

Comparison of Overtone-Induced and Electronic Photochemistry of Liquid *tert*-Butyl Hydroperoxide: Supporting Evidence for Vibrational Mode Selectivity

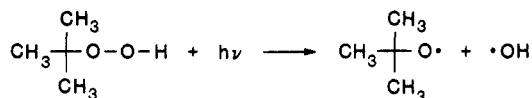
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The spectroscopy and unimolecular decomposition kinetics of *tert*-butyl hydroperoxide have been studied both in neat liquid and diluted in carbon tetrachloride. The data show that the tail of a transition to a repulsive electronic state extends to 540 nm but it is insignificant at longer wavelengths. The peak cross section of the 6-0 O-H overtone of *tert*-butyl hydroperoxide at 535 nm is estimated to be 5-24 times more intense than the electronic tail. *tert*-Butyl alcohol can be observed when photolyzing on the electronic tail, but no vibration-induced effect can be observed when photolyzing on the 5-0 O-H overtone. This study supports the contention that a small mode-selective effect is present in the gas-phase unimolecular decomposition of *tert*-butyl hydroperoxide when the 5-0 O-H overtone is excited by excluding the possibility of the electronic tail contributing to the nonstatistical component. Furthermore, the lifetime of this nonstatistical component is estimated to be longer than 0.1 ps.

Introduction

Vibration-induced mode-selective photochemistry appears to be the exception rather than the rule.¹ Some evidence for nonstatistical behavior has been presented in a few isolated systems, but doubts remain if all alternative possibilities have been excluded.²⁻⁹ One such example is *tert*-butyl hydroperoxide (*t*-BuOOH) decomposition:



Both the 5-0 and 6-0 overtones of the O-H stretch in *tert*-butyl hydroperoxide have been used to induce this reaction in the gas phase by using pulsed^{8,10} and continuous lasers.^{3,4} The results of Chandler et al.,³ where the 5-0 O-H overtone of *tert*-butyl hydroperoxide was excited by using a CW laser, showed a Stern-Volmer plot with dramatic curvature above 40 Torr. The data were interpreted as indicating two contributions to the observed reaction rate with approximately 99% occurring via a statistical channel and 1% occurring via a prompt nonstatistical channel. It was estimated that the lifetime of the nonstatistical channel was 10-100 ps.

The decomposition has also been studied by excitation of the 6-0 O-H overtone of *tert*-butyl hydroperoxide using both CW and pulsed lasers. The results of Chuang et al.,⁴ using CW lasers, produced flat Stern-Volmer plots showing no curvature with pressure. The analysis of these data suggested 10-30% of the reaction proceeded via a prompt nonstatistical channel. When the laser was detuned from the overtone feature, no reaction was observed above background. The study by Crim and co-workers^{8,9} using pulsed excitation also showed a prompt component, but this persisted when the laser was tuned off the overtone transition. There was good agreement with the rate of the statistical com-

ponent observed by Chuang et al.⁴

However, Crim and Troe have raised the possibility of a transition to a repulsive electronic state contributing to the observed prompt reaction.⁸ Thus the electronically induced photodissociation of *tert*-butyl hydroperoxide could account for the prompt component in the decomposition rate observed previously. It was clear from the Faraday discussions of 1983^{4,8} that further experiments were needed to determine whether a nonstatistical vibrational induced effect was being observed in the 5-0 and 6-0 overtones or an effect due to excitation to a repulsive electronic state. We report here the study of *tert*-butyl hydroperoxide decomposition in the liquid phase in order to investigate the relative contributions of overtone induced and electronically induced photochemistry.

Experimental Section

Sample Preparation. Ninety percent *tert*-butyl hydroperoxide (Aldrich) was dried over molecular sieves and then fractionally distilled to remove the impurities (5% H₂O and 5% *t*-BuOH).

Spectroscopy. The overtone spectra were recorded by using a Hewlett-Packard 8450 A diode array spectrometer. The spectra were used to calculate the absorption cross sections of the overtone features pumped in the photolysis experiments. There is a problem in matching exactly the Rayleigh scattering in the sample and reference cells. This causes sloping nonzero base lines. Care was taken to minimize this effect by judicious choice of reference solvent. Cyclohexane was found to be best in the 400-500-nm region.

Kinetic Measurements. The photolysis experiments were performed with both neat samples of *tert*-butyl hydroperoxide and samples diluted in carbon tetrachloride. For the experiments performed with CW lasers (either a Coherent 599 linear dye laser or the direct output from a Spectra-Physics argon ion laser) the photolysis cells were made of Teflon and were 3.22 cm in length with a bore of 0.3175 cm. The photolysis experiments were performed extracavity with one sample cell in the laser beam and one identical reference cell kept adjacent to the sample cell. No background reaction was ever observed in the reference cell. The cells used for reference and sample were randomly switched, and no difference between the results was observed.

For the experiments performed with a 532-nm light from a Quanta Ray Nd:YAG laser two different-size Teflon cells were used. One cell had a length of 4.87 cm and a bore of 1.43 cm, and the other had a length of 3.9 cm and a bore of 2.58 cm. The experiments were performed with the beam unfocused (~1/2-in. diameter) and also expanded (1-in. diameter) in order to check the absence of local heating and nonlinear effects.

Kinetic Analysis. The product yield was determined by infrared spectroscopy with an IBM 98 FTIR. The O-H stretches of the

(1) Crim, F. F. *Annu. Rev. Phys. Chem.* **1984**, *35*, 657 and references cited therein. Lupo, D. W.; Quack, M. *Chem. Rev.* **1987**, *87*, 181 and references cited therein.

(2) Reddy, K. V.; Berry, M. J. *Chem. Phys. Lett.* **1977**, *52*, 111.

(3) Chandler, D. W.; Farneth, W. E.; Zare, R. N. *J. Chem. Phys.* **1982**, *77*, 4447.

(4) Chuang, M. C.; Baggott, J. E.; Chandler, D. W.; Farneth, W. E.; Zare, R. N. *Faraday Discuss. Chem. Soc.* **1983**, *75*, 301.

(5) Natzle, W. C.; Moore, C. B.; Goodall, D. M.; Frisch, W.; Holzworth, J. F. *J. Phys. Chem.* **1981**, *85*, 2882.

(6) Schwebel, A.; Brestel, M.; Yogev, A. *Chem. Phys. Lett.* **1984**, *107*, 579.

(7) Goodall, D. M.; Chetwood, I. *Chem. Phys. Lett.* **1986**, *129*, 291.

(8) Rizzo, T. R.; Hayden, C. C.; Crim, F. F. *Faraday Discuss. Chem. Soc.* **1983**, *75*, 350. Troe, J. *Faraday Discuss. Chem. Soc.* **1983**, *75*, 350.

(9) Rizzo, T. R.; Crim, F. F. *J. Chem. Phys.* **1982**, *76*, 2754.

(10) *Organic Peroxides*; Wiley: New York, 1971; Vol. II.

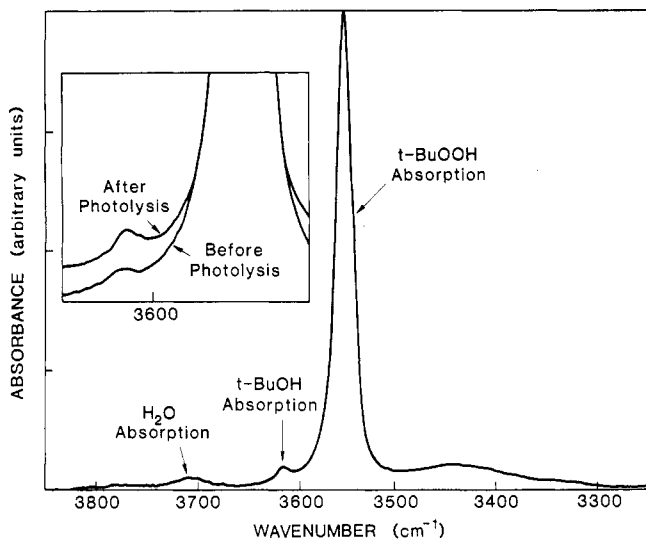


Figure 1. Infrared spectrum of *tert*-butyl hydroperoxide and *tert*-butyl alcohol diluted in carbon tetrachloride showing the two distinct O-H absorption features. Typical experimental data showing the *tert*-butyl alcohol O-H absorption before and after photolysis are inset.

tert-butyl hydroperoxide and *tert*-butyl alcohol (the product of the reaction) diluted in carbon tetrachloride are separated in the 3800–3300-cm⁻¹ spectral region as shown in Figure 1. The relative peak absorption coefficients for *tert*-butyl hydroperoxide and *tert*-butyl alcohol were measured as 31.7 and 22.4, giving a ratio of peak absorption coefficients:

$$\sigma(t\text{-BuOH})/\sigma(t\text{-BuOOH}) = 0.709 \pm 0.015$$

Since the yield of *tert*-butyl alcohol was low in all the experiments performed, the infrared spectra between 3300 and 3800 cm⁻¹ can be used to measure the mole fraction of *tert*-butyl alcohol formed. The quantum yield can then be calculated from

$$\phi = \frac{\Delta x V N h \nu}{\epsilon I_0 \tau L} \quad (1)$$

where ϕ is the quantum yield, Δx is the change in mole fraction of *tert*-butyl alcohol, V is the cell volume, L is the cell length, τ is the photolysis time, ν is the frequency of the photolysis light, I_0 is the incident light intensity which is approximately equal to the transmitted light intensity, ϵ is the extinction coefficient of the absorption feature pumped, N is Avogadro's number, and h is Planck's constant.

Although acetone is a possible reaction product, no acetone absorption features were observed in the infrared spectrum of the photolyzed samples of any experiment.

Results

Spectroscopy. The spectroscopy of *tert*-butyl hydroperoxide is complicated in the liquid phase by the presence of hydrogen-bonded dimers.¹⁰ The dimerization constant for the monomer-dimer equilibrium in carbon tetrachloride has been measured as 1.90¹¹ and 1.0 M⁻¹.¹² The overtone spectra were recorded in dilute carbon tetrachloride and in neat liquid in order to distinguish between monomer and dimer absorption features. The spectra and assignments are shown in Figures 2 and 3. The sloping base lines are due to the fact that the samples were referenced to air or carbon tetrachloride. The slopes are *not* due to any electronic absorption as will be demonstrated later. A Birge-Sponer plot of the data is shown in Figure 4. From the slope and intercept of the plots w_e and $w_e x_e$ were determined as shown in Table I. The gas-phase values from ref 1 are listed for comparison.

Figure 5 shows the spectra of the observed electronic tail in the region 325–500 nm for neat *tert*-butyl hydroperoxide. Figure

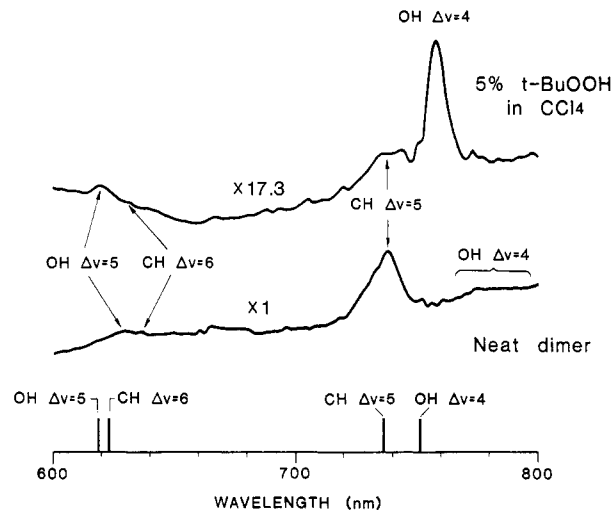


Figure 2. Visible overtone spectra of *tert*-butyl hydroperoxide monomer and dimer. The positions of the gas-phase absorption features are also shown as solid lines.

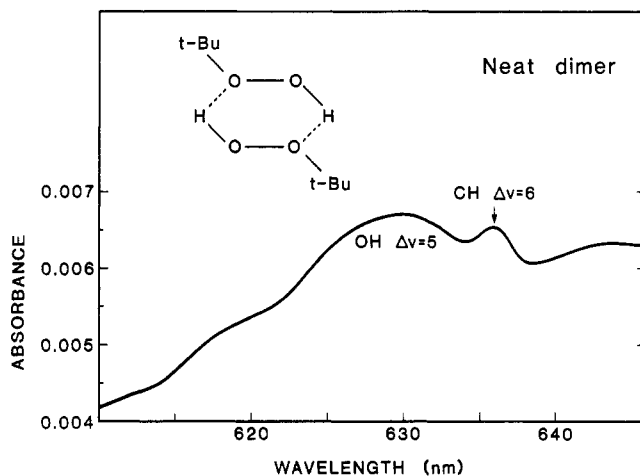


Figure 3. Visible overtone spectrum of *tert*-butyl hydroperoxide between 610 and 645 nm. The absorption cells used were 2 cm long, and carbon tetrachloride was used as the reference sample.

TABLE I: Spectroscopic Constants (cm⁻¹) Obtained from Birge-Sponer Plots of Overtone Spectra of *tert*-Butyl Hydroperoxide

		w_e	$w_e x_e$
C-H	dimer	3029.0	66.3
C-H	monomer	3056.9	72.7
C-H	gas phase ^a	2975	54
O-H	monomer	3645.9	88.5
O-H	gas phase ^a	3690	91

^a Taken from ref 1.

6 shows the region between 400 and 650 nm in more detail. The 7–0 C–H overtone is also visible at 557 nm. The 5–0 O–H overtone at 626 nm and the 6–0 C–H overtone at 636 nm are also clearly apparent. An enlargement of the spectrum between 460 and 540 nm is shown in Figure 7. The rise at 540 nm is due to the edge of the 7–0 C–H overtone. It is clear from these spectra that the electronic tail is not detectable past 540 nm. This spectrum was used to measure the extinction coefficients in this region. The extinction coefficients obtained from these measurements at 514 and 532 nm had error bars of $\pm 50\%$. These spectra were obtained by referencing the sample cell to a reference cell containing cyclohexane, which has no measurable electronic absorption above 300 nm. Cyclohexane is close in size to *tert*-butyl hydroperoxide and scatters light to the same extent, thus giving a flat base line close to zero. It was not possible to obtain spectra of the diluted *tert*-butyl hydroperoxide below 600 nm due to the weakness of the absorptions. We also recorded the overtone spectra using pulsed photoacoustic spectroscopy. This method

(11) Walling, C.; Heaton, L. *J. Am. Chem. Soc.* **1965**, *87*, 48.

(12) Zharkov, V. V.; Rudnevskii, N. K. *Opt. Spectrosc.* **1962**, *12*, 264.

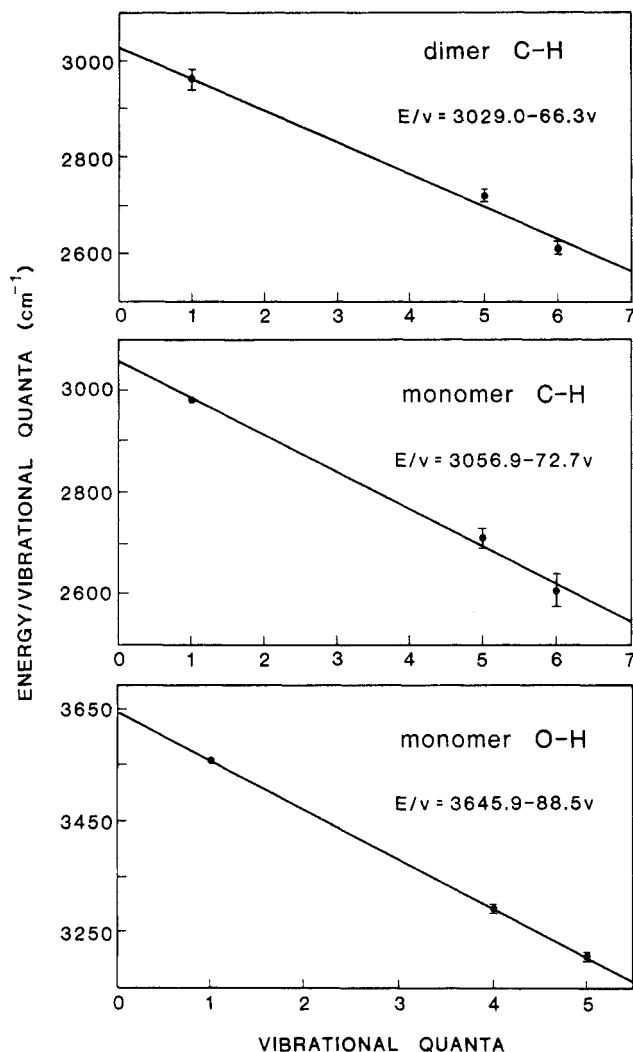


Figure 4. Birge-Sponer plots for the C-H and O-H oscillators in *tert*-butyl hydroperoxide monomer and the C-H oscillator in the dimer.

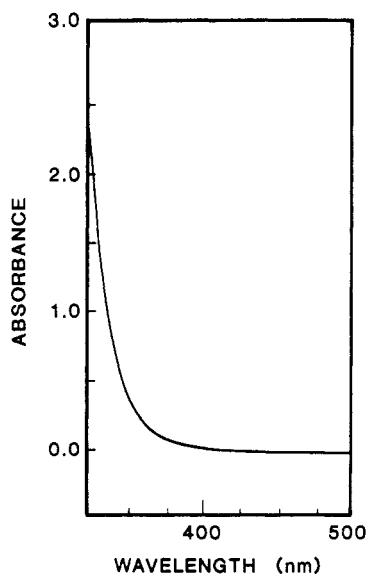


Figure 5. Visible absorption spectrum of pure (99%) *tert*-butyl hydroperoxide. The absorption cells used were 2 cm long, and cyclohexene was used as the reference sample.

enabled us to reproduce the 7-0 C-H overtone of neat *tert*-butyl hydroperoxide shown in Figure 6, but the sensitivity was no higher than using a visible spectrometer to measure the absorption directly. It also should be noted that the electronic transition to a repulsive state will result in a smaller photoacoustic signal than

TABLE II: Results of Kinetic Experiments

concn, M in CCl ₄	photolysis time, h	laser power, W	λ, nm	quantum yield
0.375	1.0	1.2	488	2.8 ± 0.3
0.375	17.5	1.2	488	3.0 ± 0.5
3.914 × 10 ⁻²	21.05	1.48	514	6.7 ± 1.2
5.681 × 10 ⁻²	2.0	1.9	514	6.5 ± 1.5
7.623 × 10 ⁻²	2.0	1.9	514	3.8 ± 1.6
7.623 × 10 ⁻²	2.0	1.9	514	3.0 ± 0.9
0.1911	2.0	1.9	514	2.7 ± 1.1
0.4665	1.52	1.17	514	2.8 ± 2.0
0.4665	1.55	0.55	514	1.3 ± 2.3
0.4665	1.68	1.9	514	2.5 ± 0.9
0.4729	19.5	1.08	514	2.7 ± 0.3
neat	14.0	0.4	514	0.87 ± 0.64
3.77 × 10 ⁻²	9.5	1.9 ^a	532	6.7 ± 9.7
3.77 × 10 ⁻²	9.5	1.0 ^a	532	no change
3.77 × 10 ⁻²	9.5	1.9 ^a	532	12.4 ± 8.1
0.4729	16.27	0.105	626.6	≤ 7 × 10 ^{-3b}
0.4729	24.0	0.120	626.6	≤ 7 × 10 ^{-3b}
neat	14.17	0.166 (2 passes)	630.5	≤ 7 × 10 ^{-3b}
neat	20.43	0.150 (2 passes)	630.5	≤ 7 × 10 ^{-3b}

^a Average power of pulsed laser. ^b Assuming chain length of 3.0.

an overtone transition since a large fraction of the absorbed energy is used to break the bond and is not available to heat the sample. This makes the electronic tail undetectable using photoacoustic spectroscopy.

Product Quantum Yield. Table II shows initial concentration of *tert*-butyl hydroperoxide, the photolysis time, the photolysis power, and the quantum yield calculated from eq 1. For the photolysis at 532 nm only the extinction coefficient for the electronic tail was used to calculate the quantum yield. The larger error bars for the 532-nm data are entirely due to the fact that the photolysis cells used had larger diameters than the cell used to obtain the 514-nm data, thus reducing the signal to noise ratio. In the case of the photolysis experiments performed at 626.6 and 630.5 nm no products were detected, and an upper bound on the quantum yield is given assuming a chain length of three, which was measured for other wavelengths.

Discussion

Spectroscopy. The line positions of the overtones of *tert*-butyl hydroperoxide are slightly shifted to the red of the gas-phase values and also broadened, as has been observed by other workers for benzene¹³ and methanol.¹⁴ There is also no evidence of a strong solvent interaction from the spectra. The O-H overtones of the hydrogen-bonded dimer are very broad, again like methanol.¹² This explains why it is possible to observe the 7-0 C-H overtone of the dimer but not the 6-0 O-H overtone of the dimer in Figure 6.

The electronic absorption between 325 and 540 nm is fit well by a Gaussian. The fit is shown in the region of the electronic tail in Figure 6. This enables the electronic contribution to the photolysis data at 626.6 and 630.5 nm to be estimated. The electronic absorption cross section is estimated to be at least 10⁴ times less intense than the overtone absorptions at 626.6 and 630.5 nm. Although the electronic tail fits well a Gaussian, we also attempted to fit it to a Lorentzian which is the worst possible case. Despite the fact that the fit is very poor the electronic absorption is estimated to be less than 5 × 10³ times as intense as the overtone absorptions at 626.6 and 630.5 nm.

As shown in Figures 6 and 7, there is still a very weak detectable electronic tail at 532 nm but not beyond 540 nm. Since it was not possible to record the spectra of *tert*-butyl hydroperoxide diluted in carbon tetrachloride in this wavelength region, it is only possible to estimate the relative values of the peak cross section of the 6-0 O-H overtone of the monomer (estimated to be at 535 nm from the Birge-Sponer plot in Figure 4) and the electronic

(13) Bray, R. G.; Berry, M. J. *J. Chem. Phys.* **1979**, *71*, 4909.

(14) Swofford, R. L.; Long, M. S.; Burberry, M. S.; Albrecht, A. C. *J. Chem. Phys.* **1977**, *66*, 664.

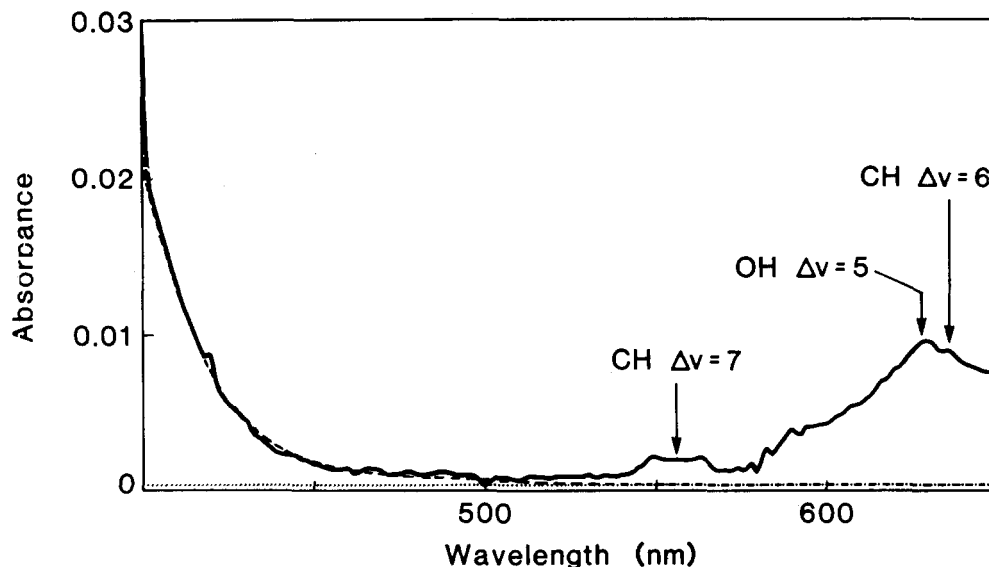


Figure 6. Visible absorption spectrum of pure *tert*-butyl hydroperoxide taken under conditions identical with those of Figure 5. The dotted line is the estimated base line. The dashed line is the fit to the electronic absorption by using a Gaussian.

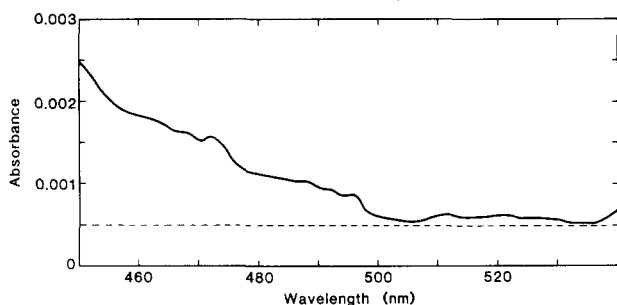


Figure 7. Visible absorption of pure (99%) *tert*-butyl hydroperoxide taken under conditions identical with those of Figure 5. The dashed line is the estimated base line.

tail in the same wavelength region.

For two different independent Morse oscillators the ratio of peak intensities for the $m=0$ and $m'=0$ overtones with the same fwhm is approximately given by¹⁵

$$\frac{I_{0m}}{I_{0m'}} \approx \left(\frac{m+1}{m+1-2/q} \right)^{2m} \left(\frac{m'+1-2/q'}{m'+1} \right)^{2m'} \frac{m'^2 w_e' q'}{m^2 w_e q} \quad (2)$$

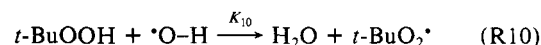
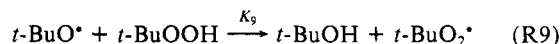
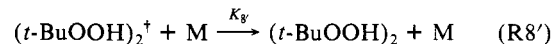
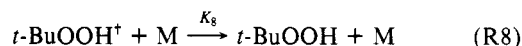
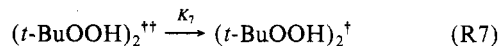
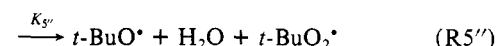
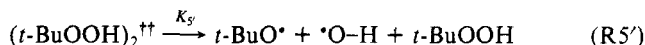
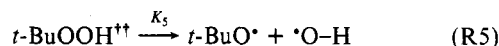
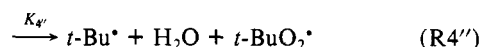
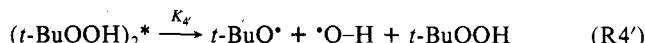
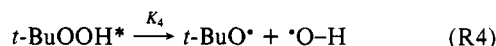
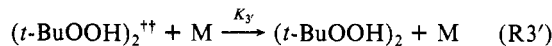
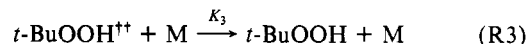
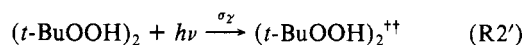
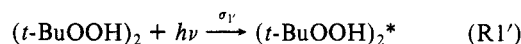
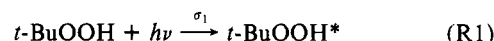
where $w_e x_e$ is the anharmonicity constant for the Morse oscillator, w_e is the mechanical frequency, and $q = w_e x_e / w_e$.

This formula predicts that if the ratio of the peak cross section of the 4-0 O-H overtone to the peak cross section of the 5-0 C-H overtone is p , then the ratio for the 5-0 O-H overtone to the 6-0 C-H overtone is $0.62p$ and the ratio for the 6-0 O-H overtone to the 7-0 C-H overtone is $0.43p$.

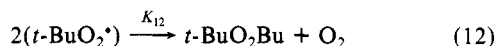
Figure 2 shows the peak cross section of the 4-0 O-H stretch of the monomer is approximately 4 times larger than the 5-0 C-H overtone and the 5-0 O-H overtone is 2-3 times stronger than the 6-0 C-H overtone as predicted by eq 2. Since the C-H overtones of the dimer are almost in the same positions as those of the monomer, it can be assumed that the peak cross sections of the C-H overtones are unaffected by dimer formation. Hence, using the ratio of the fitted electronic tail at 535 nm to the peak cross section of the 7-0 C-H stretch of the dimer at 557 nm gives an estimate that the 6-0 O-H stretch at 535 nm is 19 ± 5 times more intense than the electronic tail. If the measured spectra of the electronic tail shown in Figures 6 and 7 are used instead of the fitted electronic tail then it is estimated that 6-0 O-H stretch at 535 nm is 14 ± 9 times more intense than the electronic tail.

The conclusions from the spectroscopy are (i) There is no significant electronic tail in the wavelength region beyond 540 nm. (ii) There is an electronic tail in the region, 500-540 nm, and it is estimated that the 6-0 O-H overtone of the monomer is 5-24 times more intense than the electronic tail at 535 nm.

Kinetics. The simplest kinetic scheme which can be used to model this experiment is



(15) Kosykowski, M. L.; Noid, D. W.; Marcus, R. A. *J. Phys. Chem.* 1982, 86, 2113.



where * corresponds to electronically excited monomer or dimer, †† corresponds to nonstatistically vibrationally excited monomer or dimer, and † corresponds to statistically vibrationally excited monomer or dimer. The statistically excited monomer or dimer can only undergo collisional deactivation in the liquid since the time for unimolecular decomposition ($\sim 1 \mu\text{s}$) is far longer than the time for collisional deactivation estimated to be 0.1–1 ps.

The reaction consists of a unimolecular homolysis followed by a chain reaction. Note that once the O–O bond is broken the subsequent chemistry is independent of the type of excitation used to break the bond. In the experiments performed diluted in carbon tetrachloride, the *tert*-butyl hydroperoxide is in a bath of noninteracting spherical molecules. In this case it is expected that only isolated binary collisions will be important in vibrational deactivation, and the experiment is similar to a gas-phase experiment performed at high pressure.^{16,17} The time between collisions will be ~ 0.1 ps.^{18,19} For the experiments performed in neat *tert*-butyl hydroperoxide, multibody collisions will be important and the kinetic scheme above will be a gross simplification. The activation energy for the unimolecular reaction has not been measured in carbon tetrachloride but has been measured in water as 34 kcal mol⁻¹, in toluene as 42 kcal mol⁻¹, and in *n*-octane as 39 kcal mol⁻¹.²⁰ Since carbon tetrachloride is a nonpolar solvent, the activation energy would be expected to also be in the range 39–42 kcal mol⁻¹.

The thermal decomposition of neat *tert*-butyl hydroperoxide at 100 °C²¹ or in chlorobenzene at 140 °C²² has been found to yield *tert*-butyl alcohol and oxygen in nearly quantitative amounts. The photolytically induced decomposition in carbon tetrachloride also shows the same result.¹⁷ The chain length is dependent on viscosity because of a solvent cage effect,¹⁴ and this explains why as the concentration of *tert*-butyl hydroperoxide increases the quantum yield decreases. The results in the concentration range 0.1–0.4 M show an average quantum yield of 2.4 ± 0.6 in reasonable agreement with that measured by Martin and Norrish²³ of 3.2 (Martin and Norrish photolyzed at 313 nm, close to the peak of the electronic transition).

Our interest lies in the events taking place in the first few picoseconds. The collision time in a liquid is approximately 0.1 ps, which is long compared to the time the molecule takes to dissociate once excited onto a repulsive electronic surface. Thus the data taken by photolyzing at 514 and 488 nm on the electronic tail but off any overtone feature can be used to calibrate the experiment. The quantum yield at 514 and 488 nm for a given initial concentration of *tert*-butyl hydroperoxide can be compared with the data taken at 532 nm, photolyzing on both the electronic tail and the 6–0 O–H overtone, and the data obtained at 626.6 and 630.5 nm photolyzing only on the 5–0 O–H overtone transition. In the case of the data at 532 nm no reaction above that due to the electronic tail can be detected, and it is not possible to put an upper limit on the vibration-induced quantum yield due to the large error bars. However, in the case of the data at 626.6 and 630.5 nm the vibrational quantum yield is less than 7×10^{-3} . This means less than 1 in 150 of the molecules initially vibrationally excited decomposes. If we assume that only 1% of the initially prepared molecules react via the nonstatistical channel, the gas-phase result of Chandler et al., then less than two-thirds of the molecules react via the nonstatistical channel before the energy is removed collisionally. There have been no measurements on vibrational relaxation rates of high overtones in liquids, although

recent measurements on the fundamental O–H stretch of alcohols suggest vibrational relaxation requires less than 100 collisions.²⁴ The assumption that 1–10 collisions are required to collisionally deactivate the vibrationally excited *tert*-butyl hydroperoxide gives a lower bound on the lifetime of the nonstatistical channel of 0.15–1.5 ps.

This result suggests that the energy does not flow directly into the O–O bond from the initially excited O–H stretch, a situation that might have been expected to occur in a few vibrational periods. Rather the energy must flow by a more indirect path which takes a longer time, certainly longer than 0.1 ps—the time between collisions. The results of collisions in liquids are either to directly remove energy from the vibrationally excited molecule or to scramble the indirect path due to collision-induced intramolecular vibrational relaxation. (See the Appendix.)

Bearing on Gas-Phase Results. The experimental data from the liquid phase seem entirely consistent with that obtained in the gas phase with both CW and pulsed lasers. In the 500–540-nm region there is an electronic tail that is 5–24 times less intense than the 6–0 O–H overtone. Since there are only small shifts in line position in the liquid relative to the gas, it would be expected the electronic tail at 532 nm is still 5–24 times less intense than the 6–0 O–H overtone in the gas phase. Hence Crim and co-workers would have observed a prompt nonstatistical component when photolyzing off the overtone feature that was due to a one-photon transition to a repulsive electronic state. However, the magnitude of the prompt component should increase when photolyzing on the overtone feature although this is much harder to measure. This also explains why Chuang et al.⁴ saw no reaction above background (50% of the total reaction) when they photolyzed off the overtone absorption since the electronic tail contributes 4–20% to the laser-induced reaction and only 2–10% to the total reaction, making it undetectable in their experiment.

The spectroscopic data also strongly suggest that the results obtained by Chandler et al. at 619 nm³ were due to a vibrational effect since the electronic tail is totally insignificant at this wavelength. Hence this strongly supports the contention of Chandler et al. that a small nonstatistical effect is present in the gas-phase unimolecular decomposition of *tert*-butyl hydroperoxide when its 5–0 O–H overtone is pumped.

Acknowledgment. We thank M.-C. Chuang, C. B. Moore, J. Segall, and P. Vaccaro for helpful discussions. We thank D. Rakestraw for assistance in checking our spectra of *tert*-butyl hydroperoxide by recording the 7–0 C–H overtone by pulsed photoacoustic detection. This work was supported by the National Science Foundation under Grant NSF CHE 85-05926.

Appendix. Overtone Chemistry in Liquids: A Critique

This study is the first example of an overtone pumping experiment that has been performed in both the gas and liquid phases. Furthermore, the experiment in liquids was performed on both the monomer, which has little interaction with the solvent, and also the hydrogen-bonded dimer. The failure to observe products in the liquid phase following overtone excitation raises questions about the potential for this type of photochemistry. The following remarks, based on 6 months of experiments in this laboratory,²⁵ are intended to highlight the difficulties involved in attempting overtone-induced chemistry in the liquid phase.

There are four examples of overtone-induced chemistry to date. Natzle et al.⁵ used pulsed single-photon excitation to initiate the decomposition of water to produce H⁺ and OH⁻ ions. The laser intensities used were 1–50 MW cm⁻² and the quantum yields were in the range 2×10^{-9} to 4×10^{-5} . Schewebel, Brestel, and Yoge⁶ studied the 1,5-hexadien-3-ol rearrangement using the output of an excimer pumped dye laser focused into a capillary and end-

(16) Knudtson, J. T.; Stephenson, J. C. *Chem. Phys. Lett.* **1984**, *107*, 385.

(17) Davis, P. K.; Oppenheim, I. *J. Chem. Phys.* **1972**, *57*, 505.

(18) Fischer, S. F.; Laubereau, A. *Chem. Phys. Lett.* **1975**, *35*, 6.

(19) Oxtoby, D. W. *Adv. Chem. Phys.* **1979**, *40*, 1.

(20) Hiatt, R. *Organic Peroxides*; Wiley: New York, 1971, Vol. II, Chapter 1.

(21) Milas, N. A.; Surgeior, D. M. *J. Am. Chem. Soc.* **1946**, *68*, 643.

(22) Bell, E. R.; Raley, J. H.; Rust, F. F.; Seibold, F. H.; Vaughn, W. E. *Discuss. Faraday Soc.* **1951**, *10*, 246.

(23) Martin, J. T.; Norrish, R. G. W. *Proc. R. Soc. London, A* **1953**, *220*, 322.

(24) Heilweil, E. J.; Casassa, M. P.; Cavanagh, R. R.; Stephenson, J. C. *J. Chem. Phys.* **1986**, *85*, 5004.

(25) Experiments were performed on the proton transfer of phenylnitro-methane to water. The aliphatic 4–0 C–H overtone was pumped, and the anion product was monitored by transient absorption. No enhancement was observed, indicating a quantum yield below 10^{-4} .

product analysis to determine the quantum yields. Pumping the 5-0 and 6-0 C-H overtones produced product with quantum yields 5×10^{-4} and 1.8×10^{-3} , respectively, but no product was observed when photolyzing on the 4-0 and 5-0 O-H overtones, indicating a mode-selective effect. Goodall and Chetwood⁷ focused the output of Nd:YAG laser Raman shifted in carbon disulfide into a 1-cm square cuvette in order to study the proton transfer of nitromethane to water. Iodine scavenging was used to measure the rate enhancement, and a quantum yield of $(3 \pm 1) \times 10^{-5}$ was found pumping the 3-0 C-H overtone of nitromethane. Goodall, Hollis, and White²⁶ have recently extended these studies to transition-metal complexes and observed H/D exchange for $[\text{Co}(\text{NH}_3)_6]^{3+}$ when pumping the N-H 3-0 overtone. The quantum yield was $(2 \pm 2) \times 10^{-4}$.

In all four experiments the results appear to us inconclusive because all other possible effects have not been eliminated. In particular, since the high intensity focused output from pulsed lasers is used, heating in the laser-excited volume may occur before thermal equilibration. Unfortunately, the volume excited by the laser is not reported in any of the work to date, so it is not possible to evaluate how much or how little contribution this heating makes to the observed effect. However, it should be realized that a true overtone-induced enhancement should only depend on the photon flux and not the photon fluence; i.e., an overtone-induced effect should only depend on the total number of photons absorbed by the sample. While Natze et al.⁵ and Schwebel et al.⁶ did perform a power dependence experiment, it is essential to also perform an intensity dependence at fixed power in order to eliminate this possibility. The use of CW lasers should eliminate this effect, or one can study systems with more than one distinct C-H or O-H oscillator to distinguish between local heating and overtone-induced chemistry as done by Schwebel et al.⁶ Schwebel et al.³³ have also calculated that the temperature rise in their experiments is less than 1 K. To ensure overtone-induced chemistry is being observed, it is important to photolyze on and off the overtone features and perform wavelength-dependent studies as additional checks. Unfortunately, this has been rarely done in previous experiments.

The heating discussed above and also overtone-induced chemistry must be carefully distinguished from local heating which is a direct result of intermolecular vibrational relaxation in liquids. By local heating, it is meant that the molecules that absorb the photons undergo rapid collisional deactivation, typically 6-10 ps for large molecules,²⁷ resulting in a local temperature rise prior to bulk thermal equilibration (which takes several milliseconds). This has been demonstrated by Seilmer, Scherer, and Kaiser.²⁸ The only way to distinguish this from overtone-induced chemistry is to show that the reaction rate depends on which local mode in the molecule is excited and not on the amount of energy placed in the molecule.

Another problem in performing overtone-induced chemistry in liquids, for both unimolecular and bimolecular reactions, is the

size of the quantum yields. In all four experiments the measured quantum yields are very low, below 10^{-3} . Consequently, a very sensitive detection method is needed. Since we could only observe quantum yields greater than 7×10^{-3} in this study, it is possible that our sensitivity was not high enough to observe vibrationally induced photochemistry. However, our sensitivity was certainly high enough to observe electronically induced photochemistry when exciting electronic transitions with cross sections nearly 2 orders of magnitude less intense than the vibrational overtone transitions pumped! It seems that electronic excitation is much more efficient than vibrational excitation at breaking the O-O bond in *tert*-butyl hydroperoxide.

Let us consider unimolecular reactions in liquids. Since the time between collisions is ~ 0.1 ps, in order to see vibration-induced chemistry, it is best to pump either a mode corresponding to the reaction coordinate or one closely coupled to it so that the energy flows into the reaction coordinate within a few vibrations. There is theoretical evidence that energy flow is complex and dominated by nonlinear resonances, in particular Fermi resonances,^{29,30} and choosing molecules where the energy is preferentially channeled into the reaction coordinate is clearly difficult. Local modes, by their very nature, are generally not the reaction coordinate, or even closely coupled to it, so it seems overtone-induced chemistry in liquids is likely to be limited to a few specific cases. In the gas phase, there is the possibility of localizing the energy in a certain part of the molecule by using a blocking group or bottleneck to energy flow,³¹ but this approach is not viable in liquids because of their fast collisional deactivation rate.

Bimolecular reactions appear to be more attractive candidates than unimolecular reactions since they require at least a collision, and the quantum yield is determined by the ratio of inelastic to reactive collisions. Also, it is possible to pump an X-H overtone closely corresponding to the reaction coordinate in proton-transfer reactions, as suggested by Goodall and Chetwood.⁷ However, even if one pumps the reaction coordinate in a bimolecular reaction, there is still the competition between reactive collisions and nonreactive inelastic collisions.³² The low quantum yield, $(3 \pm 1) \times 10^{-5}$, measured for proton transfer of nitromethane to deuterated water is evidence that energy transfer is a much more favorable process than reaction.

The problems of the low quantum yields measured to date, coupled with designing experiments with very high sensitivity but still eliminating local heating, suggest that the observation of overtone-induced chemistry in liquids is challenging. The hope that vibrational photochemistry in liquids may one day be a useful synthetic tool seems a remote possibility at the present time.

Registry No. *t*-BuOOH, 75-91-2; *t*-BuOH, 75-65-0; (*t*-BuOOH)₂, 36563-30-1.

(26) Goodall, D. M.; Hollis, D. H.; White, M. H.; *J. Phys. Chem.* **1987**, *91*, 4255.

(27) Wondrazek, F.; Seilmeier, A.; Kaiser, W. *Chem. Phys. Lett.* **1984**, *104*, 121.

(28) Seilmer, A.; Scherer, P. O. J.; Kaiser, W. *Chem. Phys. Lett.* **1984**, *105*, 140.

(29) Uzer, T.; Hynes, J. T.; Reinhardt, W. P. *J. Chem. Phys.* **1986**, *85*, 5791. Uzer, T.; Hynes, J. T. In *Stochasticity and Intramolecular Redistribution of Energy*; Lefebvre, R.; Mukamel, S., Eds.; NATO ASI Series; 1986.

(30) Segall, J.; Zare, R. N.; Dübal, H. R.; Lewerenz, M.; Quack, M. *J. Chem. Phys.* **1987**, *86*, 634.

(31) Rogers, P. J.; Montague, D. C.; Frank, J. P.; Tyler, S. C.; Rowland, F. S. *Chem. Phys. Lett.* **1982**, *89*, 9. Rogers, P. J.; Selco, J. I.; Rowland, F. S. *Chem. Phys. Lett.* **1983**, *97*, 313.

(32) Oref, I.; Rabinovitch, B. S., unpublished results.

(33) Yogev, A., private communication.