experiment. With this method *single* lines appear on the diagonal of the two-dimensional plot and cross-peaks connect lines corresponding to dipolar coupled spins. The second approach involves double-quantum filtering and therefore single-quantum lines are removed from the spectra. A technique such as this (together with extensive phase cycling) is mandatory for natural abundance samples where the intensity of the double-quantum spectra is well below the single-quantum lines. The second method results in a display containing isotropic shifts in the F_2 dimension and sums and differences of shifts in F_1 as in the liquid-state INADEQUATE experiment.[6-9] It is clear that with improved signal-to-noise, available through dynamic nuclear polarization or low temperatures, these methods should be applicable to $^{13}C-^{13}C$ spectra and to a number of other systems, e.g., ^{187}W, etc. They should provide a powerful technique for elucidating the structure of solids.

VI. Experimental Section

The spectra discussed above were obtained on a home-built pulse spectrometer operating at ^1H and ^{13}C frequencies of 317 and 79.9 MHz, respectively. The ^1H decoupling field was 100 kHz and the ^{13}C field was 60 kHz. The glycine was 90% doubly labeled and was procured from Merck Isotopes. Rotors were of the Andrew-Beam design fabricated from Delrin.

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Heats of Formation of Radicals and Molecules by a Photoacoustic Technique[1]

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Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6. *Received September 9, 1985*

Abstract: A photoacoustic technique was used to measure heats of free radical reactions. To illustrate the method, bond dissociation energies were measured for the Sn–H bond in *n*-Bu_3SnH, for the C_3–H bond in 1,4-cyclohexadiene, and for the C_2–H bond in diethyl ether. Heats of formation of *t*-BuO$\dot{P}$$Ph_3$ and *t*-BuO$\dot{P}$(Bu-*n*)$_2$ were determined, and the method was also used to measure quantum yields for the photolysis of di-*tert*-butyl peroxide and diphenyl disulfide.

Homolytic bond dissociation energies have proved to be particularly difficult to measure. Even in the simplest cases, experiments are fraught with problems as evidenced by the controversy surrounding values for primary, secondary, and tertiary C–H bond strengths.[2] Reliable data for organometallic compounds and for those of high molecular weight are particularly rare, because these materials are inappropriate for conventional gas-phase techniques. Under these conditions, any method that represents a new source of thermochemical information should obviously be welcomed and exploited to the full.

Recently, Peters and his co-workers described a photoacoustic technique for measuring heats of reactions that were photoinitiated.[3-6] For example, they studied the thermochemistry of ion-pair formation in triplet benzophenone quenching by aniline[3] and the heat of formation of diphenylcarbene,[4] a species that is particularly short lived in solution. With their help and encouragement, we have applied the technique to free radical reactions and now report measurements of some C–H and an Sn–H bond strengths. We have also used the method in situations where the radical thermochemistry was reasonably well-known and have thus been able to derive quantum yields for bond cleavage and heats of formation of molecules. In addition, we have measured the heat of formation of a short-lived phosphoranyl radical.

Experimental Section

Materials. All of the materials used in this work were commercially available. Benzene was purified by multiple washings with concentrated sulfuric acid. It was then washed with water, dried over sodium sulfate, and finally distilled from calcium hydride. Diethyl ether was distilled from sodium benzophenone. Triphenylphosphine and *o*-hydroxybenzophenone were recrystallized twice from ethanol. Di-*tert*-butyl peroxide was washed with an aqueous solution of silver nitrate and then with water. It was dried over magnesium sulfate and was finally passed through a column of neutral alumina. Tri-*n*-butyltin hydride and 1,4-cyclohexadiene were distilled under nitrogen before use.

Apparatus. The photoacoustic apparatus is shown schematically in Figure 1 and follows the design developed by Peters et al.[3-6] Pulses from a nitrogen laser (Molectron UV 24, λ = 337.1 nm; pulse width 10 ns; power, 10 mJ per pulse; repetition rate, 5 Hz) were used to photolyze solutions of photolabile substrates contained in a standard UV flow cell (Hellma 176). An iris ensured that only a very small part of the light passed as a fine beam through the center of the cell, and a low powered lens was used to correct for the slight divergence of the beam. Neutral density filters were often employed to further attenuate the light intensity.

The heat evolved as a result of the photoinitiated reactions caused a shock wave in the solution, which was transmitted at the speed of sound to the cell wall. Here, the primary wave and its many reflections were detected in a time-resolved mode by a piezoelectric transducer (Panametrics V110, response 0.2 μs, or Model V101, response 2.0 μs). The transducer signals were amplified (Panametrics ultrasonic preamplifiers) and were recorded on a storage oscilloscope (Tektronics 7020).

A quartz plate was used to reflect part of the laser beam to a reference device, so that corrections could be made for variations in the laser power. Several devices were tried, e.g., power meter, photomultiplier tube, photodiode. However, in our hands, the most reliable reference was a second photoacoustic arrangement consisting of a cuvette and a trans-

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[1] Issued as NRCC publication No. 25426.

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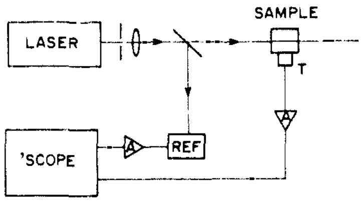

Figure 1. Block diagram of photoacoustic apparatus. T, piezoelectric transducer; A, amplifier; REF, reference cell.

ducer. The cuvette was filled with a solution of *o*-hydroxybenzophenone in isooctane (absorbance ≃ 0.5). On prolonged irradiation some drift in this device occurred, presumably because small convection currents were set up in the solution. However, the problem was easily overcome by slowly flowing the solution through the cell with a peristaltic pump. Signals from the reference transducer were amplified and were stored in a second channel of the Tektronics oscilloscope.

The time profiles of the photoacoustic waves were quite reproducible so long as the geometry of the apparatus remained unchanged. In general, the measurements from 20 laser shots were averaged to give the amplitudes of the photoacoustic waves due to sample and reference. The ratio of these amplitudes is defined as the "normalized photoacoustic response", *N*, of the system.

In the photoacoustic experiment, an important condition was that the heat evolved in a given reaction was released in a time that was short with respect to the response of the transducer. This was tested in three ways: first, by comparing the profiles of the waves due to sample and standard; second, by changing the concentrations of substrates when bimolecular reactions were studied; third, by using transducers whose response time differed by an order of magnitude. As a further check, it was normally possible to calculate the timescale for heat deposition since the reaction kinetics were generally known.[7] Only in the case of diethyl ether (vide infra) were problems due to system response encountered, but these were overcome by using high ether concentrations (>3 M) and the transducer with the slowest response.

The samples used in the photoacoustic experiments were always carefully deoxygenated by nitrogen or argon purging and were flowed through the UV cuvette so as to avoid problems associated with sample depletion and/or product formation. Samples that were oxygen-sensitive were always prepared in an inert atmosphere since oxidation generally gave rise to colored impurities which affected the optical properties of the solutions.

Results and Discussion

The photoacoustic approach to thermochemistry is conceptually simple and all of its elements can be tested experimentally.

The technique has been described in some detail by Peters and his colleagues.[3-6] Briefly, a solution of a photolabile substrate, contained in a UV cuvette, was irradiated by pulses from a nitrogen laser (pulse width, 10 ns; $h\nu = 84.8$ kcal mol^{-1}). The size of the beam was restricted with an iris so that it was small with respect to the cell dimensions. Absorbing molecules in the path of the beam gained energy corresponding to the quantum energy of the light, and the resulting physical or chemical processes released this energy as radiation or heat. The deposition of heat caused a shock wave in the cell which was transmitted through the solution to the cell walls where it was detected by a piezoelectric pressure transducer. The amplitude of the first shock wave to reach the cell wall was porportional to the heat liberated (vide infra) so that the system functioned as a simple calorimeter.

The apparatus was calibrated by filling the cell with optically dilute solutions of *o*-hydroxybenzophenone, which converts all of the light energy absorbed into heat within a few nanoseconds.[8]

Quantum Yields for Photolysis of Di-*tert*-butyl Peroxide. In the experiments described in this work, di-*tert*-butyl peroxide was used as the photolabile substrate. The excited state of the peroxide does not undergo radiative decay but is dissociative and gives two *tert*-butoxy radicals, eq 1.

$$t\text{-BuO–OBu-}t \rightarrow 2t\text{-BuO}\cdot \qquad (1)$$

Experiment and theory show that, in the gas phase, the quantum yield for photolysis is unity.[9-11] Therefore, to a first approximation the heat deposited in solution will be equal to the photon energy less the heat of the reaction, ΔH_R, which is given by the O–O bond dissociation energy of the peroxide. However, in solution the quantum yield, Φ, may be reduced by a cage effect which causes a proportion of the initially formed *tert*-butoxy radical pairs to recombine to the parent peroxide without diffusing as free radicals into the bulk solution.[12,13]

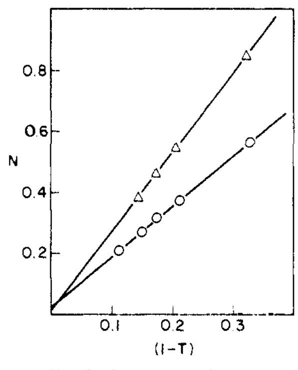

Figure 2. Plot of normalized photoacoustic response (*N*) vs. light absorbed by the sample (1 – *T*). *o*-Hydroxybenzophenone (Δ), di-*tert*-butyl peroxide (O).

The primary photochemical decomposition and any cage recombination are processes that are very fast with respect to the transducer response. Moreover, the design of the experiment was such that, in an inert solvent, the lifetimes of the free-*tert*-butoxy radicals were long with respect to the response (vide infra). Accordingly, the observed heat deposition, ΔH_{obsd}, is related to Φ by eq 2.

$$\Delta H_{\text{obsd}} = 84.8 - \Delta H_R \Phi \qquad (2)$$

The heat deposition was measured for di-*tert*-butyl peroxide photolysis in carbon tetrachloride, which served as an inert solvent. The normalized photoacoustic response, *N*, for peroxide photolysis was plotted vs. the light absorbed by the sample, Figure 2. A similar plot was then constructed for the photolysis of *o*-hydroxybenzophenone solutions which were used to calibrate the apparatus. Since the latter rapidly converts all of the light absorbed into thermal energy, the ratio of slopes a_R and a_S for reaction and standard, respectively, gave ΔH_{obsd}, eq 3, and combination of eq 2 and 3 gave eq 4.

$$\Delta H_{\text{obsd}} = 84.8(a_R/a_S) \qquad (3)$$

$$\Delta H_R = (84.8/\Phi)(1 - a_R/a_S) \qquad (4)$$

The linearity of the plots (Figure 2) indicated that the normalized photoacoustic response, *N*, was proportional to the amount of the light absorbed. In addition, the amplitude of the response was directly proportional to the intensity of the laser beam when attenuated by using neutral density filters. This confirmed that the *tert*-butoxy radicals were long-lived on the time scale of the transducer response, since any contribution to the photoacoustic wave due to bimolecular reactions of the radical would have been concentration, and hence light intensity, dependent.

The heat deposition measured in the photoacoustic experiment was 57.6 ± 1.0 kcal mol^{-1}, eq 2, 3. Since the O–O bond strength in di-*tert*-butyl peroxide is 38.3 kcal mol^{-1},[14] the quantum yield in solution, Φ, was 0.71, eq 2–4.

The fraction of radical pairs that undergo cage collapse, *F*, is by definition equal to $(1 - \Phi)$ and to a good approximation should be related to the solvent viscosity, η, via eq 5, where *A* and *B* are

$$1/F = A + B/\eta \qquad (5)$$

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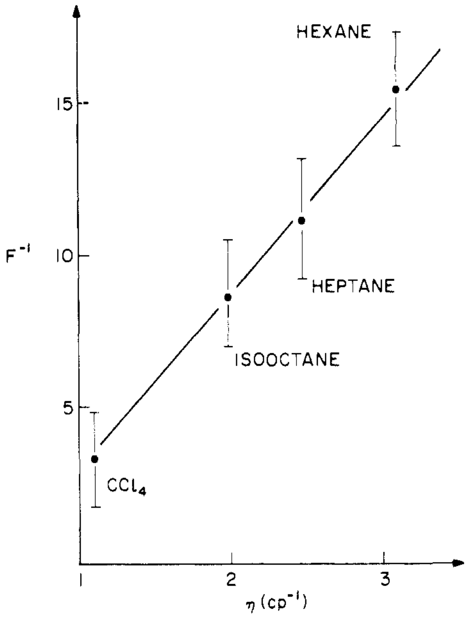

Figure 3. Dependence of cage collapse (F) for *tert*-butoxyl radical pairs on solvent viscosity η.

constants.[15] Data have been obtained on the effect of solvent viscosity on the callapse of *tert*-butoxy radical pairs which were generated by the thermolysis of di-*tert*-butyl hyponitrite.[12] These are plotted (eq 5) together with the result obtained in the present work in Figure 3. Within the limits of the experimental errors, there is clearly good agreement between the results obtained in the different systems, proving the reliability and accuracy of the photoacoustic method in this context.

A similar experiment was carried out on the photolysis of diphenyl disulfide in isooctane solution, eq 6. The observed heat

$$\text{PhS-SPh} \rightarrow 2\text{PhS} \qquad (6)$$

deposition was 74.9 ± 1.0 kcal mol^{-1}. Since the bond strength of the S-S bond in the disulfide is 55.0 ± 1.5 kcal mol^{-1},[16] it follows that the quantum yield was only 0.18 ± 0.1, eq 2-4. The quantum yield is clearly far lower than that which would be expected if a cage effect alone were operative. Moreover, since diphenyl disulfide shows almost no fluorescence, the value quoted effectively represents the efficiency of photochemical cleavage of the S-S bond.

Bond Dissociation Energies. *tert*-Butoxy radicals, obtained by photolysis of the parent peroxide, were used to abstract hydrogen at a variety of substrates R-H, eq 1, 7. The substrates were

$$t\text{-BuO}\cdot + \text{RH} \rightarrow t\text{-BuOH} + \text{R}\cdot \qquad (7)$$

chosen so that, at appropriate concentrations of R-H, reaction was fast with respect to the response of the transducers (see Experimental Section). In our system, the decay of the radicals, *R*·, was slow with respect to this response. This was tested by showing that the photoacoustic signal was proportional to the laser light intensity when the latter was varied by an order of magnitude. Under these conditions, the combined heats of reactions 1 and 7, ΔH_R, is given by eq 4 and 8.

$$\Delta H_R = 2\Delta H_f(t\text{-BuOH}) + 2\Delta H_f(\text{R}\cdot) - \Delta H_f(t\text{-BuOOBu-}t) - 2\Delta H_f(\text{RH}) \qquad (8)$$

To obtain bond dissociation energies, BDE(R-H), we combined these equations and applied literature values for the heats of formation of t-BuOH,[17] t-BuOOBu-t,[14] and H·[17] and the quantum yield, Φ, for photolysis of the peroxide in isooctane solvent,[18] eq 9, 10.

Table I. Values of ΔH_R for the Reaction between Di-*tert*-butyl Peroxide and Hydrogen Donors, RH, and Bond Dissociation Energies, BDE(R-H)

		BDE(R-H)	
R-H	ΔH_R, kcal mol^{-1}	this work, kcal mol^{-1}	lit., kcal mol^{-1}
Bu_3SnH	-24.9 ± 1.0	73.7 ± 2.0	74[a]
1,4-cyclohexadiene	-26.2 ± 1.0	73.0 ± 2.0	73 ± 5[b]
EtOEt	12.7 ± 1.0	92.5 ± 2.0	91.7 ± 0.4[c]

[a] Estimated, ref 23. [b] Estimated, ref 24. [c] Reference 25.

$$\text{BDE(R-H)} = \Delta H_f(\text{R}\cdot) + \Delta H_f(\text{H}\cdot) - \Delta H_f(\text{RH}) \qquad (9)$$

$$\text{BDE(R-H)} = \Delta H_R/2 + 86.1 \qquad (10)$$

Carefully purified samples of tri-*n*-butyltin hydride[19] and 1,4-cyclohexadiene[7,22] were chosen as substrates R-H, since only fairly crude estimates existed for their respective Sn-H[23] and C_3-H[24] bond strengths. The photoacoustic signals were independent of the concentration of RH (ca. 1.5 M in isooctane solvent) when the latter was varied by a factor of 2 or more. This demonstrated that reaction 7 was rapid with respect to the response of the transducer.[7] Values of ΔH_R and hence of BDE(R-H) for these substrates are reported in Table I together with C-H bond dissociation energy in diethyl ether, eq 11. There was good

$$t\text{-BuO}\cdot + (\text{CH}_3\text{CH}_2)_2\text{O} \rightarrow t\text{-BuOH} + \text{CH}_3\dot{\text{C}}\text{HOCH}_2\text{CH}_3 \qquad (11)$$

agreement, in all cases, between the measured and the estimates[23,24] or literature values[25] for the bond strengths in question.

Heats of Formation of Molecules. In cases where heats of formation of radicals are known, the photoacoustic technique can be used to measure heats of formation of molecules. Thus, by using n-Bu_3P as substrate[7] and by measuring $\Delta H_{(1+12)} = -5.3$ ± 0.5 kcal mol^{-1}, we determined $\Delta H_f(t\text{-BuOP(Bu-}n)_2) = -105$ ± 2 kcal mol^{-1}.[26] This value leads to $\Delta H_{12} = -24$ ± 2 kcal mol^{-1}.[14,26] Interestingly, reaction 13 could, in principle, have given different

$$t\text{-BuO}\cdot + n\text{-Bu}_3\text{P} \rightarrow t\text{-BuOP(Bu-}n)_2 + n\text{-Bu}\cdot \qquad (12)$$

$$t\text{-BuO}\cdot + n\text{-Bu}_3\text{P} \rightarrow t\text{-Bu}\cdot + \text{OP(Bu-}n)_3 \qquad (13)$$

products by a far more exothermic route[14,26,28] ($\Delta H_{13} = -48.7$ kcal mol^{-1}) yet it does not occur to a significant extent at 300 K or below.

Heat of Formation of a Phosphoranyl Radical. *tert*-Butoxy radicals react rapidly with triphenylphosphine to give the *tert*-butoxytriphenylphosphoranyl radical (I), eq 14.[29] The lifetime

$$t\text{-BuO}\cdot + \text{Ph}_3\text{P} \rightarrow \underset{\text{I}}{t\text{-BuO}\dot{\text{P}}\text{Ph}_3} \qquad (14)$$

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(19) The rate constant for hydrogen abstraction at the Sn-H bond by *tert*-butoxy[20] is ca. 2 orders of magnitude greater than the sum of rate constants for attack at all other positions.[21]

(20) Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 5399.

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(25) Kondo, O.; Benson, S. W. *Int. J. Chem. Kinet.* **1984**, *16*, 949.

(26) $\Delta H_f(n\text{-Bu}_3\text{P}) = -41.4$ kcal mol^{-1} was calculated from $\Delta H_f(\text{Et}_3\text{P})$[17] and group contributions.[20] $\Delta H_f(n\text{-Bu}\cdot) = 17.5$ kcal mol^{-1} was calculated[17] by assuming that the primary C-H bond strength in butane was equal to that in ethane.[2b] For $\Delta H_f(t\text{-BuOOBu-}t)$, see ref 14.

(27) Benson, S. W. In "Thermochemical Kinetics", 2nd Ed.; Wiley: New York, 1976.

(28) $\Delta H_f(n\text{-Bu}_3\text{PO}) - \Delta H_f(n\text{-Bu}_3\text{P})$[26] is taken to be -79.8 kcal mol^{-1} by comparison with the methyl analogues.[17] For $\Delta H_f(t\text{-Bu}\cdot)$ see ref 2b.

(29) Roberts, B. P.; Scaiano, J. C. *J. Chem. Soc., Perkin Trans. 2* **1981**, 905 and references cited therein.

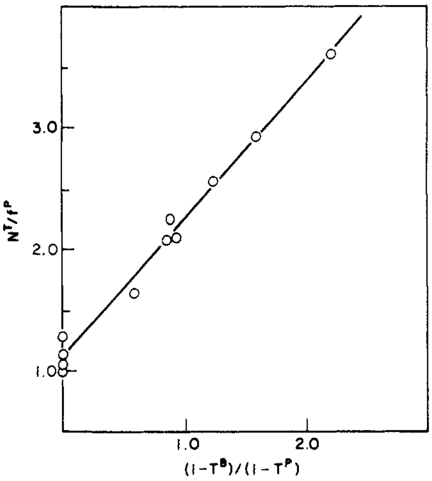


Figure 4. Plot of N^T/f^P vs. $(1 - T^B)/(1 - T^P)$ for the photoacoustic response of the triphenylphosphine/di-*tert*-butyl peroxide system.

of this radical is rather short (τ = 1.3 ms at 300 K).[29] Nevertheless, τ is long with respect to the microsecond responses of the transducers used in this work. Accordingly, the overall enthalpy change for reactions 1 and 14 could be measured by the photoacoustic technique. However, in this case a significant complication arose due to light absorption by the triphenylphosphine itself.

In the photoacoustic experiments previously described, the normalized photoacoustic response, N, due to light absorption by the sample, cell, solvent, and/or substrate were generally negligibly small compared to the response generated by the reaction of interest. Moreover, contributions from solvent and sample cell responses were eliminated by the calibration procedure. In this instance, however, light absorption by triphenylphosphine caused a substantial contribution to the photoacoustic response. In addition, as di-*tert*-butyl peroxide was added to the reaction mixture, the fraction of the laser light absorbed by the phosphine must obviously have been reduced. Accordingly, the photoacoustic data had to be corrected for contributions due to absorption by the phosphine and its dependence on the concentration of the added peroxide.

Theory, and more importantly experiment (vide supra) have established that the photoacoustic response, N, was proportional to the amount of light absorbed by the sample, i.e., $1 - T$, where T is the transmittance, eq 15, and a is a constant, cf. eq 3.

$$N = a(1 - T) \qquad (15)$$

We can apply the Beer-Lambert law for optical absorption to express the fraction, f, of light absorbed by the phosphine or the peroxide. The expression for the phosphine is given in eq 16 and 17. In these equations,

$$f^P = \alpha(1 - T^P) \qquad (16)$$

where

$$\alpha = (1 - T^T)/(2 - T^P - T^B) \qquad (17)$$

the superscripts P, B, and T refer to the phosphine, di-*tert*-butyl peroxide, and the total transmittance of the solution containing both. Thus, the observed photoacoustic response is given by eq 18.

$$N^T = N^P + N^B = a^P f^P + a^B f^B \qquad (18)$$

Clearly, the various transmittances can be measured from separate solutions of phosphine and peroxide at the concentrations used in the photoacoustic experiments. Rearranging eq 18 provides an expression which allows all of the photoacoustic data obtained at variety of phosphine (0.02–0.15 M) and peroxide (0.2–0.8 M) concentrations to be used to find the constants of interest, eq 19.

$$N^T/f^P = a^P + a^B(1 - T^B)/(1 - T^P) \qquad (19)$$

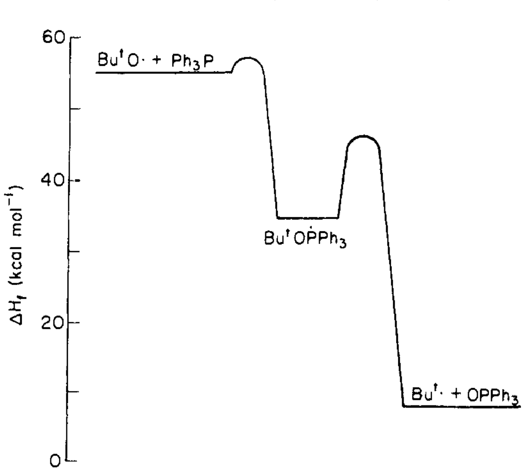
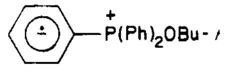


Figure 5. Enthalpy profile for the formation and decay of the *tert*-butoxy triphenylphosphoranyl radical.

The results are plotted in Figure 4 and give a^P = 1.076 ± 0.036 and a^B = 1.172 ± 0.038. As before, the apparatus was calibrated by measuring the photoacoustic response for solutions of *o*-hydroxybenzophenone which gave a^S = 1.026 ± 0.023. Substitution into eq 3 gave the thermal energy released for these processes. For light absorption by the phosphine, the energy released was 88.9 ± 4.0 kcal mol^{-1}, i.e., the laser light absorbed by the phosphine samples was completely converted into thermal energy. Similarly, the heat of reaction 14 was found to be −13.6 ± 3.8 kcal mol^{-1}, eq 3, 4. The heat of formation of I was calculated by applying literature data for the heats of formation of di-*tert*-butyl peroxide[14] and triphenyl phosphine.[30] The result was ΔH_f(I) = 30.9 kcal mol^{-1}.

The electron paramagnetic resonance spectrum of I sugests that it is best described as a benzene radical anion with a phosphonium



I

substituent since little of the unpaired spin density is to be found on the phosphorus atom. The radical decays cleanly, in a first-order reaction, to give triphenylphosphine oxide and *tert*-butyl, eq 20.

$$\text{I} \rightarrow \text{Ph}_3\text{PO} + t\text{-Bu}\cdot \qquad (20)$$

The thermochemical results can be combined with existing kinetic data[29,31] for the formation and decomposition of I to give a detailed energy profile for the reaction (Figure 5). The figure clearly shows that the formation of I, eq 14, and its subsequent decay, eq 20, are both processes that are substantially exothermic.

Summary

In this work we have demonstrated that the photoacoustic technique can be applied to a vareity of reactions and processes of interest to free radical chemists. These include measurements of quantum yields, of bond strengths for organic and organometallic substrates, and of heats of formation of molecules and radical intermediates. While the experimental errors associated with the technique are relatively high (±2 kcal mol^{-1}), the present investigation demonstrates that it shows great potential for use in areas that are inaccessible to conventional gas-phase methods.

Registry No. PhSPh, 882-33-7; *t*-BuOP(Bu-*n*)$_2$, 100813-28-3; *t*-BuO$\dot{\text{P}}$Ph$_3$, 71142-75-1; di-*tert*-butyl peroxide, 110-05-4; tri-*n*-butyltin, 688-73-3; 1,4-cyclohexadiene, 628-41-1; diethyl ether, 60-29-7.

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