

EXPERIMENTAL APPROACHES TO MEASURE THE CHEMICAL AND PHYSICAL
PROPERTIES OF RADICAL INTERMEDIATES; TIME-RESOLVED PHOTOACOUSTIC
CALORIMETRY WITH THE LAYERED PRISM CELL.

Tom Autrey and Nancy Foster-Mills

Pacific Northwest National Laboratory
Environmental Health Sciences Division
Richland, WA 99352

KEYWORDS

Thermochemistry, kinetics, radical intermediates

ABSTRACT.

Mechanistic kinetic modeling has been successfully used to elucidate the contributions of strong bond scission by various competing hydrogen transfer pathways as a function of the reaction conditions. The success of the MKM approach is limited by the availability and quality of kinetic and thermodynamic data derived from either experimental and/or theoretical methods. New and improved experimental methods to obtain quantitative information regarding the thermochemical and kinetic properties of reactive intermediates in condensed phases will facilitate the development new and improved mechanistic kinetic models. We have used time-resolved photoacoustic calorimetry, employing the Layered Prism Cell (LPC), to measure the chemical and physical properties of short-lived reactive intermediates in solution. The lifetimes and thermochemical properties of reactive radicals in the presence of various hydrogen atom donors will be presented and comparisons will be drawn to the literature.

INTRODUCTION.

Mechanistic Kinetic Modeling (MKM) is a useful experimental approach to quantify and understand the important reaction pathways occurring in a complex reaction scheme. MKM combined with traditional experimental and semi-empirical approaches have been used to investigate high temperature (> 600 K) hydrogen atom transfer pathways between hydroaromatic structures.¹⁻¹⁷ The approach is develop a model inclusive of the important reaction pathways that will "predict" (or fit) experimental observations. However, the quality of the model is limited by inclusion of the important reaction steps and the availability of thermochemical kinetic parameters to provide temperature dependent rate data. The models have evolved with enhanced methods to predict contributing reaction pathways and improvements in measuring or calculating heats of formation of transient radical intermediates. For example, inclusion of the reverse hydrogen transfer step for a thermal neutral hydrogen transfer yields a model that fits the experimental data without the need to invoke the controversial radical hydrogen transfer pathway.⁷ In another example, it was shown that varying the barrier for the initiation step for hydrogen transfer between alkyl pyrenes by less a few kcal/mol resulted in a model that fits the experimental data without the need to invoke the rht pathway.² Even the observed experimental selectivity of bond scission could be explained by a change in reaction pathways (hydrogen atoms and/or molecular assisted homolysis) with a change in solvent composition.¹

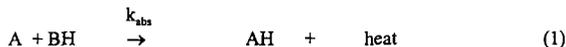
One of the goals of our research is to use experimental and theoretical approaches to measure or calculate the heats of formation of organic free radicals and to measure rate constants of reactions of reactive transient species. In this symposium new methods using time-resolved photoacoustic calorimetry to obtain rate constants for hydrogen atom transfer reactions and determinations of heats of formation of transient species will be presented.

APPROACH.

Time-resolved photoacoustic calorimetry has been used to obtain both chemical and physical properties of photo-generated reactive intermediates. Absorption of electromagnetic energy (hv) by a molecule in solution generates an electronically/vibrational excited meta-stable intermediate. The excess energy can be released from the excited state by a combination of emission, internal conversion (IC) and/or *chemical pathways*. The release of heat by either IC or chemical pathways generates an acoustic pressure pulse that can be detected with an ultrasonic transducer. The mathematical solutions describing the events leading to formation of the acoustic pressure pulse and the subsequent detection with piezoelectric transducers to yield a

photoacoustic signal,¹⁸⁻²⁰ and the methods to analyze the photoacoustic signals to obtain information on the chemical and physical properties of short-lived reactive intermediates have been studied in detail.²¹⁻²⁷

A model is useful to illustrate the time dependent response, $M(t)$, provided by an ultrasonic transducer for a simple scheme involving the reaction of a reactive intermediate A to AH as shown in equation 1. In this example A is a photo-generated reactive intermediate and B is a hydrogen donor. $M(t)$ is adequately described by a convolution (*) of the exponential release of heat $H(t)$ with a model instrument response function, $S(t)$. In our model $S(t)$ is a dampened sine wave, where ν is the resonant frequency, τ_c is the dampening constant of the transducer and K is an instrument constant. Using our model instrument response function we can demonstrate that for τ_A , ($\tau_A = 1/k_{abs}$, rate of abstraction) in $H(t)$, varied between 100 ns and 10 μ s result in a calculated response $M(t)$ that is distinguishable in shape from model instrument response $S(t)$ as shown in Figure 1.



$$M(t) = H(t) * S(t) \quad (2)$$

$$H(t) = \phi_{abs} \exp(-t/\tau_A) \quad (3)$$

$$S(t) \sim K [\exp(-t/\tau_c) \sin(\nu t)] \quad (4)$$

The experimental instrument response $R(t)$ can be obtained with a photoacoustic standard, where $\phi = 1$, and $\tau \ll \nu$. The experimentally observed photoacoustic signal $E(t)$ is therefore the convolution of $H(t)$ with the experimental instrument response $R(t)$ as shown in equation 5.

$$E(t) = H(t) * R(t) \quad (5)$$

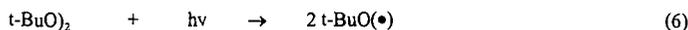
From the *shape* and *amplitude* of the experimental photoacoustic waveform, $E(t)$, we can obtain a description of the events that occurred as a consequence of the absorption of energy to generate radical intermediate A. The exponential release of heat $H(t)$ is comprised of two separable parameters, ϕ_{abs} the fraction of absorbed energy released as heat in the conversion of A \rightarrow AH, and τ_A , the lifetime of reactive intermediate A. This is an important point, the *amplitude* of the photoacoustic waveform is directly proportional to the magnitude of the fraction of absorbed energy released as heat, and the *shape* of the photoacoustic waveform is proportional to the rate of decay of A \rightarrow AH.

Deconvolution of the experimental waveform $E(t)$, with the experimentally measured instrument response, $R(t)$ can provide quantitative information regarding both the quantity of energy released in the transformation of A \rightarrow AH and the rate at which the process occurs. Both ϕ_{abs} and τ_A depend on the concentration and properties of the hydrogen atom donor BH. Importantly, these two parameters can be treated independently. Specifically, sources of heat (or volume changes) contributing to the amplitude of the photoacoustic signal need not be quantitatively discriminated if a kinetic analysis is all that is desired.

In our laboratory we have been developing methods to improve the sensitivity, enhance the time-resolution and increase experimental flexibility.²⁸⁻³¹ We have taken an approach to treat the kinetic and thermodynamic components of the experiment separately when necessary. Using optical transparent (thin) samples the kinetic information (τ) can be obtained from the shape of the waveform, even if the thermodynamic and volumetric components contributing to the amplitude of the signals are still difficult to quantify.

RESULTS.

Pulsed photolysis of di-*t*-butylperoxide in the uv generates a pair of reactive *t*-butoxyl radicals. The lifetime of the radicals is solvent dependent. The reaction scheme shown in equations 6-7 can be modeled as a sequential two step reaction pathway.



In previous work²⁸ we demonstrated the capability to obtain the lifetime of the t-butoxyl radical in binary solvent mixtures containing methanol and ethanol. Using the layered PA cell permits the a direct measure of the rate of hydrogen abstraction by measuring the volume change induced by the reaction of the alkoxy radical with the solvent (even when the thermodynamic properties of the sample and reference solutions are not matched).

To obtain quantitative thermochemical estimates a reasonable understanding of both thermal and volumetric contributions to the PA amplitude must be evaluated. There has been some effort undertaken to separate the enthalpic and volumetric contributions in organic solvents using both photoacoustic and transient grating approaches. Another potential hindrance is thermal changes brought about by changes in heats of solvation. In order to separate the ΔV_{rxn} and $\Delta \Delta H_{\text{soliv}}$ terms from the experimentally measured amplitude a few groups have used correction terms. The approach is to use a standard hydrogen donor, e.g., cyclohexadiene and assume the difference between the gas phase literature value and the experimental PA signal is constant. Then the difference between gas phase values and observed value (a correction term) can be subtracted from experimental value to arrive at an experimental measurement of the BDE. One of the assumptions used in the correction term approach is the equivalency of the solvent quality factors for an organic solvent with and without significant concentrations of peroxide. For unmatched solvents there can be a substantial difference. Additionally correction factors must be determined for each experimental condition, i.e., irradiation in a 30% peroxide solution will yield a different correction term need for a 6% peroxide solution and different corrections are necessary for various excitation wavelengths, i.e., 308 nm will yield a different magnitude correction than 355 nm.

The advantage of the layered prism cell is that a direct measure can be possible because the reaction volume change, due to peroxide bond scission, can be separated from the thermal volume change, due to an exothermic hydrogen atom abstraction, in a time-resolved manner. Unfortunately interpretation of thermochemistry data obtained in the layered cell can suffer from the same difficulties experienced with the traditional cuvette geometry in solvents where the contribution due to enthalpies of solvation of the different species can be significant. An accurate evaluation of the thermochemistry requires equivalent thermoelastic properties ($\beta/\alpha\rho C_p$) for both the sample and reference solution and the ability to separate the ΔV_{rxn} and $\Delta \Delta H_{\text{soliv}}$ from the amplitude of the signal. Results for some of our energy determinations are shown in Table 1. The lower limits determined for the BDE in polar solvents is likely due to the contribution differences in enthalpy of solvation between the alkoxy radical/donor pair and the t-BuOH/donor radical pair. The benefits and limitations of time-resolved photoacoustic calorimetry with the layered prism cell will be presented.

ACKNOWLEDGMENTS.

This work was supported by the U.S. Department of Energy, Office of Basic Energy Research, Chemical Sciences Division, Process and Techniques Branch. The work was conducted at Pacific Northwest Laboratory, which is operated for the U. S. Department of Energy under Contract DE-ACO6-76RL0 1830. Support for NFM was provided through AWU-NW under grant DE-FG06-89ER-75522 with the U.S. Department of Energy.

REFERENCES.

- (1) Autrey, T.; Albom, E. A.; Franz, J. A.; Camaioni, D. M. *Energy Fuels* 1995, 9, 420-8.
- (2) Autrey, T.; Powers, T.; Albom, E. A.; Camaioni, D. M.; Franz, J. A. *Coal Sci. Technol.* 1995, 24, 1431-4.
- (3) Autrey, T.; Albom-Cleveland, E.; Camaioni, D. M.; Franz, J. A. *Prepr. Pap. - Am. Chem. Soc., Div. Fuel Chem.* 1994, 39, 627-31.
- (4) Autrey, S. T.; Camaioni, D. M.; Ferris, K. F.; Franz, J. A. *Conf. Proc. - Int. Conf. Coal Sci., 7th* 1993, 1, 336-9.
- (5) Autrey, T.; Gleicher, G. J.; Camaioni, D. M.; Ferris, K. F.; Franz, J. A. *Prepr. Pap. - Am. Chem. Soc., Div. Fuel Chem.* 1991, 36, 521-8.
- (6) Autrey, T.; Franz, J. A. *Prepr. Pap. - Am. Chem. Soc., Div. Fuel Chem.* 1990, 35, 381-6.
- (7) Camaioni, D. M.; Autrey, S. T.; Franz, J. A. *J. Phys. Chem.* 1993, 97, 5791-2.
- (8) Camaioni, D. M.; Autrey, S. T.; Franz, J. A. *Prepr. - Am. Chem. Soc., Div. Pet.*

- Chem.* **1994**, *39*, 303-9.
- (9) Camaioni, D. M.; Autrey, S. T.; Salinas, T. B.; Franz, J. A. *J. Am. Chem. Soc.* **1996**, *118*, 2013-22.
 - (10) Savage, P. E. *Energy Fuels* **1995**, *9*, 590-8.
 - (11) McMillen, D. F.; Malhotra, R.; Tse, D. S. *Energy Fuels* **1991**, *5*, 179.
 - (12) McMillen, D. F.; Malhotra, R.; Chang, S.-J.; Fleming, R. H.; Ogier, W. C.; Nigenda, S. E. *Fuel* **1987**, *66*, 1611.
 - (13) Malhotra, R.; McMillen, D. F. *Energy Fuels* **1993**, *1993*, 227.
 - (14) Stein, S. E. *Acc. Chem. Res.* **1991**, *24*, 350.
 - (15) Autrey, T.; Linehan, J. C.; Steams, C. J.; Camaioni, D. M.; Kaune, L.; Franz, J. A. *Prepr. Pap. - Am. Chem. Soc., Div. Fuel Chem.* **1997**, *42*, 66-69.
 - (16) Autrey, T.; Linehan, J. C.; Camaioni, D. M.; Kaune, L. E.; Watrob, H. M.; Franz, J. A. *Catal. Today* **1996**, *31*, 105-111.
 - (17) Autrey, T.; Linehan, J.; Camaioni, D.; Powers, T.; Wartob, H.; Franz, J. *Prepr. Pap. -Am. Chem. Soc., Div., Fuel Chem.* **1995**, *40*, 973.
 - (18) Patel, C. K. N.; Tam, A. C. *Rev. Modern Phys.* **1981**, *53*, 517-549.
 - (19) Lai, H. M.; Young, K. *J. Acoust. Soc. Am.* **1982**, *72*, 2000-2006.
 - (20) Diebold, G. J. *J. Phys. Chem. B* **1998**, *102*, 5404-5408.
 - (21) Rudzki, J. E.; Goodman, J. L.; Peters, K. S. *J. Am. Chem. Soc.* **1985**, *107*, 7849-7854.
 - (22) Braslavsky, S. E.; Heihoff, K. *Photothermal Methods*; Scaiano, J. C., Ed.; CRC Press, 1989; Vol. 1, pp 327-355.
 - (23) Braslavsky, S. E.; Heibel, G. E. *Chemical Reviews* **1992**, *92*, 1381-1410.
 - (24) Melton, L. A.; Ni, T.; Qingzheng, L. *Rev. Sci. Instrum.* **1989**, *60*, 3217-3223.
 - (25) Arnaut, L. G.; Caldwell, R. A.; Elbert, J. E.; Melton, L. A. *Rev. Sci. Instrum.* **1992**, *63*, 5381-5389.
 - (26) Beck, K. M.; Gordon, R. J.; Tardy, D. C. *Adv. Chem. Kinetics and Dynamics* **1995**, *2B*, 299-332.
 - (27) Puchenkov, O. V.; Malkin, S. *Rev. Sci. Instrum.* **1996**, *67*, 672-680.
 - (28) Autrey, T.; Foster-Mills, N.; Klepzig, K. *Photochem. Photbio. A* **1999**. In press
 - (29) Autrey, T.; Foster, N. S.; Klepzig, K.; Amonette, J. E.; Daschbach, J. L. *Rev. Sci. Instrum.* **1998**, *69*, 2246-2258.
 - (30) Foster, N. S.; Amonette, J. E.; Autrey, T. *Applied Spectroscopy* **1999**, *53*(6), in press.
 - (31) Foster, N. S.; Autrey, T.; Amonette, J. E.; Small, J. R.; Small, E. W. *American Laboratory* **1999**, *31*(4), 96.

Table 1. Experimentally measured heats of reaction for hydrogen atom abstraction by t-butoxyl radical from a series of organic hydrogen donor solvents determined by time-resolved photoacoustic calorimetry in the layered prism cell. The calculated BDE's are compared to the literature values.

Donor	ϕ^a	Experimental		Literature BDE
		ΔH_{rxn} (kcal/mol)	BDE ^b	
MeOH	0.28	-9.2±.5	(>89.6) ^c	92-96
EtOH	0.24	-13±.7	(>90.4) ^c	>93
IPA	0.22	-13±1	(>90.7) ^c	>91
THF	0.29	-13.1±.5	(>89.1) ^c	92-95
Cyclohexane	0.31	-5.6±.8	98.6	98.2
Toluene	0.31	-16.6±.9	88.0	88.6

(a) fraction of heat released in hydrogen abstraction step. (b) calculated bond dissociation energy determined from photoacoustic measurement. (c) lower limit, see text.

Figure 1. Model of a photoacoustic signal obtained using a 1 MHz piezoelectric transducer. Comparison of the instrument response $S(t)$ with $M(t)$ with $\tau_A = 100$ ns, and $M(t)$ with $\tau_A = 10$ μ s.

