

# Hydrogen Bonding and Complex Formation in Solutions of *t*-Butyl Hydroperoxide<sup>1</sup>

Cheves Walling and LaDonne Heaton<sup>2</sup>

Contribution from the Department of Chemistry, Columbia University, New York 27, New York. Received August, 1964

Dilute solutions of *t*-butyl hydroperoxide in CCl<sub>4</sub> show a sharp -OH stretching band at 3554 cm.<sup>-1</sup> which is replaced by a lower frequency band at higher concentrations and on addition of aromatic solvents. The change is interpreted as indicating a cyclic hydrogen-bonded dimer and the formation of hydrogen-bonded complexes with the aromatics. Association constants for these complexes have been calculated. Deuterated hydroperoxide, with an -OD band at 2630 cm.<sup>-1</sup>, behaves similarly. Its dimerization constant is smaller, but it forms stronger complexes with aromatic solvents. Partition experiments of hydroperoxide between 4 M styrene-carbon tetrachloride and water give results consistent with the above equilibria. Other aromatic solvent systems show additional affinity for the hydroperoxide dimer not discernible from infrared measurements.

Although a number of workers have suggested that hydrogen bonding plays an important role in the reactions of hydroperoxides,<sup>3-6</sup> and qualitative spectral evidence for such bonding has been reported,<sup>5,7,8</sup> no quantitative study of such association in a variety of solvents has been available. Our own work on *t*-butyl hydroperoxide (TBHP) decomposition<sup>9</sup> required such data in order to estimate changes in hydroperoxide activity with solvent and concentration, and this paper reports our results, obtained by infrared spectroscopy and measurement of distribution constants.

**Infrared Spectra of *t*-Butyl Hydroperoxide.** The hydroxyl stretching band of TBHP which appears at 3554 cm.<sup>-1</sup> in dilute solution in CCl<sub>4</sub> shows significant shifts to lower frequencies at higher concentrations or in aromatic solvents, a phenomenon generally associated with the formation of hydrogen bonds.<sup>10</sup> Thus, as shown in Figure 1, addition of benzene to a 0.2 M solution of TBHP in CCl<sub>4</sub> leads to a decrease in absorbance at 3554 cm.<sup>-1</sup> and appearance of a lower frequency shoulder. In pure benzene the 3554-cm.<sup>-1</sup> peak disappears and is replaced by a broader, more intense peak at 3509 cm.<sup>-1</sup>. Other aromatic solvents show qualitatively similar results, summarized in Table I. Measurements at 70° produce little change in the 3554-cm.<sup>-1</sup> band and small decreases in the magni-

Table I. Stretching Frequencies and Band Widths for ROO-H in Various Solvents

Solvent	$\nu_{\max}$ , cm. <sup>-1</sup>	Width, <sup>a</sup> cm. <sup>-1</sup>
CCl <sub>4</sub>	3554	30
Hexane	3561	29
Cyclohexane	3556	29
<i>m</i> -C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	3530	46
<i>o</i> -C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	3530	46
C <sub>6</sub> H <sub>5</sub> Cl	3523	53
C <sub>6</sub> H <sub>6</sub>	3509	58
C <sub>6</sub> H <sub>5</sub> C(CH <sub>3</sub> ) <sub>3</sub>	3504	64
C <sub>6</sub> H <sub>5</sub> CH=CH <sub>2</sub>	3500	66
C <sub>6</sub> H <sub>5</sub> OCH <sub>3</sub>	3480, 3418	73, 114

<sup>a</sup> Band width at half-height.

tudes of the observed shifts. Qualitatively the shifts parallel the expected order of basicities of the aromatic solvents, and anisole yields a two-peak spectrum, perhaps indicating association with both the aromatic ring and the ether oxygen. Benzotrifluoride also shows a double peak.

If it is assumed that we are observing equilibrium with a hydrogen-bonded complex between TBHP and the aromatic molecule acting as a base



as has been found in other systems,<sup>10</sup> and governed by an equilibrium constant

$$K = [PB]/[P][B] \quad (2)$$

*K* may be determined from the decrease in absorbance, *A*, at 3554 cm.<sup>-1</sup>, since

$$[P] = [P]_0 A/A_0 \quad (3)$$

whence

$$K = \frac{1 - A/A_0}{(A/A_0)([B]_0 - [P]_0(1 - A/A_0))} \quad (4)$$

(zero subscripts indicating initial absorbance and total concentrations). Measurements on systems containing 0.02 M TBHP and 0.3-1.5 M aromatic base in CCl<sub>4</sub> yield consistent values of *K* at both 30 and 70° (Table II). Although *K* values vary little between solvents,

Table II. Complex Formation by TBHP in CCl<sub>4</sub> Solutions

Complex	<i>K</i> , l./mole		-Δ <i>H</i> , kcal./mole	-Δ <i>S</i> , e.u.
	70°	30°		
TBHP-styrene	0.17	0.27	2.39	10.5
TBHP-benzene	0.11	0.15	1.58	9.0
TBHP- <i>o</i> -dichlorobenzene	0.13	0.15	0.74	6.2
TBHP-chlorobenzene	0.10	...	...	...
TBHP dimer	0.60	1.90	5.95	18.4

(1) Taken from the Ph.D. Thesis of L. Heaton, Columbia University, 1963. Support of this work by grants from the National Science Foundation is gratefully acknowledged.

(2) American Cyanamid Co. Fellow, 1961-1962.

(3) L. Bateman and H. Hughes, *J. Chem. Soc.*, 4594 (1952).

(4) A. V. Tobolsky and L. R. Matlack, *J. Polymer Sci.*, **55**, 49 (1961).

(5) H. E. De La Mare, *J. Org. Chem.*, **25**, 2114 (1960).

(6) J. O. Edwards, "Peroxide Reaction Mechanisms," Interscience Publishers, Inc., New York, N. Y., 1962, pp. 70, 86 ff.

(7) O. D. Shreve, *et al.*, *Anal. Chem.*, **23**, 282 (1951).

(8) R. West and R. H. Baney, *J. Phys. Chem.*, **64**, 822 (1960).

(9) C. Walling and L. Heaton, *J. Am. Chem. Soc.*, **87**, 38 (1965).

(10) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960.

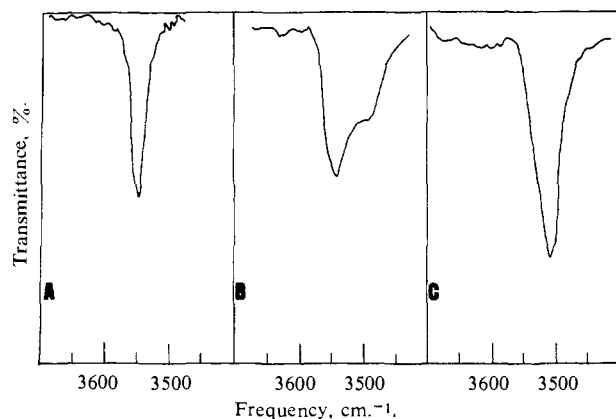
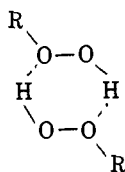


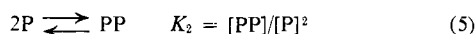
Figure 1. Frequency and intensity changes attributed to complex formation of TBHP with benzene: A,  $\text{CCl}_4$ ; B,  $\text{CCl}_4$  with added benzene; C, benzene.

$\Delta H$  and  $\Delta S$  both become increasingly negative in the order *o*-dichlorobenzene < benzene < styrene, paralleling the infrared shifts observed and increasing basicity.

The changes in spectra observed with changing TBHP concentration in  $\text{CCl}_4$  are shown in Figure 2. As concentration increases the  $3554\text{-cm}^{-1}$  peak is replaced by a broad band at about  $3400\text{ cm}^{-1}$ , which we believe is associated with a cyclic hydrogen bonded dimer perhaps together with higher polymers. The equi-



librium constant for its formation



was calculated by the method of Liddel and Becker,<sup>11</sup> which assumes a series of successive polymers, present in low enough concentration (in dilute solution) so that  $[P] \cong [P]_0$ . Under these conditions

$$\epsilon = \epsilon_0(1 - 2K_2[P]_0 - 3K_3[P]_0^2 - \dots) \quad (6)$$

where  $\epsilon$  is a measured molar extinction coefficient at  $3554\text{ cm}^{-1}$  and  $\epsilon_0$  that for monomeric TBHP. If  $\epsilon$  is plotted vs.  $[P]_0$ , the intercept yields  $\epsilon_0$ , and the slope at  $[P]_0 = 0$  then yields  $K_2$ . Plots at  $70^\circ$  and  $30^\circ$  (and also data for deuterated hydroperoxide discussed below) are shown in Figure 3. They indicate  $K_2 = 0.60\text{ l./mole}$  at  $70^\circ$  and  $1.90$  at  $30^\circ$ , from which  $\Delta H = -6\text{ kcal./mole}$  and  $\Delta S = -18.4\text{ cal./deg}$ . Both values seem consistent with the cyclic dimeric structure proposed.

**Infrared Spectra of Deuterated *t*-Butyl Hydroperoxide (TBDP).** Deuteration moves the absorption maxima of TBHP in dilute  $\text{CCl}_4$  to  $2630\text{ cm}^{-1}$ , and changes in solvent and concentration produce shifts qualitatively similar to those just described.<sup>12</sup> Equilibrium constants and thermodynamic quantities were determined as above, and are summarized in Table III. Comparison of the TBHP and TBDP results are in-

(11) U. Liddel and E. D. Becker, *Spectrochim. Acta*, **10**, 70 (1957).

(12) For all species  $\nu(\text{TBHP})/\nu(\text{TBDP}) \cong 1.35$ , consistent with observations on many other compounds with  $-\text{OH}$  and  $-\text{OD}$  bonds.

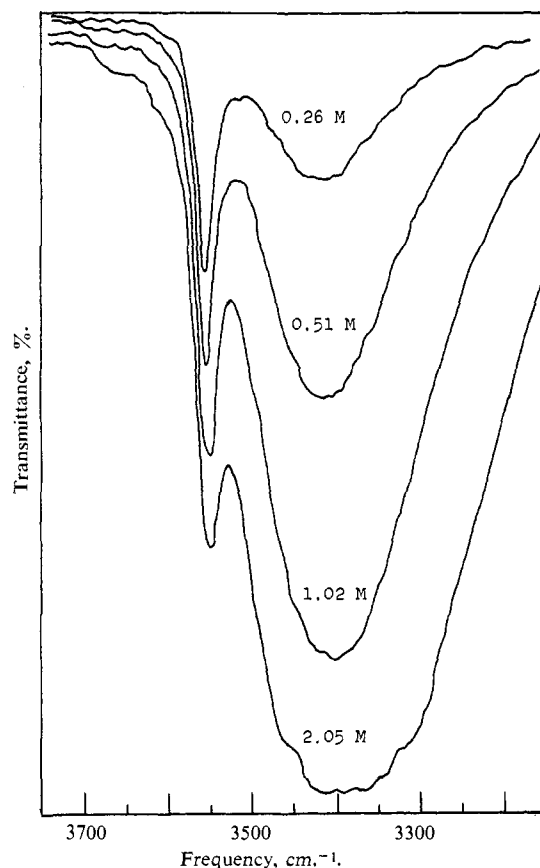


Figure 2. Effect of concentration on the absorption of free and hydrogen-bonded  $\text{ROO-H}$  in  $\text{CCl}_4$ .

teresting in that deuteration decreases the tendency to form cyclic dimers, but increases complex formation with aromatic bases. Without going into possible explanations (discussed in references cited below),

Table III. Complex Formation by TBDP in  $\text{CCl}_4$  Solutions

Complex	$K$ , l./mole		$-\Delta H$ , kcal./mole	$-\Delta S$ , e.u.
	$70^\circ$	$30^\circ$		
TBDP-styrene	0.50	0.84	2.7	9
TBDP-benzene	0.25	...	...	..
TBDP dimer	0.64	1.65	4.9	15

we may note that similar results have been observed in other systems. Thus, for example, deuteration increases the bonding of phenol to various bases<sup>13</sup> and of  $\text{CHF}_3$  to tetrahydrofuran.<sup>14</sup> On the other hand, it decreases the dimerization of phenol<sup>13</sup> and trifluoroacetic acid.<sup>15</sup>

**Partition Experiments.** Although infrared studies may indicate the nature of association phenomena, partition techniques provide a more unequivocal method of determining changes in solute activity with concentration and solvent. In addition, comparison of the two techniques shows whether additional interactions are involved not indicated by spectral changes.

(13) G. R. Plourde, *Dissertation Abstr.*, **22**, 1400 (1962).

(14) A. L. Allred and C. J. Creswell, *J. Am. Chem. Soc.*, **84**, 3966 (1962).

(15) M. D. Taylor and M. B. Templeman, *ibid.*, **78**, 2950 (1956).

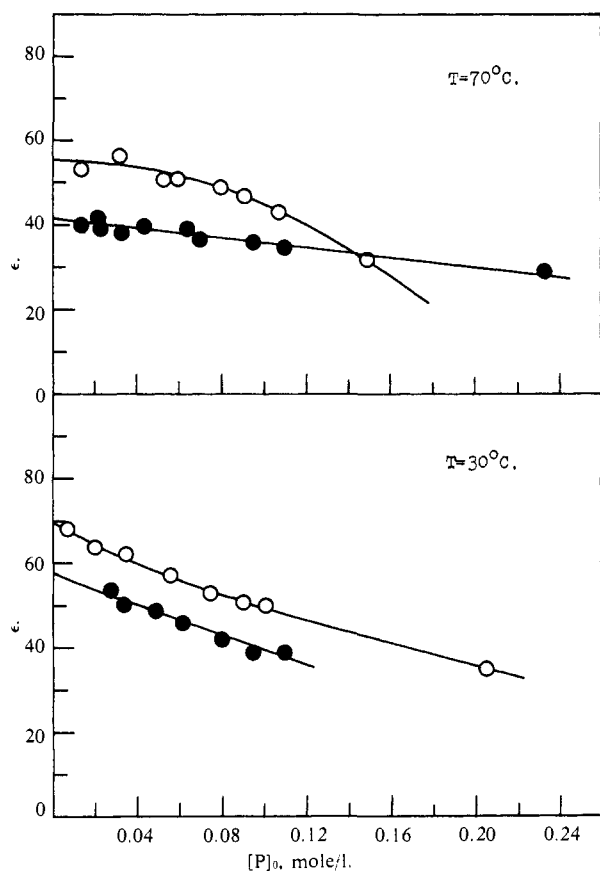


Figure 3. Dependence of  $\epsilon$  for ROO-H (○), and ROO-D (●) in  $\text{CCl}_4$  on  $[P]_0$ : upper curves, temp.  $70^\circ$ ; lower curves, temp.  $30^\circ$ .

When a hydroperoxide is partitioned between water (in which it presumably exists in a monomeric form strongly hydrogen bonded to water) and an organic solvent in which it may exist as monomer and various associated species, its distribution is determined by a distribution coefficient  $K_d$  such that

$$K_d = [P]_w((1 - \alpha)[P]_s) \quad (7)$$

where  $[P]_w$  and  $[P]_s$  represent hydroperoxide concentrations in water and organic phase, respectively, and  $\alpha$  is the fraction of peroxide existing in associated form.

In the presence of aromatic bases, association involves both dimer formation and association with the aromatic base and is governed by the equilibria 2 and 5. Substituting these expressions into eq. 7 yields the relation

$$K_d[P]_s = [P]_w(1 + K[B]) + 2K_2[P]_w^2/K_d \quad (8)$$

This expression was checked by determining the distribution of TBHP at a series of concentrations at  $34^\circ$  between water and  $3.94 M$  styrene in  $\text{CCl}_4$ . Substituting the value of  $K_2$  obtained by interpolation from our infrared measurements ( $1.67 \text{ l./mole}$ ) gave  $K_d = 2.51$  and  $K = 0.25 \text{ l./mole}$ , in good agreement with our infrared value of  $0.26$ .

Measurements in a number of other solvent systems gave less satisfactory agreement with eq. 8, the peroxide in general showing too high a solubility in the organic phase, particularly at higher concentrations. Interestingly, in every case the data could be fitted

by adding an additional term involving association of peroxide dimer with solvent. Whether such terms have any direct physical significance or simply represent empirical corrections which take into account unspecified interactions between solvent and solute molecules cannot be answered, since infrared spectra of complexed peroxide at high peroxide concentrations in aromatic solvents are too broad and diffuse to indicate changes in the species present. The empirical "complexes" and their association constants are listed in Table IV. It will be noted that all (except the simple

Table IV. Equilibrium Constants for Formation of Peroxide-Solvent Complexes Based on Distribution Data

Complex <sup>a</sup>	Solvent mixture	Peroxide	Temp., °C.	$K^b$
P-M	4 M styrene in $\text{CCl}_4$	TBHP	34	0.25
P-P-M	Bulk styrene	TBHP	30.5	0.27
P-P-S	6 M benzene- 4 M styrene	TBHP	32.5	0.14
P-P-M	4.7 M <i>o</i> -dichloro- benzene-4 M styrene	TBHP	27.5	0.32
P <sup>2</sup> -M <sup>2</sup>	4 M styrene in $\text{CCl}_4$	TBDP	24	1.3
P <sup>2</sup> -M <sup>2</sup>	Bulk styrene	TBDP	25	1.0

<sup>a</sup> P = peroxide, M = styrene monomer, and S = solvent. P<sup>2</sup>-M<sup>2</sup> denotes a hypothetical complex containing two molecules each of peroxide and styrene. <sup>b</sup> Equilibrium constants are based on concentrations in mole/l.

Table V. Distribution Data for TBHP and TBDP in Water-Solvent Mixtures

Peroxide	Solvent	Temp., °C.	$[P]_w$ , mole/l.	$[P]_s$ , mole/l.
TBHP	3.94 M styrene in $\text{CCl}_4$	34	0.2321	0.2132
			0.1900	0.1625
			0.1426	0.1217
			0.0954	0.0803
TBHP	8.47 M styrene	30.5	0.2297	0.2202
			0.1841	0.1728
			0.1396	0.1265
			0.0937	0.0831
TBHP	3.96 M styrene- 6.00 M benzene	32.5	0.2437	0.1910
			0.1903	0.1552
			0.1423	0.1194
			0.1406	0.1174
TBHP	4.03 M styrene- 4.71 M <i>o</i> -di- chlorobenzene	27.5	0.2514	0.2010
			0.2049	0.1570
			0.1541	0.1173
			0.1997	0.1622
TBHP	5.03 M styrene- 3.69 M <i>o</i> -di- chlorobenzene	27.5	0.1521	0.1193
			0.1959	0.1660
			0.1542	0.1172
			0.2974	0.2117
TBDP	4.03 M styrene in $\text{CCl}_4$	24	0.2496	0.1635
			0.1888	0.1218
			0.2620	0.2166
			0.2144	0.1690
TBDP	8.66 M styrene	25	0.2620	0.2166
			0.2144	0.1690

peroxide-styrene complex) involve two peroxide molecules, so that their perturbing effect on peroxide activity becomes very small at high dilution. This in turn is consistent with our findings<sup>9</sup> that the interpretation of the homolytic decomposition of TBHP is fairly straightforward in dilute solution, but must be

come increasingly complex as concentrations are increased.

## Experimental

*Materials* were the same as those described previously<sup>9</sup> except that styrene was used without removal of a trace of phenolic inhibitor which did not interfere with any of the physical measurements.

*Infrared spectra* were taken with a Perkin-Elmer Model 421 grating spectrophotometer, using 0.1- or 1.0-mm. NaCl cells. Measurements at room temperature were at constant temperature within 1° determined by a thermometer attached to the cell. Measurements at 70° were made by enclosing the cell in a box with NaCl windows heated by circulating hot air,  $\pm 0.5^\circ$ . The spectrum from 3800–3500 (–OH) or 2900–2600  $\text{cm}^{-1}$  (–OD) was scanned three times for each sample. During the time required for measurement there was no change attributed to evaporation or decomposition, and samples measured at 30°, heated to 70°, cooled,

and remeasured gave identical spectra. At room temperature slit widths were 135 ( $3554 \text{ cm}^{-1}$ ) and 308  $\mu$  (2630). Since the thermostating arrangement prevented considerable light from reaching the cell, 70° measurements were made with maximum source intensity and slit widths of 210 and 599  $\mu$ . Complex formation with aromatic bases was determined in  $\text{CCl}_4$  solutions 0.3–1.5 *M* in aromatic and 0.02 *M* in TBHP (or 0.03 *M* TBDP), at which concentration dimer formation was negligible.

*Distribution Experiments.* Known concentrations of TBHP in solvent (previously saturated with water) were shaken with an equal volume of water (previously saturated with solvent) in a small separatory funnel, and the phases allowed to separate. An aliquot of the organic layer was removed and titrated for peroxide, and the concentration in the water layer calculated by the difference. Experiments with TBDP were carried out in the same way using 99.5%  $\text{D}_2\text{O}$ . Results from which distribution constants were calculated are listed in Table V.

## Optical Rotatory Dispersion Studies. XCVII. Anomalous Rotatory Dispersion and Circular Dichroism Curves Associated with Thionamides. Application to Stereochemical Studies of Carboxylic Acids<sup>2</sup>

Joseph V. Burakevich<sup>3</sup> and Carl Djerassi

*Contribution from the Department of Chemistry of Stanford University, Stanford, California. Received August 5, 1964*

*In the past, a number of "chromophoric" derivatives containing the thione moiety ( $\text{C}=\text{S}$ ) have been successfully employed for stereochemical correlations. However, these derivatives all had the structural feature that the thione was separated from the asymmetric center by one or two atoms. In the thionamide derivative ( $-\text{C}(\text{S})\text{NRR}'$ ), prepared by reaction of phosphorus pentasulfide with an amide, the thione is adjacent to the asymmetric center. This favorable situation produces more reliable and pronounced Cotton effects when a thionamide is used as a "chromophoric" derivative for carboxylic acids than the formerly employed acylthiourea derivative ( $-\text{C}(\text{O})\text{NHC}(\text{S})\text{NR}'_2$ ). In general, a correlation can be made between the absolute configuration (*R* or *S*) of the asymmetric center closest to the chromophore and the sign of the Cotton effect associated with the derivative's low extinction ultraviolet absorption maximum near 330  $\text{m}\mu$ . The operation of free rotation in thionamides is demonstrated by circular dichroism measurements over the range  $-192$  to  $+168^\circ$ .*

(1) Paper XCVI: C. Djerassi, *Proc. Chem. Soc.*, 314 (1964).

(2) Supported by Grants No. GM-06840 and CA-07195 from the National Institutes of Health of the U. S. Public Health Service.

(3) Taken from part II of the Ph.D. Thesis of J. V. B., Stanford University, 1964.

The stereochemistry of many optically active compounds which are transparent in the 210–700- $\text{m}\mu$  region such as alcohols, amines, and carboxylic acids has been successfully investigated through optical rotatory dispersion measurements of Cotton effects associated with "chromophoric" derivatives. These derivatives contain the required low intensity and conveniently measurable absorption bands, and give rise to anomalous optical rotatory dispersion and circular dichroism curves. Dithiocarbamates ( $-\text{NHC}(\text{S})\text{SR}'$ ), xanthates ( $-\text{OC}(\text{S})\text{SR}'$ ), and acylthioureas ( $-\text{C}(\text{O})\text{NHC}(\text{S})\text{NR}'_2$ ) thus serve as useful "chromophoric" derivatives for amino acids, alcohols, and carboxylic acids, respectively.<sup>4</sup>

The three sulfur derivatives all possess a low intensity ultraviolet absorption maximum at 330–350  $\text{m}\mu$  which most likely arises from transitions in which the thione plays the principal role; the isolated thione is known to have a low intensity band at about 500  $\text{m}\mu$ .<sup>5</sup> Since it is this grouping which is responsible for the long wave

(4) For leading references to these and many other "chromophoric" derivatives, see Table I in ref. 1.

(5) See C. Djerassi and D. Herbst, *J. Org. Chem.*, **26**, 4675 (1961); R. Mayer, G. Hiller, M. Nitzschke, and J. Jentzsch, *Angew. Chem. Intern. Ed. Engl.*, **2**, 370 (1963).