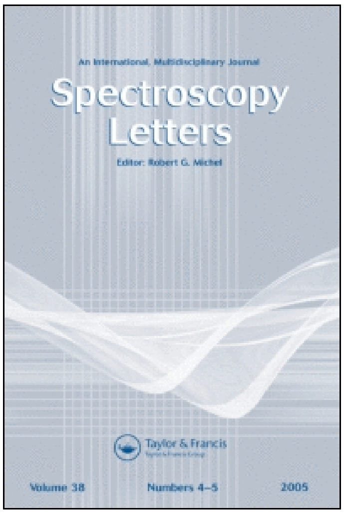

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Determination of Reaction Enthalpy and Conformational Volume Changes by Photoacoustic Spectroscopy

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DETERMINATION OF REACTION ENTHALPY AND CONFORMATIONAL VOLUME CHANGES BY PHOTOACOUSTIC SPECTROSCOPY

Key words: photoacoustic spectroscopy, reaction enthalpy change, conformational volume change, 5'-deoxyadenosylcobalamin (AdoCbl)

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Abstract: The reaction enthalpy and conformational volume changes can be qualitatively estimated by means of the temperature-dependent pulsed photoacoustic spectroscopy. The curves for heat-releasing fraction and conformational volume changes with different temperatures are presented. The simultaneous equations for determination of the enthalpy and volume changes are established based on temperature-dependent measurements, and applied to study the photolysis of coenzyme system.

INTRODUCTION

Pulsed photoacoustic spectroscopy has been proved useful for studying the physical and chemical properties of various systems[1,2]. In the experiment a low-energy laser pulse is used to initiate a reaction which, upon excitation, releases heat and may undergo a volume change in molecular conformation. Both of the processes give rise to a transient acoustic pressure pulse which is detected by a piezoelectric transducer. The observed photoacoustic signal reflects the energetics as well as the kinetics for processes that occur on the nanosecond to microsecond scale. By analyzing the amplitude and profile of the photoacoustic signals, several research groups have obtained important information involving chemical [3-6] and biological systems [7-12].

In a photoinitiated reaction of a solution there are two possible contributions to the total volume change: the thermal expansion (ΔV_{th}) and the molecular conformational volume change (ΔV_{con}) of the system. In organic solvents the former usually dominates, though the latter may be significant. Both components can be separated by measuring the dependence of the photoacoustic signal on the thermal expansivity of different solvents [5], or expansion coefficient of the solvent at different temperatures. In aqueous system the temperature-dependent measurement is often employed for determination of the reaction enthalpy and conformational volume changes [2,7-13]. The detected photoacoustic signal must be linear to the excitation pulse energy for the experimental temperatures.

In this paper the heat-releasing fraction and the conformational volume changes are qualitatively predicted by means of the temperature-dependent photoacoustic spectroscopy. The simultaneous equations for determination of the enthalpy and volume changes are established based on this method, and used for investigation of the photolysis of coenzyme system.

ANALYSIS

The observed photoacoustic signal, S, is produced by a change in volume, ΔV, of the irradiated sample due to an expansion or a contraction of the system.

$$S = K\Delta V \qquad (1)$$

where, K is an instrumental constant, ΔV, the total volume change, may come from two sources. One is the thermal component ΔV_{th} , which is induced by the heat release, Q, to the solvent as nonradiative process,

$$\Delta V_{th} = (\beta / C_p \rho) Q \qquad (2)$$

where, β is the thermal expansion coefficient for the solvent, C_p is the heat capacity, and ρ the density of the solution. ΔV_{th} gives a thermally generated signal, S_{th},

$$S_{th} = K \Delta V_{th} \qquad (3)$$

The second source contributing to ΔV within the system is a conformational volume change of the reacting molecules, ΔV_{con} , which also produces an acoustic signal, S_{con} ,

$$S_{con} = K \Delta V_{con} \qquad (4)$$

Therefore, the total photoacoustic signal is expressed as

$$S = K[(\beta / C_p \rho) Q + \Delta V_{con})] \qquad (5)$$

For elimination of the constant K, a reference compound is used, which converts all of the absorbed photon energy, $E_{h\nu}$, into heat on a time scale faster than that of transducer response, and has no intrinsic volume change, ΔV_{con} , thus

$$S_{rf} = K(\beta / C_p \rho) E_{h\nu} \qquad (6)$$

The ratio of the signal amplitudes for the sample of interest to the reference compound, ϕ, is as,

$$\phi = Q / E_{h\nu} + (\Delta V_{con} / [(\beta / C_p \rho) E_{h\nu}]) \qquad (7)$$

Thus, by plotting ϕ *vs.* $(C_p \rho)/\beta$, one can obtain Q and ΔV_{con} by measuring the intercept and slope of the plot, provided that both remain constant for temperature changes or the series of solvents used. For each waveform (see Fig. 1), the amplitude of the photoacoustic signal, S, taken as the distance between the first peak and trough is measured in order to reduce the relative errors.

ESTIMATION OF HEAT-RELEASING FRACTION AND CONFORMATIONAL VOLUME CHANGE

Pre-estimation of the thermal release Q and molecular volume change ΔV_{con} is very helpful for further study. We define the heat-releasing fraction α and the temperature-

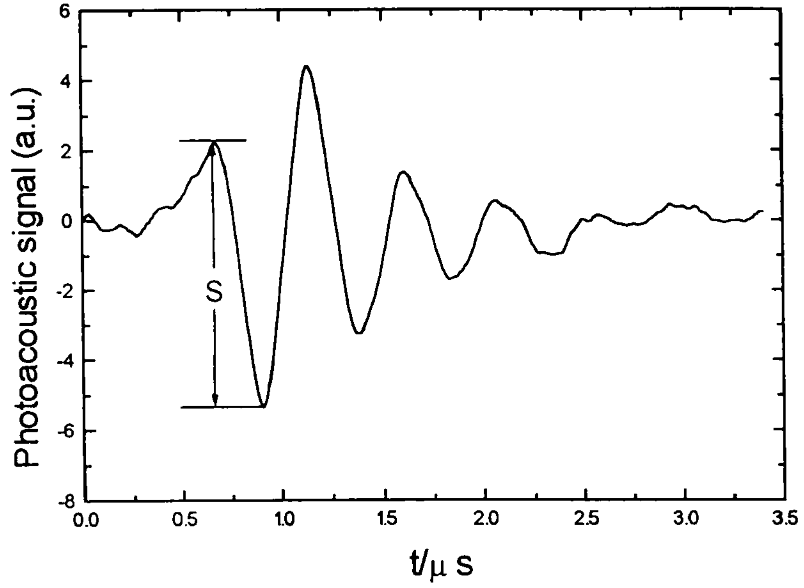

Fig. 1. A profile of photoacoustic signal from a reference, $K_2Cr_2O_7$, at 20 °C.

dependent (or solvent-dependent) factor χ as

$$\alpha = Q / E_{h\nu} \tag{8}$$

$$\chi = \frac{1}{(\beta / C_p \rho)} \tag{9}$$

which lead to, upon rearrangement,

$$\phi = \alpha + \Delta V_{con} \chi / E_{h\nu} \tag{10}$$

$$S = \alpha S_{rf} + K \Delta V_{con} \tag{11}$$

ϕ and χ are changed with temperature or solvent, α and ΔV_{con} are to be estimated.

In the linear range of response to excitation energy, the amplitude of photoacoustic signal resulting from heat deposition is proportional to $\beta / C_p \rho$. β is greatly changed with

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temperature in aqueous system, and close to be zero at 3.9°. At β=0 temperature, the amplitude of observed signal should be neatly the measure of the conformational volume change, ΔV_{con}, which may be expansive or contractive. It is noted that α may be small or large, and ΔV_{con} may be positive (expansion) or negative (contraction). If the amplitude curve of reference (whose α is unity, and ΔV_{con} is zero) is firstly determined by equation (6) from the temperature range of 3.9°C to 30°C, a set of amplitude curves of the samples with different values of α and ΔV_{con} can be proportionally plotted according to equation (11) in this temperature range. The values of α and ΔV_{con} and the correspondent curves are shown in Fig.2 and Fig.3, respectively.

SIMULTANEOUS DETERMINATION OF REACTION ENTHALPY AND CONFORMATIONAL VOLUME CHANGES

Plot of the signal amplitude *vs.* excitation energy creates the slope which represents the magnitudes of photoacoustic signal. In the linear response range the ratio of the slopes for sample to reference at a temperature T_i is expressed as

$$k_e^i = \alpha + \frac{\Delta V_{con}\chi^i}{E_{h\nu}} \tag{12}$$

$$k_e^i = k_s^i / k_{rf}^i \tag{13}$$

where, k_s^i and k_{rf}^i are the slopes of plotting the signal amplitude *vs.* excitation energy for sample and reference, respectively. From Eqs. (12) and (13) we can derive the ralations which produce the heat-releasing fraction and conformational volume change,

$$\alpha = k_e^2 - \frac{\chi^2(k_e^2 - k_e^1)}{\chi^2 - \chi^1} \tag{14}$$

$$\Delta V_{con} = \frac{(k_e^2 - k_e^1)E_{h\nu}}{\chi^2 - \chi^1} \tag{15}$$

EXPERIMENTAL AND RESULTS

The experimental system of pulsed laser photoacoustic spectroscopy has been described in detail [14]. The acoustic transducer made of a cylindrical piezoelectric tube

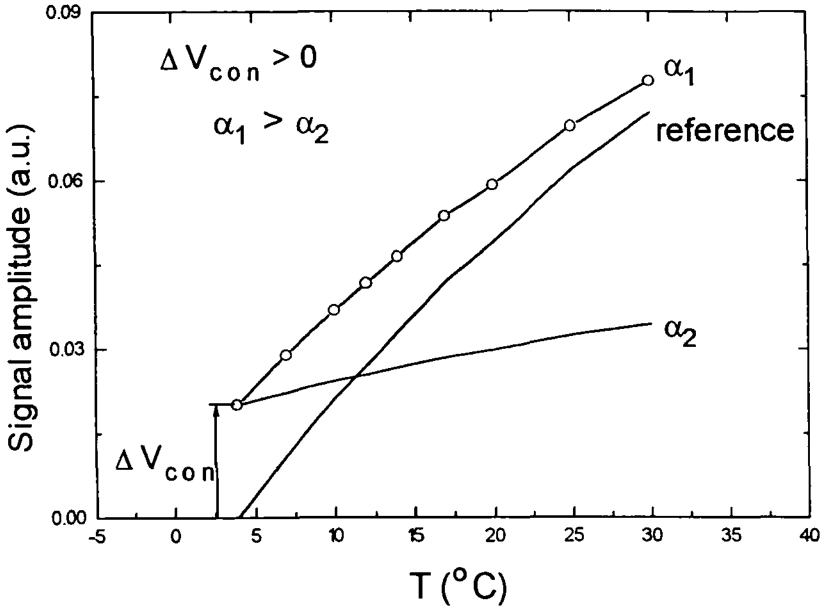

Fig.2. ΔV_{con} is positive (expansion).

which has a resonance mode in thickness (ν=2 MHz). Dilute sample is filled in the tube which serves as a photoacoustic chamber. There is a thermoelement in the chamber to detect the temperature of solution. A Q-switched Nd:YAG laser (Continuum NP70) with pulse duration of 8 ns operating at third harmonic (355 nm) and a repetition rate of 10 Hz is the excitation source. The laser beam passing along the axis of the cylinder is with a diameter of 9 mm which determines the time resolution of the experiment. The excitation energy is varied by means of a neutral filter and recorded by a transient radiometer (DigiRad. R-752 and P-444). The photoacoustic signal is pre-amplified (HP-8447F), recorded (HP-54510B), and then transfered to a laboratory computer for further processing. Each acoustic waveform is an average of the signals from about 100 pulse excitations.

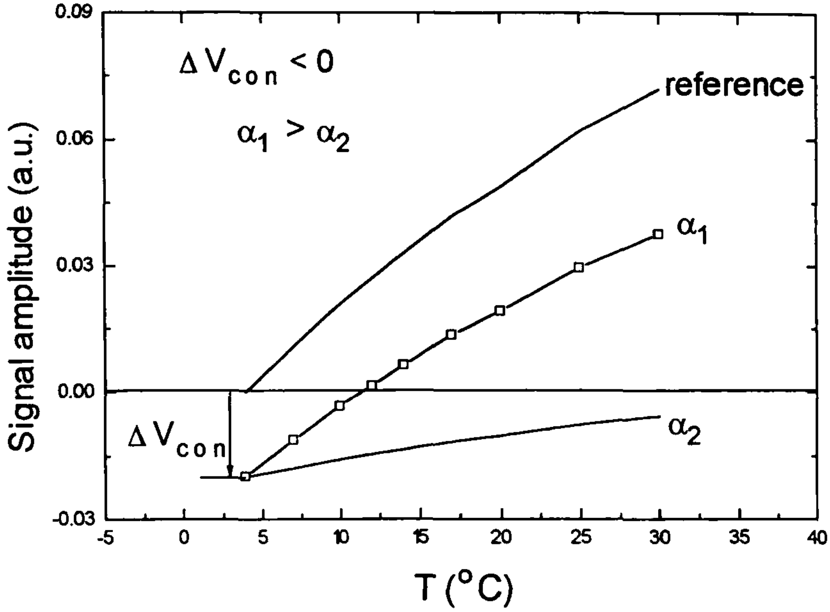

Fig.3. ΔV_{con} is negative (contraction).

For calibration of the system response, $K_2Cr_2O_7$ solution is chosen as a calorimetric reference due to its totally prompt heat release and no conformational volume changes [2,12]. Care is taken to keep the same conditions for the reference as for the sample (absorbance, solvent, instrumental geometry, and temperature). The absorbance is $A_{355} = 0.24\pm0.01$ for both of the reference and sample solutions. The test sample, Coenzyme B_{12} (5'- deoxyadenosylcobalamin, AdoCbl), is a natural cofactor for a number of enzymatic reactions and extremely sensitive to light radiation. Homolysis of the cobalt-carbon bond occurs to give a cobalt (II) complex and a free radical in photoreduction process described as

$$\mathrm{Ado-Co} \xrightarrow{h\nu,\, k_1} \mathrm{Ado\cdot + Co(II)} \qquad (16)$$

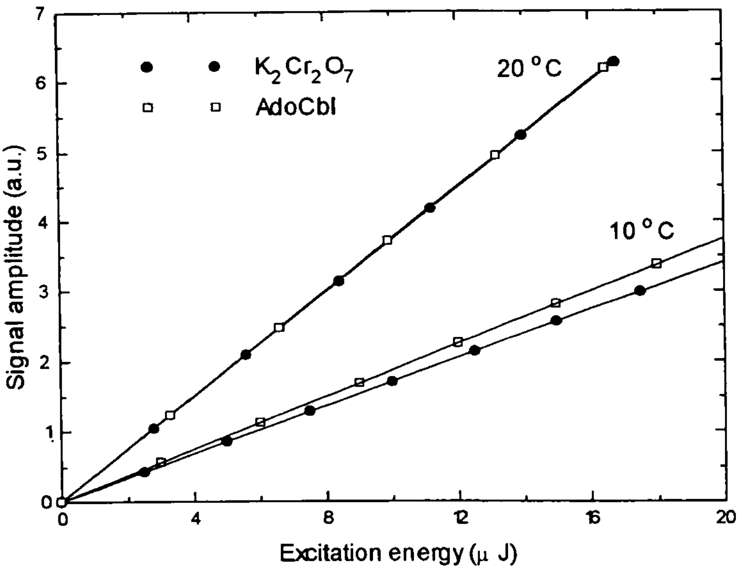

Fig.4. Plots of photoacoustic response amplitude *vs.* excitation energy for AdoCbl and $K_2Cr_2O_7$ in aqueous solutions.

Light-induced dissociation and spontaneous dissociation may have similar mechanisms both in vitro and in vivo. Previous study showed that the rate of photolysis is about 10^8-10^9 s^{-1} [15]. The lifetime of the radical is long with respect to the response time of the transducer, so it is suitable to employ this experimental system to study the reaction enthalpy and conformational volume changes (if the changes occur) of the homolytical process.

Measurements are performed at different temperatures, i.g., 10 °C and 20 °C. Plots of photoacoustic signal amplitude *vs.* excitation energy in linear response range for AdoCbl and $K_2Cr_2O_7$ solutions are shown in Fig.4. From their slopes at T_1 and T_2 , ratios of k_e^1 and k_e^2 are produced as 1.101 and 0.995, respectively. Taking k_e^i into Eqs. (14) and (15) with $\chi^1 = 47.62$ kJ/ml (at 10 °C) and $\chi^2 = 20.41$ kJ/ml (at 20 °C) [16], the heat-

TABLE 1. Results of reaction enthalpy and conformational volume changes

	ΔV_{con} (ml/mol)	ΔV_{rxn} (ml/mol)	α	ΔH_{rxn} (kJ/mol)
Adocbl	1.27	6.35[a]	0.919	114.3[a], 103.8[b]

[a] Φ in aqueous solution is estimated as 0.2±0.05 taken from E. Chen et al. [15].

[b] data obtained by J. Halpern et al.[17].

releasing fraction and conformational volume changes can be calculated and listed in Table 1. When the nonradiative decay is the only mechanism that competes with the reaction of interest, then

$$\Delta H_{rxn} = (1-\alpha)E_{h\nu}/\Phi \tag{17}$$

$$\Delta V_{rxn} = \Delta V_{con}/\Phi \tag{18}$$

Use of simultaneous equations for determination of reaction enthalpy and conformational volume changes may be explicit and effective.

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