*J. Am. Chem. Soc.* **1989,** *111,* 1849–1854

acylated hydrazines has been provided by comparison of vertical ionization potentials with formal redox potentials for several compounds,[23] including 1,2-dimethyl-3-pyrazolidone, which is structurally similar to **1** and **2**. By analogy, perhaps some degree of internal reorganization is required in the electron exchange between a pyrazolidone anion and its radical, and this accounts for the fact that $k_{22}$ is approximately 100 times smaller than $k_{11}$ and other one-electron self-exchange rate constants for "normal" organic systems. Unfortunately, there is insufficient structural detail available for anion and radical to make a valid argument that such reorganization should be expected. Results of semiempirical calculations (AM1), however, do indicate that the geometry at the anilino nitrogen in 1-phenyl-3-pyrazolidone ($R^1 = R^2 = R^3 = H$) is nearly flat, while the corresponding geometry in the anion is more pyramidal. The calculated average bond angle around the anilino nitrogen is 119.7° in the radical and 114.5° in the anion. For tetraalkylhydrazines the geometrical differences between the parent and radical are even greater[21,22] and the electron self-exchange process is correspondingly slower.

**Acknowledgment.** The author thanks Elizabeth Cilano for her invaluable experimental assistance. Thanks also to Dr. Dan Kapp for useful discussions and for providing the AM1 calculations.

**Supplementary Material Available:** A listing of all pseudo-first-order rate constants determined at varying reactant concentrations, sulfite concentrations, and pH (4 pages). Ordering information is given on any current masthead page.

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# Determination of the Enthalpy and Reaction Volume Changes of Organic Photoreactions Using Photoacoustic Calorimetry

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**Abstract:** Photoacoustic calorimetry (PAC) can be used to measure both the thermal and reaction volume changes for photoinitiated reactions. The photoreactions of 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH), diphenylcyclopropenone (DPC), and *trans*-stilbene (TS) are investigated by PAC. The resolution of these experimental volume changes is accomplished by either a temperature dependence or a binary solvent mixture method. The thermal volume changes yield the enthalpies of reaction in solution, which can be compared to literature values. In two cases (DPH and DPC), the values are more endothermic than those predicted from gas-phase heats of formation. The differences can possibly be attributed to differential solvation of the reactants and products in the polar solvents employed. Absolute reaction volume changes for the photoreactions are also obtained for the photoreactions. PAC is a useful alternative technique to pressure-dependence studies to obtain this information. These volume changes can further be time-resolved to provide kinetic information about the photoprocesses.

The effect of pressure on chemical equilibria and reaction rates has received much attention over the past two decades.[1,2] Attention has been primarily concerned with thermal reactions. Recently, reports have appeared which describe the influence of pressure on photophysical rate constants and the empirical derivation of activation volumes.[3,4] Unfortunately, little information on the reaction volumes of photochemical processes is available. This is due in part to the difficulty in measuring the requisite effect of pressure on the equilibrium constant in photochemical reactions. In selected cases, indirect methods have been used. For example, the reaction volumes of excimer and exciplex formation have been determined by fluorescence intensity measurements.[5] However, these methods are usually quite restrictive in their application to photochemical systems. Data can be obtained from partial molar volume data or by means of dilatometry, but only when both the reactants and products are stable and isolable. Consequently, it would be quite useful to develop a general methodology to measure photochemical reaction volume changes which involve reactive intermediates.

In this context, we report the use of time-resolved photoacoustic calorimetry (PAC) as an alternative approach to measure reaction volumes of photochemical processes.[6] PAC is extremely sensitive to the volume changes of a chemical system following photoexcitation. These volume changes are caused by both the thermal deposition of energy and the photoinitiated reaction volume change. This paper describes two methods by which these two contributions can be separated and analyzed to provide both enthalpic *and* reaction volume information about the photochemical reaction. In particular, three compounds, 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH), diphenylcyclopropenone (DPC), and *trans*-stilbene (TS), are examined by PAC to illustrate these methods and demonstrate the importance of reaction volume changes in the photoacoustic experiment.

## Background

The principles of the photoacoustic effect have been well established.[7,8] When a molecule absorbs a photon, the energy may

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be converted into thermal energy, $E_{th}$, which will result in an increase in temperature along a cylinder defined by the path of the excitation beam through the sample. This rise in temperature, $\Delta T$, increases the volume of the solution, $\Delta V_{th}$, along the irradiated cylinder, generating an outwardly propagating pressure wave. If all of the photon energy is converted into thermal energy, the increase in $E_{th}$ along the laser beam is expressed as

$$E_{th} = E_0(1 - 10^{-A}) \quad (1)$$

where $A$ is the absorbance of the sample and $E_0$ is the energy of the laser pulse. The increase in temperature is given by

$$\Delta T = E_{th}/\rho C_p V_0 \quad (2)$$

where $\rho$ is the density of the solution, $C_p$ is its heat capacity, and $V_0$ is the initial volume. The volume change is related to the temperature change by the thermal coefficient of expansion of the solution, $\beta$:

$$\Delta V_{th} = \beta V_0 \Delta T \quad (3)$$

For chemical systems of interest, photolysis produces intermediates whose energetics relative to the reactants are unknown. The energetics of the intermediate are established by comparison of the acoustic wave generated by the nonradiative decay of the excited state to create the intermediate, producing thermal energy $E_{th}$, with that of a reference or calibration compound whose excited-state decay converts the entire photon energy into heat, $E_{th}$(ref). The ratio of acoustic wave amplitudes, $\alpha_{th}$, represents the fraction of the photon energy that is converted into heat:

$$\alpha_{th} = E_{th}/E_{th}(\mathrm{ref}) \quad (4)$$

The enthalpy of the intermediate relative to the reactant, $\Delta H$, is given by

$$\Delta H = E_{h\nu}(1 - \alpha_{th}) \quad (5)$$

where $E_{h\nu}$ is the photon energy.

The above discussion assumes unit quantum efficiency for the photochemical reaction. Consider the more general case where the excited state either undergoes a photochemical reaction with quantum yield $\Phi$ or decays back to its ground state with quantum yield $(1 - \Phi)$. The enthalpy of reaction is expressed as

$$\Delta H = E_{h\nu}(1 - \alpha_{th})/\Phi_r \quad (5')$$

The acoustic wave detector, a piezoelectric transducer, is sensitive to both the amplitude and the temporal profile of the acoustic wave.[6-9] Whereas the amplitude of the wave provides the desired enthalpic information, the temporal profile reveals the dynamics of the decay processes of the intermediate. Photoacoustic calorimetry (PAC) has been applied to a variety of photochemical systems to provide both enthalpic and kinetic information.[6-12]

## Experimental Section

Photoexcitation is conducted at 337 nm (PRA nitrogen laser, Model LN 1000). The sample cuvette is held in a thermostated (Haake A80 circulating bath) aluminum block. The acoustic waves are detected by a lead zirconate-lead titanate piezoelectric transducer (Panametrics, Model A125S, 2.25 MHz or home modified to be ~0.5 MHz[8]). The signal is amplified (Panametrics preamp, Model 5676), digitized (LeCroy 9400), and transferred to a laboratory computer. Each acoustic wave is normalized to the laser energy, which is measured by a Laser Precision, Rj-7000, pyrolytic probe. The sample absorbances are determined with a second pyrolytic probe positioned behind the sample. Each photoacoustic waveform is an average of 50–100 laser pulses. Evaluation of the acoustic waveforms, 400 data points, is done by a computer program. A more extensive description of the experiment and computer program has recently been given.[6]

Experiments are done on argon-degassed samples at room temperature. The optical densities of the calibration compound and sample are ~0.3 and adjusted to be within 2% of each other in order to avoid different concentration gradients of heat-producing transients. The reference waveform is obtained from photoexcitation of 2-hydroxybenzophenone (2-HBz).

The quantum yields are determined with phenylglyoxlic acid actinometry.[34] The disappearance of DPC and DBH is followed by UV–vis spectroscopy: in acetonitrile, $\epsilon_{330}$(DBH) = 110 and $\epsilon_{337}$(DPC) = 1740; in SDS solution (0.06 M), $\epsilon_{330}$(DBH) = 110 and $\epsilon_{337}$(DPC) = 909. A monochromater was used to isolate the 337-nm excitation beam.

The 2,3-diazabicyclo[2.2.1]hept-2-ene, DBH, is prepared by the literature procedure[13] and sublimed immediately prior to use. Sodium dodecyl sulfate (Bio-Rad), 2-HBz (Aldrich), and *trans*-stilbene (Aldrich) are recrystallized before use. Cetyltrimethylammonium chloride (CTAC, American Tokyo KASEI Inc.), diphenylcyclopropenone (Aldrich), and black ink (Reform, West Germany) are used as received. Spectrograde acetonitrile is used as received.

## Results and Discussion

In previous photoacoustic experiments[6-12] it has been assumed that the experimental volume change resulted only from thermal deposition of energy to the solvent. In such cases, the ratio of the volume change of the sample to that of the reference compound, $\alpha_{th}$, could be related to the enthalpy of reaction with eq 4 and 5. However, most photochemical reactions also undergo a reaction volume change, which will also contribute to the observed acoustic wave. Complexation, ionization, covalent-bond formation or breakage, and conformational changes can all contribute to the photochemical reaction volume change.[1] The total acoustic wave, $\Delta V$, may be produced by two different types of volume changes

$$\Delta V = \Delta V_{th} + \Delta V_{rx} \quad (6)$$

where $\Delta V_{th}$ and $\Delta V_{rx}$ are the thermal and reaction volume changes, respectively.[35] If the reaction volume change is positive due to volume expansion, the acoustic wave will be larger than anticipated if only thermal expansion for the system is considered. This would result in an erroneous value for $\Delta H$. From eq 3, the total volume change is expressed as

$$\Delta V = \beta V_0 \Delta T + \Delta V_{rx} \quad (7)$$

If these two volume contributions can be resolved, then both the enthalpy of reaction and the photochemical reaction volume can be determined. Two different methods can be used to experimentally separate these two contributions. The dependence of the thermal contribution on an adjustable experimental parameter is used in both methods. In the first method, the ratio of solvents in a binary mixture is varied, which effectively changes the solvent properties, $\beta$, $\rho$, and $C_p$. In the second method, the photochemical reaction is conducted in water and the temperature is varied. The thermal-expansion coefficient of water, $\beta$, is temperature dependent, so the thermal component will vary accordingly. This approach has been previously used by us and others.[6b,14] The obvious limitation of this method is that the organic photoreaction must be done in water, which requires at least moderate solubilities of the reactants. In this study, we use micellar solutions to increase the reagents' solubility. The photoacoustic signal obtained in these solutions is also temperature dependent. Importantly, both these methods can be used to provide the same experimental information. This should serve as an internal check

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on the validity of the methods and hopefully the accuracy of the data.

The reference or calibration compound undergoes no net photochemistry; therefore, its excitation generates an acoustic wave due only to thermal expansion from the conversion of the photon energy into heat, $\Delta V(\text{ref}) = \Delta V_{1h}(\text{ref})$. With use of eq 4 and 6

$$\alpha_{\text{eff}} = \Delta V/\Delta V(\text{ref}) = \Delta V_{1h}/\Delta V_{1h}(\text{ref}) + \Delta V_{rx}/\Delta V_{1h}(\text{ref}) \quad (8)$$

$$= \alpha_{1h} + \Delta V_{rx}/\Delta V_{1h}(\text{ref}) \quad (9)$$

where $\alpha_{\text{eff}}$ is the experimental ratio of the total volume change of the sample to the total volume change of the reference in a given solvent mixture or at a given temperature and $\alpha_{1h}$ represents the thermal contribution to $\alpha_{\text{eff}}$. $\Delta V_{1h}$ and $\Delta V_{1h}(\text{ref})$ are the thermal volume changes of the sample and the reference, and $\Delta V_{rx}$ is the reaction volume change for the sample. Let $X = \Delta V'_{1h}(\text{ref})/\Delta V_{1h}(\text{ref})$, where $\Delta V'_{1h}(\text{ref})$ is the thermal volume change of the calibration compound in either a reference solvent mixture or at a reference temperature, then

$$\alpha_{\text{eff}} = \alpha_{1h} + X[\Delta V_{rx}/\Delta V'_{1h}(\text{ref})] \quad (10)$$

Defining

$$\alpha'_{rx} = \Delta V_{rx}/\Delta V'_{1h}(\text{ref}) \quad (11)$$

where $\alpha'_{rx}$ is the ratio of the reaction volume change of the sample to that of the thermal volume change for the calibration compound in the reference solvent mixture or at the reference temperature. Then

$$\alpha_{\text{eff}} = \alpha_{1h} + \alpha'_{rx}X \quad (12)$$

Assuming the photochemical reaction volume change, $\Delta V_{rx}$, is independent of changes in temperature or the binary solvent system employed, a plot of $\alpha_{\text{eff}}$ versus $X$ should be linear with a slope of $\alpha'_{rx}$ and an intercept of $\alpha_{1h}$. Importantly, the *ratio* of the thermal volume change of the sample to that of the reference, $\alpha_{1h}$, is independent of temperature and variation of the binary solvent mixture.[15] However, the ratio of the reaction volume change of the sample to the thermal volume change of the reference, $\alpha'_{rx}X$, does change. $\alpha_{\text{eff}}$ and $X$ are determined experimentally as a function of either the temperature or the binary solvent mixture. The $\alpha_{\text{eff}}$ value is obtained from the ratio of the amplitude of the photoacoustic signal obtained from the sample to that from the calibration compound at a given temperature or in a given solvent. Similarly, the ratio of the photoacoustic signal for the calibration compound at the reference temperature or in the reference solvent to that at other temperatures or in other solvent mixtures yields $X$.

The ratio $\alpha'_{rx}$ can be converted into an absolute reaction volume change. From eq 1–3, the volume change for the reference compound due to thermal relaxation is

$$\Delta V'_{1h}(\text{ref}) = \beta E_0(1 - 10^{-A})/(C_p\rho) \quad (13)$$

Normalizing $\Delta V'_{1h}$ to the moles of photons absorbed gives

$$\Delta V''_{1h}(\text{ref}) = E_{h\nu}\beta/(C_p\rho) \quad (14)$$

where $\Delta V''_{1h}(\text{ref})$ is the thermal volume change of the reference per mole of photons absorbed. With use of eq 11,

$$\Delta V''_{rx} = \alpha'_{rx}E_{h\nu}\beta/(C_p\rho) \quad (15)$$

where $\Delta V''_{rx}$ is the molar reaction volume change of the compound (mL/mol). In the more general case, the molar reaction volume change for a photoreaction with quantum efficiency $\Phi_r$ is

$$\Delta V''_{rx} = \alpha'_{rx}E_{h\nu}\beta/(C_p\rho\Phi_r) \quad (15')$$

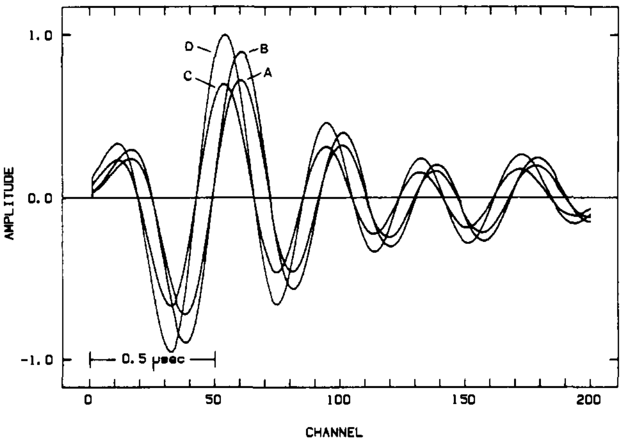
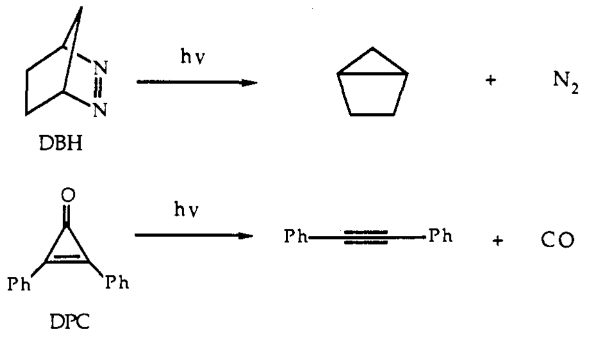


Figure 1. The experimental acoustic waves obtained from the photoexcitation of the calibration compound 2-HBz and DBH in different acetonitrile/water mixtures: (a) 2-HBz, acetonitrile; (b) DBH, acetonitrile; (c) 2-HBz, 1:2 acetonitrile/water; and (d) DBH, 1:2 acetonitrile/water.

**Scheme I**



The photochemistry of the three examined compounds, DBH, DPC, and TS, has been previously investigated.[16–18] DBH and DPC both undergo rapid, <10 ns, highly efficient, $\Phi_r \approx 1$, photoelimination reactions to give bicyclo[2.1.0]pentane and diphenylacetylene, respectively (Scheme I). *trans*-Stilbene photoisomerizes to *cis*-stilbene, $\Phi_r = 0.5$, via the singlet excited state, $\tau \cong 100$ ps.

The enthalpy change of the three photoreactions can be calculated with known literature values. With use of $\Delta H_f°(\text{DBH}) = 49.6$ kcal/mol[19] and $\Delta H_f°(\text{bicyclo[2.1.0]pentane}) = 37.0$ kcal/mol,[20] the calculated $\Delta H$ for the photoreaction of DBH is −12.6 kcal/mol. With use of $\Delta H_f°(\text{DPC}) = 76.0$ kcal/mol,[17b] $\Delta H_f°(\text{diphenylacetylene}) = 92.0$ kcal/mol,[21] and $\Delta H_f°(\text{CO}) = -26.4$ kcal/mol,[22] the calculated $\Delta H$ for the photoreaction of DPC is −10.4 kcal/mol. The enthalpy difference between *trans*- and *cis*-stilbene has recently been determined.[23] The $\Delta H$ value, 4.59 kcal/mol, is based on temperature-dependence equilibrium studies.[24]

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[15] The ratio of the thermal volume change of the sample to that of the reference is proportional to the ratio of the respective temperature changes and consequently to the ratio of the enthalpies of reaction. This statement assumes that the ratio of the enthalpies of reaction is independent of temperature and variation in the binary solvent mixture. For the photoreactions investigated, this appears to be a reasonable assumption. However, if the photoreaction involves intermediates whose energies are highly solvent dependent, this may not be the case.

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**Table I.** Values Obtained from the $\alpha_{eff}$ versus $X$ Experimental Plot with the Binary Solvent Mixture Method[a-c]

| compd | $\alpha_{1h}$ | $\Delta H$, kcal/mol | lit. $\Delta H$, kcal/mol | $\alpha'_{rx}$ | $\Delta V''_{rx}$, mL/mol[g] |
|---|---|---|---|---|---|
| DBH | $1.06 \pm 0.03$[d] | $-5.2 \pm 2.5$ | $-12.6$ | $0.18 \pm 0.03$ | $51.2 \pm 8.3$ |
| DPC | $0.96 \pm 0.03$ | $+4.2 \pm 2.5$ | $-10.4$ | $0.19 \pm 0.03$ | $65.0 \pm 8.3$ |
| TS | $0.90 \pm 0.03$ | $+8.4 \pm 5.6$[f] | $+4.6$ | $-0.01 \pm 0.02$ | *e* |

[a] For a detailed discussion, see the text. [b] 337-nm excitation, <20 μJ, 300 K, ~0.3 OD, 2-hydroxybenzophenone is used as the calibration compound. [c] The binary solvent mixtures ranged from neat acetonitrile to 1:2 acetonitrile/water. Neat acetonitrile is used as the reference solvent, $X = 1$. [d] Errors are 1σ from at least three experimental runs. [e] Contribution is not resolved. [f] See ref 27. [g] Error is based solely on the PAC value and not $\Phi_r$ or $\Phi_f$.

The acoustic waves obtained from photoexcitation of DBH and the reference compound 2-hydroxybenzophenone (2-HBz) in different acetonitrile/water solvent mixtures are shown in Figure 1. The thermal expansion coefficient, $\beta$, is significantly less for water than for acetonitrile [$\beta^{298}(H_2O) = 2.6 \times 10^{-4}$ K$^{-1}$, $\beta^{298}(CH_3CN) = 1.4 \times 10^{-3}$ K$^{-1}$].[25c] Increasing the water concentration decreases the amplitude of the acoustic wave. Importantly, it is this change in amplitude with solvent composition which permits the resolution of the thermal and reaction volume components of the experimental acoustic wave. Increasing the water concentration increases the speed of sound in the solvent mixture and consequently produces the observed phase shift of the acoustic wave. However, no phase shift is observed between the acoustic wave from the calibration compound and DBH (Figure 1), DPC, or TS in any solvent mixture. This indicates that no heat deposition occurs during the time-resolved response time of the transducers employed (50 ns–3 μs), in agreement with the known photochemistry of the compounds.[6]

The ratio of the amplitude of the acoustic waves from DBH, DPC, and TS to that from the reference compound, $\alpha_{eff}$, is determined separately in five different solvent mixtures, ranging from pure acetonitrile to 1:2 acetonitrile/water. The ratio of the amplitude of the acoustic wave from the reference compound in acetonitrile to that from the reference compound in the other solvent mixtures yields the $X$ values. The same ratios are obtained with either the 2.25-MHz (Figure 1) of the ~0.5-MHz piezoelectric transducer as the detector. Representative plots of $\alpha_{eff}$ versus $X$ for DBH, DPC, and TS are shown in Figure 2. The linear correlation between $\alpha_{eff}$ and $X$ for the three compounds indicates that $\alpha'_{rx}$ and $\Delta V_{rx}$ are relatively insensitive to the change in solvent composition. The $\alpha_{1h}$ and $\alpha'_{rx}$ values for each compound are determined from the intercept and slope of the plots (eq 12) and are given in Table I. The values represent the average of at least three experimental runs. The reaction enthalpies, $\Delta H$, are calculated with eq 5′ and the experimental $\alpha_{1h}$ and $\Phi_r$ values (Table I).[26,27] The reaction volume changes, $\Delta V''_{rx}$, are determined with eq 15′ and the experimental $\alpha'_{rx}$ and $\Phi_r$ values (Table I).[25a,26,27]

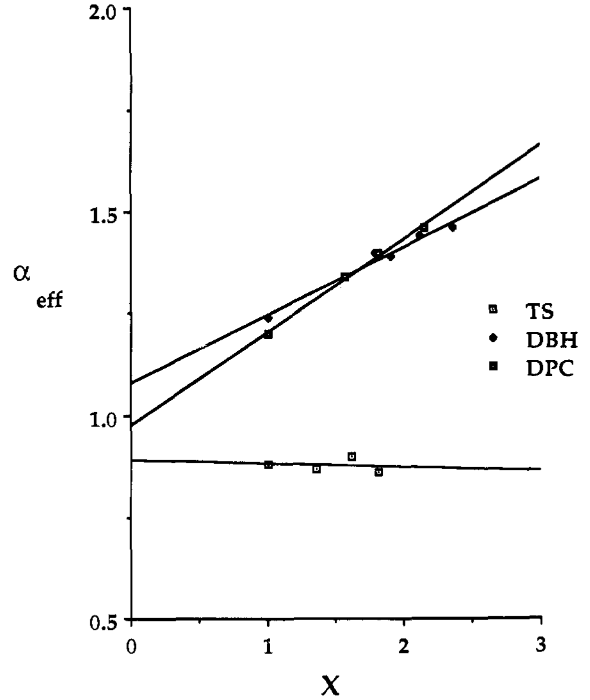

**Figure 2.** Representative plots of $\alpha_{eff}$ versus $X$ for DBH, DPC, and TS. The binary solvent mixture range is from acetonitrile ($X = 1$) to 1:2 acetonitrile/water. The calibration compound is 2-HBz.

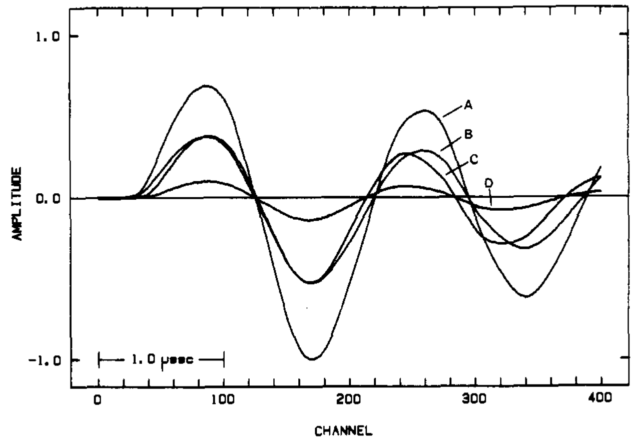

**Figure 3.** The experimental acoustic waves obtained from the photoexcitation of the calibration compound 2-HBZ and DBH in SDS (0.06 M) solution at different temperatures: (a) 2-HBz, 40 °C; (b) DBH, 40 °C; (c) 2-HBz, 10 °C; and (d) DBH, 10 °C.

The effect of temperature on the acoustic waves obtained from DBH and the calibration compound 2-HBz, in micellar solution (0.06 M SDS), is shown in Figure 3. As anticipated, the acoustic waves decrease in amplitude as the temperature decreases. The plot of the amplitudes of the acoustic waves obtained from the calibration compound in the micellar solution at various temperatures, 10–40 °C, against the corresponding distilled-water $\beta$ values is linear, as predicted by eq 3. At each temperature, no phase shift is observed between the acoustic waves from the calibration and sample compounds.

The ratio of the amplitude of the acoustic wave from the sample compound to that from the calibration compound, $\alpha_{eff}$, in micellar

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(24) For these photoreactions, the differential heat of solution between reactants and products should be negligible. Therefore, the gas-phase and solution reaction enthalpies should be quite similar.

(25) (a) Using $\beta = 1.37 \times 10^{-3}$ K$^{-1}$, $C_p = 21.9$ cal K$^{-1}$ mol$^{-1}$, and $\rho = 0.782$ g cm$^{-3}$, at 20 °C for acetonitrile.[25c] (b) Using $\beta = 0.207 \times 10^{-3}$ K$^{-1}$, $C_p = 18.0$ cal K$^{-1}$ mol$^{-1}$, $\rho = 0.998$ g cm$^{-3}$ at 20 °C for water.[25c] (c) Riddick, J. A.; Bunger, W. B.; Sankano, T. K. *Organic Solvents, Physical Properties and Methods of Purification*; Wiley: New York, 1986; Vol. 2.

(26) (a) In acetonitrile, $\Phi_r(DBH) = 0.98$, $\Phi_r(DPC) = 0.83$, and $\Phi_r(TS) = 0.5$.[18] In SDS solution (0.06 M), $\Phi_r(DBH) = 0.81$ and $\Phi_r(DPC) = 0.67$. In CTAC solution (0.014 M), $\Phi_r(TS) = 0.45$, assuming equal probability for decay of the twisted singlet to cis and trans isomers.[28] (b) It is assumed that the quantum yields for the photoreactions and/or fluorescence are not highly dependent on the solvent mixture or temperature, i.e. $\Phi_r$ does not change. Curvature in the experimental plots of $\alpha_{eff}$ vs X would have been observed if the quantum yields were altered appreciably.

(27) The calculated value $\Delta H$ for the photoisomerization of TS from $\alpha_{eff}$ must include a correction for fluorescence and partial isomerization. The corrected equation is $\Delta H = (1 - \Phi_f - \alpha_{eff})E_{h\nu}/\Phi_r$. In acetonitrile, the fluorescence yield, $\Phi_f$, for TS is ~0.05.[17] In the CTAC solution, it is assumed $\Phi_f = 0.1$.[28]

(28) Suddaby, B. R.; Brown, P. E.; Russell, J. C.; Whitten, D. G. *J. Am. Chem. Soc.* **1985**, *107*, 5609.

**Table II.** Values Obtained from the $\alpha_{\mathrm{eff}}$ versus $X$ Experimental Plot with the Temperature-Dependence Method[a-c]

| compd | $\alpha_{1h}$ | $\Delta H$, kcal/mol | lit. $\Delta H$, kcal/mol | $\alpha'_{rx}$ | $\Delta V''_{rx}$, mL/mol[h] |
|---|---|---|---|---|---|
| DBH[d] | 1.07 ± 0.02[f] | −7.1 ± 1.7 | −12.6 | 1.56 ± 0.15 | 48.5 ± 5.3 |
| DPC[d] | 0.98 ± 0.03 | +2.5 ± 2.5 | −10.4 | 1.56 ± 0.12 | 60.1 ± 4.5 |
| TS[e] | 0.86 ± 0.03 | +7.5 ± 5.0[g] | +4.6 | 0.14 ± 0.10 | 5.6 ± 4.3 |

[a] For a detailed discussion, see the text. [b] 337-nm excitation, <40 μJ, 300 K, ~0.3 OD, 2-hydroxybenzophenone is used as the calibration compound. [c] The temperature range for the experiments is 10–40 °C. The reference temperature is 20 °C, $X = 1$. [d] 0.06 M SDS in water. [e] 0.014 M CTAC in water. [f] Errors are 1σ from at least three experimental runs. [g] See ref 27. [h] Error is based solely on the PAC value and not $\Phi_r$ or $\Phi_f$.

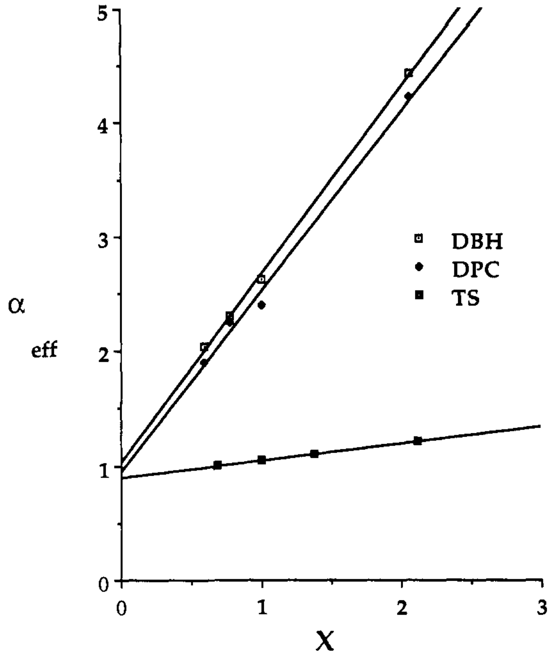

**Figure 4.** Representative plots of $\alpha_{\mathrm{eff}}$ versus $X$ for DBH, DPC, and TS. The temperature ranges from 10 to 40 °C, with 20 °C ($X = 1$) as the reference. The calibration compound is 2-HBz.

solutions is determined separately at four temperatures, 10–40 °C. The ratio of the amplitude of the acoustic wave from the calibration compound at the reference temperature 20 °C to that at the other temperatures gives the $X$ values. Representative plots of $\alpha_{\mathrm{eff}}$ versus $X$ for DBH, DPC, and TS are shown in Figure 4. The linear correlation between $\alpha_{\mathrm{eff}}$ and $X$ for the three compounds indicates that $\alpha'_{rx}$ and consequently $\Delta V_{rx}$ for the three compounds is temperature independent, 10–40 °C.[29a] The $\alpha_{1h}$ and $\alpha'_{rx}$ values for each compound are obtained from the intercept and slope of the plots (eq 12 and Table II). The values represent the average of at least three experimental runs.

The reaction enthalpies, $\Delta H$, are calculated with eq 5′ and the experimental $\alpha_{1h}$ and $\Phi_r$ values (Table II).[26,27] To calculate the absolute reaction volume changes, the appropriate value of $\beta/(C_p\rho)$ for the micellar solutions, SDS (0.06 M) or CTAC (0.014 M), must be determined. This is done by measuring the ratio of the amplitude of the acoustic wave from black ink, in the SDS or CTAC solutions, to that in pure water, at the reference temperature 20 °C.[30] The experimental ratios, 1.45 ± 0.05 and 1.13 ± 0.04, multiplied by the $\beta/(C_p\rho)$ value for pure water at 20 °C, 0.21,[25b] corrects the $\beta/(C_p\rho)$ values for the SDS, 0.30 ± 0.01, and CTAC, 0.24 ± 0.01, solutions. With these values, the experimental $\alpha'_{rx}$ and $\Phi_{rx}$ values, and eq 15′, the molar reaction volume changes are determined (Table II).[26,27] The value of $\Delta V''_{rx}$ does not depend on the arbitrarily chosen reference temperature; i.e., the same $\Delta V''_{rx}$ value is obtained at any reference temperature.

Similar $\alpha_{1h}$ and calculated $\Delta H$ values are obtained for the three compounds studied by using either of the two methods to resolve the thermal contribution. In addition, the calculated $\Delta V''_{rx}$ values are also similar with either method. This provides an internal check on the validity of each method. In two photoreactions (DBH and DPC), the enthalpies of reaction in solution are more endothermic than those predicted with the appropriate gas-phase heats of formation. The PAC values measure the difference in the heats of formation between reactants and products in solution and necessarily include the differential enthalpies of solvation between the reactants and products. The photoreactions of DBH and DPC involve reactants which are probably more polar than the products. In the polar solvents employed, acetonitrile and micellar solution, the heat of solvation of the reactants may indeed be significantly greater than that of the products. Consequently, the PAC $\Delta H$ values would be anticipated to be more endothermic than those calculated with gas-phase heats of formation. This may account, in part, for the observed difference between the gas phase and solution enthalpies of reaction. In the third photoreaction (TS), the PAC enthalpy value is in good agreement with the literature value which suggests, that the differential enthalpy of solvation between *cis* and *trans*-stilbene is small.

Although the photochemical reaction volumes of DBH and DPC are not known, the magnitude of the observed changes seem reasonable. The retro-Diels–Alder reaction may serve as a reasonable model for the DBH and DPC photoreactions. The reaction volume values for this reaction are quite large, 30–50 mL/mol,[1] and are similar in magnitude to those determined by PAC for the DBH and DPC photoreactions. The reaction volume change for the photoisomerization of TS is estimated to be ~2.3 mL/mol, using a van der Waals volume of 91 mL/mol for TS and the experimental finding that the molar volume of *cis*-stilbene is larger than that of TS by only 2.5%.[31] This small reaction volume increase is in accordance with the experimental value.

Although both described methods can resolve the reaction volume contribution, the temperature-dependence approach is much more sensitive and able to resolve significantly smaller reaction volume changes. As evidence, the small reaction volume change for the isomerization of TS is only resolved by the temperature-dependence method. This is because the $\beta/(C_p\rho)$ term for water is quite temperature dependent, so the range of experimental $\alpha_{\mathrm{eff}}$ values is large (Figure 3). In contrast, the variation in the $\beta/(C_p\rho)$ term and the range of experimental $\alpha_{\mathrm{eff}}$ values for the binary solvent mixtures is small (Figure 1). In general, a given reaction volume change will have a larger slope for the experimental plot of $\alpha_{\mathrm{eff}}$ vs $X$ with the temperature dependence method than the binary solvent mixture method.

Micellar solutions greatly facilitate the study of organic photochemical reaction volume changes. These highly solubilizing solutions have a temperature-dependent volume response similar to that of water. Assuming the photoreaction occurs in micelle solubilization sites, the water acts as a coupling medium by which the acoustic effect is propagated. Both anionic (SDS) and cationic (CTAC) micelles have been used and yield similar experimental results for both the DBH and DPC photoreactions. Care should

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(29) The quantum yields for fluorescence and isomerization of TS are temperature dependent in micellar solutions.[28] This should cause curvature in the experimental plot of $\alpha_{\mathrm{eff}}$ vs X. However, given the linearity of the plot, this curvature must be small over the temperature range of the experiment, 10–40 °C.

(30) It is not required that the water-soluble black ink deposit all of the absorbed photon energy as heat to the surroundings. In fact, it probably does not. However, it is required and assumed that the ink does deposit the same fraction of the photon energy to solution in the micellar solution and pure water, i.e. undergoes the same photochemistry in both media. In support, other water-soluble compounds give similar ratios.

(31) (a) Victor, J. G.; Torkelson, J. M. *Macromolecules* **1987**, *20*, 2241. (b) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441. (c) von Auwers, *Ber. Dtsch. Chem. Ges. B* **1935**, *68*, 1346.

be taken to account for the possibility that the specific properties of the solubilizing medium may alter the photochemical reaction.

The contribution of the reaction volume change to the total volume change can be significant. The failure to account for it may yield erroneous thermochemical data. For example, assuming $\Delta V'_{1h} = \Delta V_{1h} + \Delta V_{rx}$, where $\Delta V'_{1h}$ is the uncorrected thermal volume change which includes both the reaction and thermal volume changes, then the uncorrected enthalpy change, $\Delta H'$, is given by

$$\Delta H' = E_{h\nu}[1 - (\alpha_{1h} + \alpha'_{rx})]/\Phi_r \qquad (16)$$

The uncorrected $\Delta H'$ values for the DBH, DPC, and TS photoreactions in acetonitrile are −20.7, −15.3, and +5.1 kcal/mol, whereas in water at 20 °C, the uncorrected $\Delta H$ values are −170.6, −194.9, and +8.5 kcal/mol, respectively.[32] The uncorrected values of DBH and DPC are *significantly* different than the corrected enthalpy values determined by PAC *with* the resolution of the thermal and reaction volume components. In contrast, the reaction volume change of TS in acetonitrile is negligible so the difference is small.

The difference between the corrected and uncorrected enthalpy values, $\Delta\Delta H$, is $\Delta V_{rx} C_p \rho / \beta$. The larger the photochemical reaction volume change or the smaller the $\beta/(C_p\rho)$ value of the solvent, the larger the difference. The micellar solutions have a very small $\beta/(C_p\rho)$ value, 0.2–0.3, so ΔΔH is large. In contrast, the $\Delta\Delta H$ for the photoreactions in acetonitrile is significantly less than in water because its $\beta/(C_p\rho)$ value is quite large, 3.3. In general, $\Delta\Delta H$ for photoreactions will be smaller in organic solvents than in aqueous solutions because of the relative $\beta/(C_p\rho)$ values. Consequently, if either the solvent employed is water or $\Delta V_{rx}$ is large, the thermal and reaction volume changes can and should be experimentally resolved, preferably by the temperature-dependence method. Simply, if the photochemical reaction volume change is of interest, conduct the reaction in micellar solutions and resolve the change. To minimize its contribution to the total volume change, conduct the reaction in organic solvents with high $\beta/(C_p\rho)$ values. Clearly, we have chosen the photoreactions of DBH and DPC to dramatize the potential contribution of reaction volume changes to the total volume change. The magnitude of this contribution will obviously depend on the photoreaction and the solvent employed, but in general, the contribution will be considerably smaller than that observed for DBH and DPC.

Photoacoustic calorimetry has several advantages over conventional methods to measure photochemical reaction volume changes. These changes can be obtained either from partial molar volume data or by means of dilatometry only if the reactants and products are stable and isolable.[1] Such stability is not a requirement for PAC. Indeed, either the reactants or the products may be reactive intermediates and reaction volumes can be obtained. The interpretation of pressure-dependence measurements to obtain $\Delta V_{rx}$ are often complicated by assumptions.[1] No assumptions are necessary to determine the reaction volumes other than $\Delta V_{rx}$ is independent of either temperature or solvent composition. This seems justified given the linear plots and the small temperature range required for these experiments. Furthermore, these reaction volume changes can be time-resolved to provide information about the structural nature of reactive intermediates. For example, the rate and magnitude of the reaction volume change associated with excimer and exciplex formation can be determined.[33]

In conclusion, we have demonstrated the use of PAC to measure both thermal and reaction volume changes for photoinitiated reactions. The use of either the temperature-dependence or the binary-solvent method allows for the resolution of these two contributions to the total volume change. This technique has great potential in its applicability to a wide variety of chemical systems to provide thermodynamic, kinetic, and reaction volume information.

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**Registry No.** DBH, 2721-32-6; DPC, 886-38-4; TS, 103-30-0.

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[32] A previous photoacoustic experiment was done on DPC which did not account for the reaction volume change.[11] The observed uncorrected $\Delta H$ value for the photodissociation of DPC in benzene was −9.9 kcal/mol, in good agreement with our uncorrected value of −15.3 kcal/mol in acetonitrile.

[33] Herman, M. S.; Goodman, J. L., unpublished results.

[34] Defoin, A.; Defoin-Straatmann, R.; Hildenbrand, K.; Bittersmann, E.; Kreft, D.; Kuhn, H. J. *J. Photochem.* **1986**, *108*, 99.

[35] This treatment classifies all nonthermal expansion contributions to the total acoustic wave as photochemical reaction volume changes. Consequently, the photochemical reaction volume changes will only be meaningful values if other nonthermal expansion contributions are small. Possible contributions, electrostriction, breakdown, or plasma formation, should be small for the systems examined.

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# Photooxygenation of Ascorbic Acid Derivatives and Model Compounds

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**Abstract:** Photooxygenation of ascorbic acid derivatives and model compounds produces hydroperoxy ketones as initial products. The reaction rate and initial product distribution depend on the acidity of the hydroxy group; the more acidic group reacts more readily. The C-2 carbonyl group of the 3-hydroperoxy ketones reacts readily with methyl alcohol to give a hydroperoxy hemiketal. Both the hydroperoxy ketones and their hemiketals decompose to oxalate esters upon warming to room temperature. The structure of oxalate **11a** was confirmed by X-ray crystal analysis. Hydroperoxy ketones **31** and **32** are in equilibrium at low temperature and give only one hemiketal (**34**) in $CD_3OD$. Analogous photooxygenation products and similar decomposition pathways occur with 2-hydroxytetronic acid derivatives. The presence of fluoride ion affects both the reaction of enediols with singlet oxygen and the decomposition of the unstable products.

L-Ascorbic acid (vitamin C) serves as a biological antioxidant. Previous study has centered on its importance as a reductant which can undergo reversible oxidation and reduction with the formation of free-radical intermediates.[1] Another role is as a redox buffer,

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