

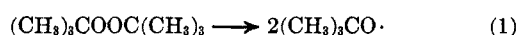
Effects of Solvent on the Unimolecular Decomposition of *t*-Butyl Peroxide<sup>1</sup>EARL S. HUYSER AND RICHARD M. VANSCOY<sup>2</sup>

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The activation parameters  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  calculated from the first-order reaction rate constants found for decomposition of *t*-butyl peroxide in various solvents show that this decomposition reaction is influenced by the solvent. An isokinetic relationship ( $\Delta H^\ddagger = \beta \Delta S^\ddagger$ ) was observed where  $\beta$  is 437°K. The heats of solvation of *t*-butyl peroxide in the solvents used for the kinetic studies were shown to be similar, indicating that differences in interactions of the solvent with the transition state of the decomposition reaction are mainly responsible for the observed differences in the activation parameters. The nature of the solvent effect is discussed in terms of the interactions of the solvent with the ground state of the peroxide and the transition state of the decomposition of the peroxide.

The rate of thermal decomposition of *t*-butyl peroxide yielding *t*-butoxy radicals (eq 1) was reported



initially to be essentially the same in the gas phase and in solution.<sup>3</sup> More recent work has shown that this peroxide was subject to induced decompositions by radicals derived from certain compounds, namely primary and secondary alcohols,<sup>4</sup> and primary and secondary amines.<sup>5</sup> The structural requirement for solvent-derived radicals to induce the decomposition of this dialkyl peroxide is that the radical site be an atom bonded to either a hydroxy group or to an amino group having at least one hydrogen bonded to the nitrogen. This article is concerned with the effects of solvents not capable of inducing the decomposition of *t*-butyl peroxide on the unimolecular decomposition of the peroxide into two *t*-butoxy radicals.

### Results

The first-order reaction rate constants for the decomposition of *t*-butyl peroxide in various solvents (Table I), determined from least-squares treatment of the decomposition rate data obtained by the gas chromatographic method described previously<sup>4</sup> showed that the rate of decomposition was somewhat faster in polar and protic solvents than in nonpolar solvents. The rates of decomposition of the peroxide at any one temperature, however, did not vary by more than a factor of about three in these solvents. However, the activation parameters determined from these first-order reaction rate constants (given in Table II with the calculated probable error<sup>6</sup>) show that the solvent apparently does have a marked effect on the decomposition reaction. Examination of these activation parameters shows that a change in  $\Delta H^\ddagger$  is always accompanied by a concurrent change in  $\Delta S^\ddagger$ . This linear correlation (see Figure 1), where  $\Delta H^\ddagger = \beta \Delta S^\ddagger$ , is referred to as an isokinetic relationship<sup>7</sup> and  $\beta$  is the isokinetic tempera-

ture, the temperature at which enthalpy and entropy factors have opposite but compensating effects on the reaction rate. A decrease in  $\Delta H^\ddagger$  due to a solvent interaction at the isokinetic temperature, which would be expected to increase the reaction rate, is accompanied by a decrease  $\Delta S^\ddagger$  which retards the rate to an extent that compensates for the increase expected from the decrease in  $\Delta H^\ddagger$  and *vice versa*. The isokinetic temperature calculated from our data for the decomposition of *t*-butyl peroxide in various solvents is 437°K (164°), a temperature just somewhat higher than those where the reaction rate constants were determined. At temperatures below the isokinetic temperature, decreases in  $\Delta H^\ddagger$  resulting from solvent interaction result in increases in rate that are not completely compensated for by the decrease in  $\Delta S^\ddagger$ . The reaction rate constants in solvents having low  $\Delta H^\ddagger$  are consequently somewhat higher than those with higher heats of activation. Furthermore, the difference is more pronounced at 120° than at 135°, the higher temperature being closer to the isokinetic temperature. Similar isokinetic relationships have been reported by Leffler and his coworkers for the radical-forming decompositions of various azo compounds in different solvents.<sup>8</sup>

The activation parameters measure only the energy difference between the ground state of the peroxide in solution and the transition state of the decomposition reaction. Measuring the heats of solvation of the peroxide in these solvents (Table III) showed that only small differences in the interactions of the peroxide in the ground state with the solvent existed. Although the heats of solution were measured at 25° and the decomposition rate studies made at 115–135°, it is probably quite safe to assume that the heats of solution at the higher temperatures may be quite similar to those determined at 25°. The conclusion reached is that the differences in  $\Delta H^\ddagger$  must be for the most part the result of differences in interaction of the solvent with the transition state of the decomposition reaction rather than differences in interactions of the solvents with the peroxide in the ground state.

### Discussion

The differences in the activation parameters for the decomposition reaction of *t*-butyl peroxide in these

(1) Taken in part from the thesis submitted by R. M. V. in partial fulfillment of the requirements for the Ph.D. Degree from the University of Kansas, 1966.

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TABLE I  
 FIRST-ORDER REACTION RATE CONSTANTS ( $k \times 10^5 \text{ sec}^{-1}$ ) FOR DECOMPOSITION OF *t*-BUTYL PEROXIDE

Solvent	115°	120°	125°	130°	135°
Cyclohexane	...	$0.63 \pm 0.06^a$	$1.52 \pm 0.07$	$2.59 \pm 0.30$	$4.64 \pm 0.12$
Triethylamine	...	$0.79 \pm 0.03$	$1.69 \pm 0.07$	$3.15 \pm 0.10$	$5.55 \pm 0.20$
Dimethylaniline	...	$0.96 \pm 0.02$	$1.89 \pm 0.04$	$3.41 \pm 0.09$	$5.84 \pm 0.08$
Cyclohexene	...	$0.76 \pm 0.02$	$1.38 \pm 0.02$	$2.81 \pm 0.10$	$4.41 \pm 0.10$
Tetrahydrofuran	...	$0.97 \pm 0.03$	$1.84 \pm 0.03$	$3.39 \pm 0.06$	$5.76 \pm 0.06$
<i>t</i> -Amyl alcohol	...	$1.26 \pm 0.04$	$2.34 \pm 0.06$	$4.47 \pm 0.16$	$6.80 \pm 0.13$
Nitrobenzene	...	$1.31 \pm 0.02$	$2.39 \pm 0.03$	$4.28 \pm 0.03$	$7.20 \pm 0.08$
Ethyl benzoate	...	$1.07 \pm 0.04$	$1.92 \pm 0.04$	$3.39 \pm 0.04$	$5.90 \pm 0.08$
Benzene	...	$1.10 \pm 0.02$	$1.99 \pm 0.06$	$3.22 \pm 0.11$	$6.19 \pm 0.22$
<i>t</i> -Butyl alcohol	...	$1.41 \pm 0.05$	$2.49 \pm 0.06$	$4.30 \pm 0.07$	$7.32 \pm 0.17$
Acetic acid	$1.20 \pm 0.03$	$2.19 \pm 0.05$	$2.98 \pm 0.06$	$6.29 \pm 0.14$	...
Acetonitrile	$1.19 \pm 0.04$	$2.21 \pm 0.07$	$3.47 \pm 0.04$	$5.63 \pm 0.12$	...

<sup>a</sup> Standard deviation.
 TABLE II  
 ACTIVATION PARAMETERS FOR DECOMPOSITION  
 OF *t*-BUTYL PEROXIDE IN VARIOUS SOLVENTS

Solvent	$\Delta H^\ddagger$ , kcal/mol	Probable error	$\Delta S^\ddagger$ , eu <sup>a</sup>	Probable error
Acetonitrile	$31.0 \pm 0.9^b$	0.8	$-1.54 \pm 0.06$	1.99
Acetic acid	$33.4 \pm 0.5$	0.7	$4.58 \pm 0.08$	1.74
<i>t</i> -Butyl alcohol	$34.3 \pm 0.07$	0.9	$5.89 \pm 0.02$	2.25
Benzene	$35.3 \pm 1.1$	0.9	$7.96 \pm 0.32$	2.25
Ethyl benzoate	$35.5 \pm 0.02$	0.8	$8.42 \pm 0.00$	2.08
Nitrobenzene	$35.6 \pm 0.4$	0.4	$9.04 \pm 0.12$	0.95
<i>t</i> -Amyl alcohol	$35.7 \pm 1.4$	0.8	$9.33 \pm 0.49$	2.15
Tetrahydrofuran	$37.1 \pm 0.5$	0.6	$12.3 \pm 0.2$	1.6
Cyclohexene	$37.3 \pm 1.4$	0.7	$12.4 \pm 0.6$	1.9
Dimethylaniline	$37.6 \pm 0.8$	0.5	$13.6 \pm 0.4$	1.2
Gas phase <sup>c</sup>	38.0		14.0	
Triethylamine	$40.6 \pm 1.2$	1.2	$20.9 \pm 0.7$	2.9
Cyclohexane	$40.8 \pm 2.2$	2.1	$21.1 \pm 1.4$	5.2

<sup>a</sup> Calculated for 125°. <sup>b</sup> Standard deviations. <sup>c</sup> From ref 3.
 TABLE III  
 HEATS OF SOLUTION OF *t*-BUTYL PEROXIDE (25°)

Solvent	$\Delta H_{\text{sol}}$ , kcal/mol
Cyclohexene	~0
Triethylamine	~0
Tetrahydrofuran	+0.236
Decahydronaphthalene	0.268
Cyclohexane	0.307
Benzene	0.400
Ethyl benzoate	0.575
N,N-Dimethylaniline	0.866
<i>t</i> -Amyl alcohol	0.949
Acetic acid	1.08
Nitrobenzene	1.15
<i>t</i> -Butyl alcohol	1.33
Acetonitrile	1.55

solvents possibly results from a combination of three different factors. These factors are (1) differences in the solvent interactions with the alkoxy radicallike transition state, (2) different solvent cavity requirements for the transition state, and (3) different amounts of cage recombination of the *t*-butoxy radicals.

It may be illustrative at this point to consider the expected differences between the ground state of the peroxide and the transition state of the decomposition reaction. *t*-Butyl peroxide in the ground state has much hydrocarbon character since the two oxygens of the peroxide linkage are protected by the *t*-butyl groups from direct interaction with the solvent. This is reflected by the lower heats of solution of the peroxide in the nonpolar hydrocarbon solvents than observed in the

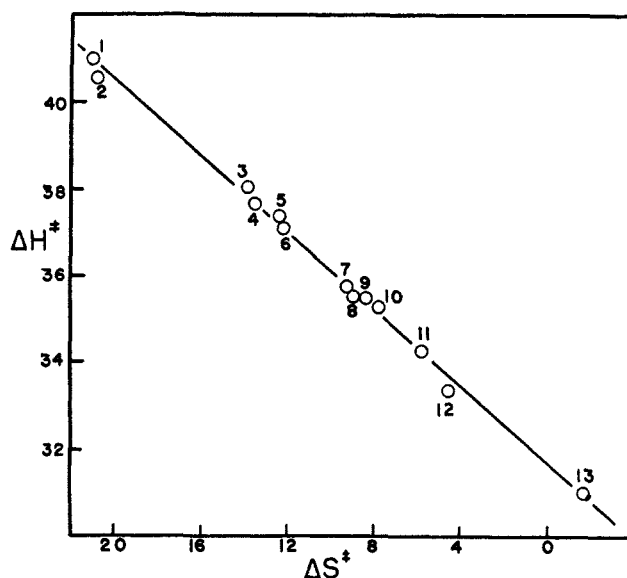
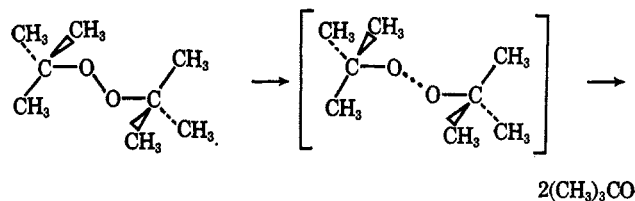


Figure 1.—Linear correlation of activation parameters for decomposition of *t*-butyl peroxide in various solvents: 1, cyclohexane; 2, triethylamine; 3, gas phase; 4, dimethylaniline; 5, cyclohexene; 6, tetrahydrofuran; 7, *t*-amyl alcohol; 8, nitrobenzene; 9, ethyl benzoate; 10, benzene; 11, *t*-butyl alcohol; 12, acetic acid; 13, acetonitrile.

polar and protic solvents. However, the transition state of the decomposition reaction may be quite different.



The activation enthalpy requirement for the gas phase decomposition and the bond dissociation energy of the oxygen-oxygen linkage of the peroxide ( $37.5 \pm 0.5 \text{ kcal/mol}$ )<sup>9</sup> are essentially identical, the latter being determined from the former on the assumption that complete bond breaking occurs in the transition state of the decomposition reaction and the barrier to recombination in the gas phase is negligible. The transition state, therefore, will not only have considerable free *t*-butoxy radical character but the oxygens of the per-

(9) T. L. Cottrell, "The Strength of Chemical Bonds," Academic Press Inc., New York, N. Y., 1958, pp 64-66.

oxide linkage will be more exposed to possible interactions with solvent molecules. Furthermore, the solvent cavity requirement for the transition state will be different from that of the ground state possibly both in size and shape. It is also probable that the dipolar character of the *t*-butoxy moieties will be more pronounced in the transition state where they are more separated than in the ground state.

Comparing the activation parameters found in these solvents with those observed in the gas phase decomposition suggests that the transition state is solvated in certain of these solvents, namely those in which  $\Delta H^\ddagger$  is lower than that for the gas phase reaction. The observed decrease in the  $\Delta S^\ddagger$  relative to that of the gas phase reaction is also consistent with a solvated transition state. Certain of these solvents, namely acetic acid and acetonitrile, have been reported to solvate free *t*-butoxy radicals effectively<sup>10</sup> and might therefore be expected to solvate the transition state of the decomposition reaction of the peroxide if the transition state has *t*-butoxy radical character. Our data would indicate that tertiary alcohols and aromatics also solvate the transition state of the decomposition reaction.

Comparison of the activation parameters found in cyclohexane, a solvent which does not interact with alkoxy radicals, and cyclohexene suggests solvation of the transition state by the latter compound. This observation is consistent with the reported complexing of alkoxy radicals by alkenes.<sup>10</sup>

Somewhat surprising, however, is the observation that in cyclohexane and triethylamine the activation parameters are larger than those observed in the gas phase reaction. These compounds might be expected to solvate the ground state of the peroxide owing to the hydrocarbonlike character of the peroxide, but would not be expected to solvate either the transition state of the reaction or the *t*-butoxy radicals produced in the reaction. Indeed, an increase in the dipolar character of the *t*-butoxy moieties in the transition state relative to the ground state may result in some desolvation in the transition relative to the ground state and may account, in part, for the somewhat higher activation parameters. Another difference between the ground state of the peroxide and the transition state of the reaction may be an increase in size of the solvent cage required to accommodate the transition state. An increase in the size of the solvent cage requirement without any compensating solvation of the transition state could also be responsible in part (see below) for the somewhat higher  $\Delta H^\ddagger$  requirement in these solvents compared with that of the gas phase reaction. The increase in  $\Delta S^\ddagger$  over that in the gas phase reaction observed in cyclohexane and triethylamine may be the result of disrupting the liquid structure in the vicinity of the solvent cage when its size is increased. Changes in the nature of the solvent cavity relative to the ground state should also be expected in solvents where the transition state is highly solvated. In such solvents, the volume change of the solvent cavity for the transition state relative to the ground state possibly is not so large, but the solvent cage may have a different shape from that required for solvents which do not interact with the transition state.

Recent reports by Walling and Waits,<sup>11</sup> Hiatt and

Traylor,<sup>12</sup> and Pryor<sup>13</sup> indicate that cage recombinations of the *t*-butoxy radicals occur in decomposition reactions of *t*-butyl peroxide in solution. Cage recombination, as expected, is important in viscous solvents in which the *t*-butoxy radicals diffuse out of the solvent cavity slowly. Cage recombination may also play a role in determining the activation parameters observed for the decomposition of *t*-butyl peroxide in various solvents. The transition state of the decomposition reaction must closely resemble two free *t*-butoxy radicals in the solvent cavity. If the *t*-butoxy radicals are effectively more solvated than the ground state of the peroxide, this solvation might be expected to be in the vicinity of the oxygen moieties of the radicals. As cage recombination would then require release of the solvent, it is likely that the solvated *t*-butoxy radicals diffuse rapidly from each other into the solution. Consequently, cage recombination in such solvents (*i.e.*, acetic acid, acetonitrile, *t*-alkyl alcohols) is probably unimportant. However, in solvents such as cyclohexane or triethylamine cage recombination could occur. The analytical procedure employed for obtaining rate data measures only decompositions that result in formation of free *t*-butoxy radicals. The somewhat slower rates observed in solvents that do not interact with the transition state could result from solvent cage recombination of some of the *t*-butoxy radical pairs produced by decomposition of the peroxide. The energy required for the *t*-butoxy radicals to diffuse from the solvent cage in these solvents may be reflected in values for  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  being larger than found for the gas phase reaction.

The activation parameters we found for the decomposition of *t*-butyl peroxide in these various solvents probably more than anything else provide a relative measure of the interactions of the solvents with *t*-butoxy radicals. Strong interactions of the solvent with the *t*-butoxy radicals, as reflected by low values for the activation parameters, result in extensive solvation of the transition state with the consequential solvent cavity requirement for such a transition state as well as little cage recombination. At the other extreme, little or no interaction of solvent with *t*-butoxy radicals results in higher values for the activation parameters owing to a larger solvent cavity requirement for the transition state as well as some cage recombination. Between the extremes of acetonitrile, which apparently solvates the transition state effectively and cyclohexane and triethylamine, both of which we might assume do not interact to any extent with the transition state, are solvents which interact with the transition state to a lesser extent than acetonitrile. It should not be assumed that those solvents for which the activation parameters are very nearly the same as those for the gas phase reaction do not interact in any way with the peroxide in its decomposition reaction. In these solvents the interaction of the solvent with the transition state is smaller than in others, but the same factors pertain. The similarity of the values for the activation parameters to those in the gas phase is fortuitous and not indicative of no solvent interaction with the transition state of the decomposition reaction.

(11) C. Walling and H. P. Waits, *J. Phys. Chem.*, **71**, 2361 (1967).

(12) R. Hiatt and T. G. Traylor, *J. Amer. Chem. Soc.*, **86**, 1911 (1964).

(13) W. A. Pryor, personal communication.

(10) C. Walling and P. Wagner, *J. Amer. Chem. Soc.*, **86**, 3363 (1964).

### Experimental Section

All reagents were commercial materials and redistilled before use.

**Determination of the Rate of Decomposition of *t*-Butyl Peroxide in Solvents.**—A master solution of a solvent and *t*-butyl peroxide (TBP) was carefully weighed out in a 5:1 molar ratio. About 1.5 ml of this solution was delivered to each of eight tubes prepared by sealing one end of a 27-cm length of 9-mm-o.d. Pyrex tube. The tubes were then sealed and immersed in an oil bath maintained at the required temperature  $\pm 0.03^\circ$ . Tubes were removed from the bath at appropriate time intervals and immediately quenched in cold tap water. The time intervals were adjusted so that the final tube in a run was taken from the bath near the end of the first half-life of the peroxide.

Each of the samples was analyzed for its *t*-butyl peroxide content by the following gas chromatographic method. The solution from the tube was poured into a tared 2-dram vial and weighed. An amount of a suitable internal standard was added, and the vial was weighed again. This mixture was subjected to gas chromatographic analysis (F & M Model 700) to obtain the peak areas of peroxide and internal standard. Three gas chromatographic column systems were used: (1) a commercial 4-ft, 10% silicone rubber column (F & M Scientific Corp.) operating at a column temperature of  $55^\circ$  using chlorobenzene as the internal standard; (2) several 15-ft columns packed with 15–17% E-600 (Dow Chemical Co.) on Chromosorb W operating at a column temperature of  $65^\circ$  using ethyl acetate as the internal standard; and (3) a 12-ft column packed with didecyl phthalate on Chromosorb W operating at a column temperature of  $70^\circ$  using 2-pentanone as the internal standard. Exit port flow rates were adjusted to 60 ml/min in each case. The last system was found to be the best from the standpoint of speed and reproducibility.

The amount of *t*-butyl peroxide remaining was calculated by mmol of peroxide/g of soln =

$$\frac{K \times \text{wt of I.S.} \times \text{peak area of peroxide} \times 1000}{\text{mol wt of peroxide} \times \text{sample wt} \times \text{peak area of I.S.}}$$

where *K*, the correction factor relating peak areas of peroxide to internal standard (I.S.), is obtained by chromatographing a known mixture of peroxide and internal standard.

Millimoles of peroxide remaining after the various time intervals were used to calculate the reaction rate constant shown in Table I.

**Determination of Heats of Solution.**—The equipment used for determining the heats of solution was an apparatus described by Tyson, McCurdy, and Bricker<sup>14</sup> for performing differential thermometric titrations. The design of this apparatus is similar in most respects to that described by Arnett, *et al.*<sup>15</sup> differing somewhat only in the calorimeter setup. The procedure employed for obtaining the heats of solution is essentially that described in detail by Arnett, *et al.* It consisted of first calibrating a chart recorder to an input of heat into the calorimeter containing to solvent. When calibrated, a small, but accurately measured, amount of *t*-butyl peroxide is introduced into the rapidly stirred solvent by means of 100- $\mu$ l Hamilton syringe fitted with a Cheney adapter. The heat change in the mixture resulting from solution of the peroxide was recorded on the chart recorder, and the heat of solution is calculated from this recorded heat and the amount of peroxide added. These heats of solution are partial molal heats of solution at infinite dilution. Normally three injections of peroxide were made, and in no case did a definite trend in the magnitude of the measured values indicate that the solutions were no longer "infinitely dilute." The heats of solution determined by this method are given in Table III.

**Registry No.**—*t*-Butyl peroxide, 110-05-4.

**Acknowledgment.**—We wish to acknowledge the National Institutes of Health for support of part of this work. We also wish to express our gratitude to Professor C. E. Bricker for use of equipment for determining the heats of solution and to Dr. Harriet Benson for invaluable assistance in the calculations of the rate constants and activation parameters.

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(15) E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. M. Duggleby, *J. Amer. Chem. Soc.*, **87**, 1541 (1965).

## Reactions of Ester Free Radicals. The 2-Carbomethoxy-2-propyl Radical

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The reactions of the 2-carbomethoxy-2-propyl radical (VI) were investigated *via* the dehydrodimerization of methyl isobutyrate and the decomposition of dimethyl 2,2'-azobisisobutyrate. Products from both reactions were identified, and mechanistic pathways were formulated. In the dehydrodimerization process, efficiencies were found to decrease with increasing peroxide concentration. This was attributed to enhanced interaction of VI with the *t*-butoxy radical and subsequent telomerization. It was determined that coupling and disproportionation of 2-carbomethoxy-2-propyl radical proceeded with little difference in activation energies. Over the range  $90\text{--}165^\circ$ ,  $E_C - E_D = 0.21 \text{ kcal mol}^{-1}$ . The site of radical attack on a series of aliphatic esters was determined by the corresponding free-radical additions to norbornene.

The site of free-radical attack on carboxylic esters poses an interesting question of directive effects. Walling and Mintz<sup>1</sup> have recently shown that aliphatic esters are notably inert to attack by *t*-butoxy radicals. This they ascribed to the electron-withdrawing effect of the carboxy group and, in turn, the lowering of electron density of adjacent carbon-hydrogen bonds. This and related polar effects argue for strong polar contributions to the transition state of hydrogen abstraction.<sup>1,2</sup> Earlier workers<sup>3</sup> interpreted such ef-

fects as being partly electrostatic in nature, with an actual repulsion exerted between the incoming radical and the electronegative ester group.

Opposing this unfavorable polar effect is a counterbalancing resonance effect. The driving force for the formation of a carbonyl-adjacent radical is a resonance stabilization of the order of  $4 \text{ kcal mol}^{-1}$ .<sup>4</sup> Experimentally it has been shown that attack by methyl radicals occurs at a carbon-hydrogen bond adjacent to

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