

## Time-resolved photoacoustic calorimetry

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**Abstract** – Time-resolved photoacoustic calorimetry is an experimental method that provides both the dynamics and energetics of reactive intermediates that are produced in photochemical reactions. With the present apparatus, dynamics on the timescale spanning 10 nanoseconds to 50 microseconds can be resolved. The enthalpy sensitivity is + 1.0 kcal/mole. This technique has been applied to the hydrogen atom abstraction reaction of *t*-butoxy radical with phenol. Also, the strain enthalpy of 1-phenyl-*trans*-cyclohexene has been measured.

### INTRODUCTION

Photochemists have long recognized the necessity of having reliable thermochemical data that can be used in the formulation of reaction mechanisms. Unfortunately, it has been almost impossible to obtain thermochemical information for reactive intermediates with lifetimes on the nanosecond or microsecond timescales. For example, it has been extremely difficult to discuss the effect a substituent may have on the stability of a radical or carbene, or how the medium may effect the energetics of an ionic intermediate.

During the past two years, we have been developing the experimental method of time-resolved photoacoustic calorimetry whereby both the energetics and dynamics for photochemically generated reactive intermediates can be obtained on timescale spanning 10 nanoseconds to 50 microseconds (ref. 1). Similar methods have been developed in the laboratory of Braslavsky (ref. 2). In this report, we will discuss the most recent developments, and present two chemical problems to which the technique has been applied.

### THEORY

The theory of time-resolved photoacoustic calorimetry has recently been presented (ref. 3). Consequently, only a brief discussion of the theory will follow. In order to understand the response of a transducer to an acoustic wave, we have modeled the photoacoustic experiment with a point source of heat and a point detector. The heat source was assumed to have a analytic form  $(1/\tau) \exp(-t/\tau)$  where  $\tau$  is the lifetime of the transient and the pre-exponential term  $1/\tau$  is a normalization factor. The transducer was defined to be sensitive to longitudinal displacement waves and was modeled as an underdamped harmonic oscillator. The Green's function analysis, involving the time domain convolution of the heat source and detector, gave the result, equation 1,

$$V(t) = \frac{h_0 A}{4\pi r_0} \frac{v/\tau}{v^2 + (1/\tau')^2} e^{-t/\tau} - e^{-t/\tau_0} \left[ \cos(vt) - \frac{1}{v\tau'} \sin(vt) \right] \quad (1)$$

where  $V(t)$  is the detector response,  $h_0 A / \pi r_0$  is an experimental constant,  $v$  is the characteristic frequency of the transducer,  $\tau_0$  is the relaxation time of the transducer,  $\tau$  is the lifetime of the transient, and  $1/\tau' = 1/\tau - 1/\tau_0$ .

We have modeled equation 1 for a transducer with the properties  $v = 10^6$  Hz,  $\tau_0 = 1$  msec, and for a transient with varying lifetime,  $\tau$ , ranging from 1 nanosecond to 100 microseconds, Figure 1. For times shorter than 1 nanosecond as well as times longer than 100 microseconds the transducer cannot time-resolve the acoustic waves. However, for transients with lifetimes ranging from 10 nanoseconds to 50 microseconds, the acoustic wave gives rise to a unique waveform.

Many of the experimental systems of interest involve several transient intermediates. The goal of time-resolved photoacoustic calorimetry is then to obtain the amplitude factor,  $\phi_k$  which represents the fraction of the photon energy that is released as heat during the decay of the transient,  $T_k$ . The  $\phi_k$  and  $T_k$  are obtained by a deconvolution procedure of the acoustic wave,  $C_{\text{exp}}(t)$ , the details of which can be found in reference 1. The experimental waveform,  $C_{\text{exp}}(t)$ , is the convolution of a time-dependent heat source,  $E(t)$ , with the transducer function,  $T(t)$ .

$$C_{\text{exp}}(t) = E(t) * T(t) \quad (2)$$

The transducer response function  $T(t)$  may be obtained by generating an impulse function by photoexciting a calibration compound, such as ferrocene, which decays within 1 nanosecond

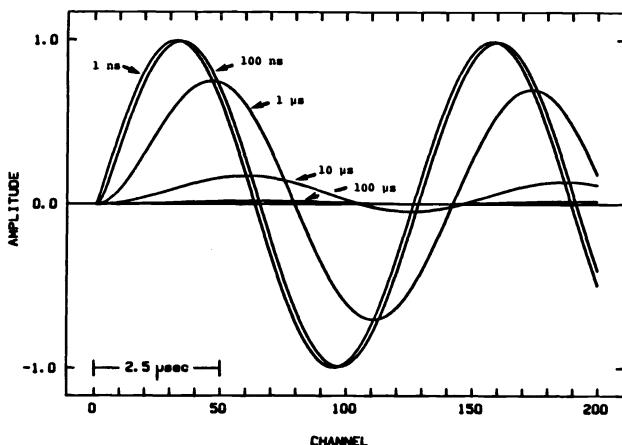


Fig. 1. The model of equation 1 with varying  $\tau$ , and  $v=10^6$  Hz,  $\tau_0 = 1$  msec.

and converts all the photon energy into heat. The deconvolution procedure involves calculating an  $E(t)$  wave assuming a set of parameters,  $\phi_k$  and  $\tau_k$ . The calculated heat wave  $E(t)$  is then used to produce  $C_{\text{calc}}(t)$  wave. The  $C_{\text{calc}}(t)$  wave is then compared to the experimental  $C_{\text{exp}}(t)$  wave by evaluation of the sum of the residuals. The fitting parameters  $\phi_k$  and  $\tau_k$  are then varied to minimize the residuals.

## EXPERIMENTAL

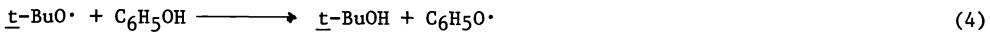
The details of the experiment have recently been presented (ref. 1). A nitrogen laser (Lumonics TE-261, 5 nsec pulse) is used for photoexcitation of the sample. The incident energy per pulse upon the sample is varied between 2 to 20 microjoules, as measured by a Laser Precision (RJ-7000) energy meter. The acoustic wave is detected by a piezoelectric transducer, amplified with a Panametrics ultrasonic preamp and a Princeton Applied Research 113 amplifier. The output is digitized by a LeCroy (WD8256) waveform recorder and the data is transferred to a Digital MINC laboratory computer for data processing.

## PHOTOCHEMICAL STUDIES

### Radical reactions

One potential application of time-resolved photoacoustic calorimetry is to the study of the reactions of carbenes and radicals in the condensed phase. To illustrate the feasibility of studying the chemistry of reactive intermediates in the condensed phase, we have investigated the hydrogen atom abstraction from phenol by t-butoxy radical.

The irradiation of di-tert-butyl-peroxide in the presence of phenol, with benzene as a solvent, leads to the following reactions.



The objective of the present study is to measure the reaction enthalpy associated with the hydrogen abstraction by t-butoxy radical from phenol, reaction 4. Knowing the heat of reaction for 4, and the oxygen-hydrogen bond enthalpy for t-butanol, the oxygen-hydrogen bond enthalpy for phenol can be obtained, providing the differential heat of solution for the reactants and products is zero. It is thus anticipated that at least two transient decays will be observed in the photoacoustic waveform, corresponding to reaction 3 and 4.

The irradiation of di-tert-butyl-peroxide at 337 nm in the presence of 0.06 M phenol results in the acoustic wave, E-wave, shown in Figure 2A. The first positive excursion of the acoustic wave amplitude for the E-wave is shifted in time by approximately 100 nanoseconds with respect to the transducer wave from ferrocene, T-wave. The ratio of the amplitudes of the E-wave to the T-wave is 1.01.

From the time-shift of the E-wave with respect to the T-wave it is evident that a reaction has occurred on the timescale of the transducer. Therefore, a minimum of two transients are required to produce the E-wave. For the deconvolution procedure, we assumed a model of two sequential decays with time constants  $\tau_1$  and  $\tau_2$ . Associated with each decay will be an amplitude factor  $\phi_1$  and  $\phi_2$ , corresponding to the fraction of the photon energy (84.7 kcal/mole for 337 nm) that is released as heat during the decay. In the deconvolution  $\tau_1$  was held constant at 1 nsec. The analysis of 30 E-wave/T-wave separate combinations resulted in an average value of  $\phi_1=0.622 \pm .011$ ,  $\phi_2=0.410 \pm .013$  and  $\tau_2=175 \pm 13$  nanoseconds

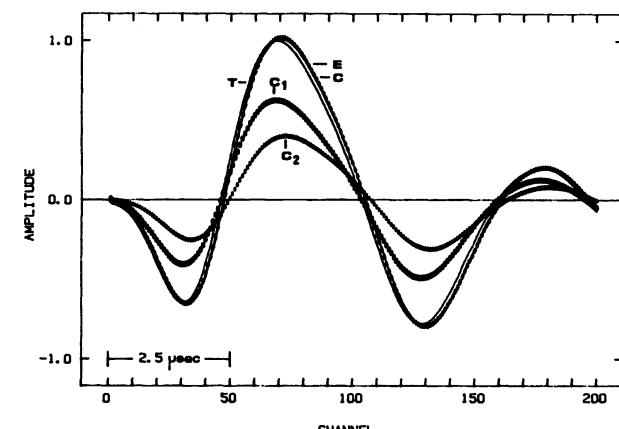


Fig. 2A. Deconvolution of the waveform from the 337 nm irradiation of a 1:7 mixture of di-*tert*-butyl-peroxide:benzene with 0.06M phenol. T-wave is ferrocene; E-wave (solid line) - peroxide/phenol; C-wave (dotted line) =  $C_1(\phi_1=0.627, \tau_1=1\text{nsec}) + C_2(\phi_2=0.41, \tau_2=186\text{ nsec})$

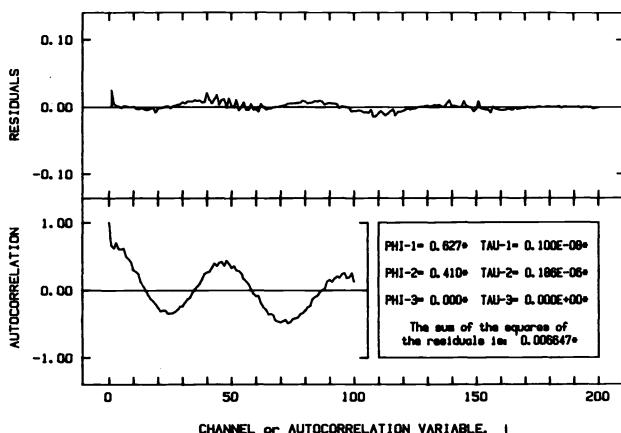


Figure 2B. The diagnostics of the convolution shown in Figure 2A.

where the minimum residual for each set is .006. A single E-wave/T-wave deconvolution is shown in Figure 2A. The calculated wave, the C-wave, is essentially superimposable with the E-wave, the difference only being manifested by the residual analysis, Figure 2B. The two components to the C-wave,  $C_1$  and  $C_2$  are also shown in Figure 2A.

The quantum yield for reaction 3 may be obtained from  $\phi_1$  and the value for the O-O bond enthalpy of di-*tert*-butyl-peroxide, 38.0 kcal/mole (ref. 4). The measured heat released during  $\tau_1$  is attributed to the sum of the decay of the excited state of the peroxide to give *t*-butoxy radical with quantum yield Q and decay of the excited peroxide to give ground state peroxide with quantum yield 1-Q. Thus, the heat released is expressed as

$$\Delta H_1 = \phi_1 \times 84.7 \text{ kcal/mole} = Q(46.7 \text{ kcal/mole}) + (1-Q)(38.0 \text{ kcal/mole}) \quad (5)$$

Thus, the quantum yield for cage escaped *t*-butoxy radical is  $Q = 0.84$ .

The enthalpy for the reaction of *t*-butoxy radical with phenol, reaction 4, is calculated as

$$\Delta H_2 = \frac{84.7 \text{ kcal/mole} \times \phi_2}{Q \times 2} \quad (6)$$

With a value of  $\phi_2 = .41$  and  $Q = .84$ , then  $\Delta H_2 = 20.6 \text{ kcal/mole}$ . Assuming an O-H bond enthalpy of 105 kcal/mole for *t*-butanol (ref. 4), the O-H bond enthalpy for phenol is  $84.4 \pm 1.0 \text{ kcal/mole}$ . This is in good agreement with the experimentally determined value of  $86.5 \pm 2.0 \text{ kcal/mole}$ . We therefore conclude from these initial experiments that time-resolved photoacoustic calorimetry will become an important methodology for the study of radical reactions in the condensed phase.

#### Strain energy of *trans*-1-phenyl-cyclohexane

The concept of strain energy has long fascinated organic chemists. Though much has been learned in recent years about strain in polycyclic compounds, there is little experimental information available regarding torsional strain around double bonds that are contained in rings. *trans*-Cyclooctene has been isolated and its strain energy was determined to be 9 kcal/mole greater than *cis*-cyclooctene (ref. 6). *trans*-Cycloheptene has been prepared by low temperature photolysis ( $-78^\circ\text{C}$ ) from the *cis* compound, but since the *trans* olefin is unstable at  $0^\circ\text{C}$ , its strain energy has not been determined.

Recently, there has been a report of the photochemical generation of 1-phenyl-*trans*-cyclohexene prepared by triplet energy transfer from xanthone to 1-phenyl-*cis*-cyclohexene (ref 7). The triplet state of the *cis* olefin decays in 65 nanoseconds to produce the *trans* compound,  $\tau_2$ , in Scheme 1. The quantum yield for *trans* formation is  $0.36 \pm .01$  (ref. 8) with the remaining triplet decaying back to the *cis* compound. The lifetime for the *trans* olefin is 9 microseconds,  $\tau_3$ , decaying to the *cis* form.

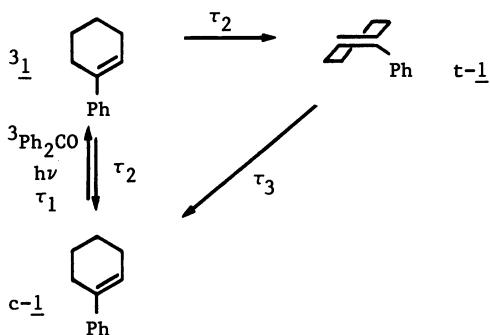
**Scheme 1**

TABLE 1. Deconvolution fitting parameters for the photosensitized isomerization of 1-phenyl-*cis*-cyclohexene in methanol.

$\phi_1 = 0.34 \pm .04$	$\tau_1 = 1 \text{ nsec}$
$\phi_2 = 0.47 \pm .03$	$\tau_2 = 64 \pm 7 \text{ nsec}$
$\phi_3 = 0.19 \pm .02$	$\tau_3 = 9.7 \pm 2.0 \mu\text{sec}$

In collaboration with Professor Caldwell at the University of Texas at Dallas, we have examined the photoacoustic waveform produced by the photosensitized isomerization of 1-phenyl-*cis*-cyclohexene. Irradiation (337 nm) of benzophenone ( $10^{-3}\text{M}$ ) in the presence of 1-phenyl-*cis*-cyclohexene (.1M) in methanol produces a photoacoustic spectrum which required three transients in the deconvolution procedure in order to obtain an acceptable fit to the experimental data, Table 1.

In the first decay process, where  $\tau_1 = 1 \text{ nsec}$  was held constant, the decay amplitude  $\phi_1 = 0.34$  corresponds to the relaxation of the benzophenone excited state and triplet energy transfer to 1-phenyl-*cis*-cyclohexene to produce the triplet state of the alkene in its thermally relaxed form. From  $\phi_1$  and the photon energy (84.7 kcal/mole), the thermally relaxed triplet energy of the alkene is  $E_T = 56.0 \pm 3.4 \text{ kcal/mole}$ .

The second decay, with  $\tau_2 = 64 \pm 7 \text{ nsec}$ , is attributed to the relaxation of the alkene triplet to produce a mixture of both *cis* and *trans* 1-phenyl-cyclohexene. This value of  $\tau_2$  is in excellent agreement with the value obtained from laser flash photolysis (ref. 7).

Finally, the third decay,  $\tau_3 = 9.7 \pm 2.5 \text{ sec}$ , is due to the isomerization of *trans* alkene back to the *cis* alkene. The heat released during this process is just the difference in strain energy between the *trans* and *cis* forms once the value is normalized to the quantum yield for the formation of the *trans* isomer, Q.

$$E_{CT} = \phi_3 \times 84.7 \text{ kcal/mole} \times (1/Q) \quad (7)$$

Thus, the strain energy of 1-phenyl-*trans*-cyclohexene relative to 1-phenyl-*cis*-cyclohexene is  $E_{CT} = 44.7 \pm 5.0 \text{ kcal/mole}$ .

These values of  $E_T$  and  $E_{CT}$  are the first experimental measure of a thermally relaxed triplet state of an alkene and the strain energy of a *trans* cyclohexene (ref. 8). Furthermore, this is a clear demonstration that time-resolved photoacoustic calorimetry can be applied to rather complex photochemical reactions that involve as many as three transient decays.

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