V$  is determined as 39.8 ml/mol. Using the reported quantum yield,  $\phi = 0.78$ ,  $\Delta H$  and  $\Delta V$  are obtained for ether formation from DPDM, and they are listed in Table 1.

### 3.2. Ether formation from other diazo compounds

Similar TG and PA measurements were performed for other diazo compounds listed in Scheme 1. The features of the TG and PA signals are similar to the case of DPDM. Following the same steps as described in Section 3.1,  $\phi\Delta H$  and  $\phi\Delta V$  are determined.

The quantum yields of the reaction were mea-

sured by the disappearance of the ground-state absorption after photoexcitation with a known number of photons. (Quantum yield of the disappearance of DPDM is used as a reference.)  $\Delta H$  and  $\Delta V$  obtained for these samples are summarized in Table 1.

### 3.3. Enthalpy and volume changes

Previously, the  $\Delta H$  of ether formation from DPDM was measured by the PA method but without considering the volume contribution in the signal [3]. If we analyze our PA signal without considering the volume effect, apparent  $\Delta H$  is  $-214$  kJ/mol, which is close to the previously reported  $\Delta H = -227$  kJ/mol [3]. However, as shown in Section 3.1, this assumption is not correct. The volume change contributes considerably to the signal intensity.

The partial molar volume of  $N_2$  (50 ml/mol) is larger than that reported in water (35.7 [23] and 34.3 ml/mol [24]) by the density measurement. The difference may be due to the solvent dependence of the partial molar volume. It is known that the molecular volume increases with increasing the isothermal compressibility for non-interacting molecules [25]. For example, the partial molar volume of  $CH_4$  is calculated to be 37.5 ml/mol in water, while the volume is 49.7 ml/mol in methanol [25]. Furthermore,  $V_N$  in  $CCl_4$  was reported to be 58.1 ml/mol [26]. Considering these facts, we conclude that  $V_N$  determined by this TG method is a reasonable partial molar volume.

In the previous papers [12,13], we suggested that this TG method could be a very convenient way to determine the partial molar volumes of small gas molecules in solution, which is a rather difficult task using traditional methods. In those papers, a photodissociation reaction of diphenylcyclopropanone was used to produce carbon monoxide (CO), and the

Table 1

$\Delta V$ ,  $\Delta H$ , the quantum yield for the formation of ethers ( $\phi$ ) from diazo compounds and the diffusion constants of diazo compounds ( $D$ ) and  $N_2$  ( $D_N$ )

	$\Delta V$ (ml/mol)	$\Delta H$ (kJ/mol)	$\phi$	$D$ ( $\times 10^{-9}$ , $m^2 s^{-1}$ )	$D_N$ ( $\times 10^{-9}$ , $m^2 s^{-1}$ )
diazo-1 (DPDM)	51	-127	0.78	1.9	5.3
diazo-2	22	-118	0.42	1.7	5.3
diazo-3	40	-162	0.75		

partial molar volume of CO was measured. The decomposition reaction of a diazo compound is a useful way to produce  $N_2$  in solution. Diffusion constant of  $N_2$  ( $D_N = 5.3 \times 10^{-9} \text{ m}^2/\text{s}$ ) is close to what is expected from literature values in  $\text{CCl}_4$  ( $3.4 \times 10^{-9} \text{ m}^2/\text{s}$  [27]) with a correction of the solution viscosity ( $5.5 \times 10^{-9} \text{ m}^2/\text{s}$ ).

The  $\Delta H$  of ether formation is similar for DPDM and diazo-2 but slightly larger for diazo-3. The difference may be explained in terms of the geometries of these compounds. As shown later in this section, the optimum orientations of the phenyl groups are different between the diazo and ether forms if they can freely move. The configuration of the phenyl groups can be relaxed with the diazo-ether transformation for DPDM, but rigidly fixed for diazo-2. Diazo-3 is an interesting case. A preliminary semi-empirical MO calculation shows that the configuration of the phenyl groups determined by the ethylene groups of diazo-3 is unstable for the diazo form but is stable for the ether form. Hence, the  $\Delta H$  for ether formation is larger for diazo-3 compared with the other diazo compounds. A more elevated calculation will be needed to understand fully various  $\Delta H$  for these compounds.

It is important to note that the volume changes depend on the diazo compounds. The volume change decreases in an order of  $\text{DPDM} > \text{diazo-3} > \text{diazo-2}$ , and this order is the same as the decrease of flexibility of the phenyl groups. This fact may suggest that the volume change is induced by rearrangement of the phenyl groups between the reactant and product. In fact, if we calculate the Van der Waals volume change by the method of atom increment [28], it predicts a negligibly small change. Therefore, the volume change cannot be due to change in the intrinsic molecular volume. Fig. 4 depicts the energetically optimized geometries of DPDM, diphenylmethy methyl ether, diazo-2 and ether by the PM3 method of the MOPAC program. Apparently, the geometries of the phenyl groups are different for these species. The phenyl groups are closer or compact for DPDM, while they are almost parallel to each other and widely open for ether. An increase of the void volume around the phenyl groups could be the main cause of the relatively large volume increase by the reaction. Naturally, the relative arrangement of the phenyl groups of diazo-2 is fixed

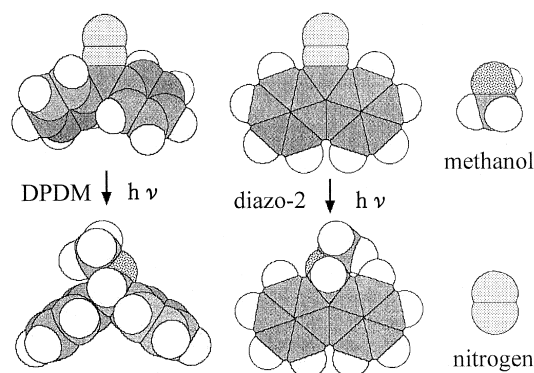


Fig. 4. Optimized geometries of DPDM, diphenylmethy methyl ether, diazo-2, and ether from of diazo-2.

and it cannot produce an additional void volume by the reaction.

In summary, we analyzed in detail the TG signal observed after photoexcitation of diazo compounds in methanol and determined the reaction enthalpy, reaction volume, partial molar volume of nitrogen molecule, diffusion constant of  $N_2$ , and diffusion constant of diazo compounds. The reaction volume contributes significantly to the signal and any analysis without this contribution should lead an unreasonable enthalpy change as previously reported. The large volume change was attributed to rearrangement of the phenyl moieties induced by the reaction from the diazo compounds to the ethers.

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