

## ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF MICHIGAN, ANN ARBOR, MICH.]

The Mechanism of the Thermal Decomposition of Di-*t*-butyl Diperoxycarbonate

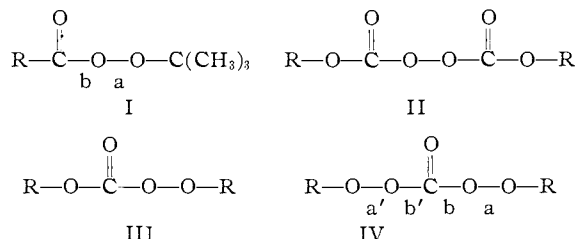
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A study has been made of the free radical decomposition of di-*t*-butyl diperoxycarbonate. The reaction involves a two-step, non-concerted loss of carbon dioxide in which only one of the peroxidic bonds undergoes homolytic cleavage. The activation parameters are  $\Delta H^*$  31.8 kcal. and  $\Delta S^*$  7.1 e.u.

## Introduction

The recent work of Bartlett's laboratory<sup>1-5</sup> has contributed greatly to the understanding of the mechanism of the decomposition of peresters. In this series of papers the factors which cause the decomposition to proceed in stepwise or concerted fashion are established. It is found that the degree of simultaneity of the cleavage of bonds a and b in peresters of the type I depends upon the stability of the incipient radical R.



When R is phenyl or methyl, the decomposition is stepwise, involving initial cleavage of bond a to give a carboxylate radical, which then decarboxylates by subsequent cleavage of bond b. When R is benzyl, however, the decomposition is concerted, bonds a and b cleaving simultaneously to generate carbon dioxide in the rate-determining step. Bartlett and Hiatt<sup>1</sup> go further to develop an interesting correlation between the enthalpy of activation,  $\Delta H^*$ , and the entropy of activation,  $\Delta S^*$ . They find that as the concerted nature of the decomposition increases,  $\Delta H^*$  decreases, due to greater stabilization of the transition state, but only at the expense of  $\Delta S^*$ , since the resonance stabilization of the incipient alkyl radical and *trans* elimination to give carbon dioxide restrict the rotation of certain bonds.

These considerations have not been applied to the peroxidic derivatives of carbonic acid, three types of which are known: II<sup>6-8</sup> (dialkyl peroxydicarbonates), III<sup>6</sup> (dialkyl monoperoxycarbonates) and IV<sup>8,9</sup> (dialkyl diperoxycarbonates). In fact, the work of Cohen and Sparrow,<sup>7</sup> in which it is

found that diisopropyl peroxydicarbonate (II, R = isopropyl) decomposes in a stepwise fashion to give carbon dioxide and isopropoxy radicals, is the only mechanistic work of any kind involving these compounds.

The goal of this work was to establish the mechanism of the decomposition of di-*t*-butyl diperoxycarbonate (IV, R = *t*-butyl). This compound poses several interesting questions, the essence of which concerns the effect of one peroxidic bond upon the cleavage of the other, situated as they are. If both peroxidic bonds a and a' should cleave either simultaneously or stepwise, the hypothetical species, neutral CO<sub>3</sub>,<sup>10</sup> would result. On the other hand, if bonds a and b' cleave, then a peroxidic molecular species would have decomposed by a process in which a non-peroxidic bond, b', has cleaved in preference to a peroxidic bond, a'.

## Experimental

**Materials.** Chlorobenzene from the Eastman Kodak Co. was distilled, b.p. 130-131°, shaken with three portions of concentrated sulfuric acid, once with water, three times with 5% sodium bicarbonate, again with water, dried successively over calcium chloride, calcium sulfate and phosphorus pentoxide and distilled, b.p. 130-130.5°.

*o*-Dichlorobenzene from the Eastman Kodak Co. was distilled, b.p. 179-180°.

Toluene from the Baker Chemical Co. was shaken twice with sulfuric acid, once with water, once with 5% sodium bicarbonate, again with water, was dried over calcium sulfate, then phosphorus pentoxide, and distilled from phosphorus pentoxide; b.p. 110-110.5°.

Cumene from the Eastman Kodak Co. was distilled, b.p. 151-152°.

Diisopropyl ether was dried over calcium hydride, and distilled, b.p. 67-68°.

*t*-Stilbene from the Eastman Kodak Co. was used without further purification, m.p. 123.5-124°.

**Di-*t*-butyl Diperoxycarbonate.**—Phosgene (9.9 g., 0.1 mole), which had been condensed in a trap cooled in a Dry Ice-acetone-bath, was allowed to distil into a mixture of 18.0 g. (0.2 mole) of *t*-butyl hydroperoxide, 16.0 g. (0.2 mole) of pyridine and 100 ml. of petroleum ether (40-60°), cooled in an ice-water-bath, with stirring. About 40 minutes was required for all of the phosgene to distil out of the trap at room temperature into the reaction flask. Stirring at 0° was continued for 30 minutes subsequent to completion of addition. Then 100 ml. of cold water was added to the mixture, the organic layer was separated, washed twice with 100-ml. portions of water, dried over sodium sulfate, and concentrated at room temperature at aspirator pressure on a rotating concentrator. The residue was distilled twice through a 10-inch Vigreux column; b.p. 48° (0.3 mm.), yield 9 g. (44%).

**Procedure for Kinetic Runs.**—A weighed sample of the di-*t*-butyl diperoxycarbonate in a 10.00-ml. volumetric flask was dissolved in a suitable solvent, and 1.00-ml. aliquots transferred to ampoules, which were then sealed. No effort was made to conduct the reactions under a nitrogen atmosphere, since oxygen did not affect the results. A

- (1) P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.*, **80**, 1398 (1958).
- (2) P. D. Bartlett and D. M. Simon, *ibid.*, **82**, 1753 (1960).
- (3) P. D. Bartlett and C. Rüchardt, *ibid.*, **82**, 1756 (1960).
- (4) P. D. Bartlett, E. P. Benzing and R. E. Pincock, *ibid.*, **82**, 1762 (1960).
- (5) P. D. Bartlett and R. E. Pincock, *ibid.*, **82**, 1769 (1960).
- (6) F. Strain, W. E. Bissinger, W. R. Dial, H. Rudoff, B. J. DeWitt, H. C. Stevens and J. H. Langston, *ibid.*, **72**, 1254 (1950).
- (7) S. G. Cohen and D. B. Sparrow, *ibid.*, **72**, 611 (1950).
- (8) H. C. McBay and O. Tucker, *J. Org. Chem.*, **19**, 869 (1954).
- (9) A. G. Davies and K. J. Hunter, *J. Chem. Soc.*, 1809 (1953).

- (10) A. D. Walsh, *ibid.*, 2301 (1953).

sample of this solution was considered to represent zero time. The ampoules were immersed simultaneously in an oil-bath maintained at a constant temperature within  $\pm 0.05^\circ$ . Ampoules were removed periodically from the oil-bath, chilled in ice-water, opened, and the solutions stored at  $5^\circ$  until analyzed. Points were taken until up to 80 or 90% of the original perester had decomposed. One ampoule was kept in the bath until decomposition was complete. This aliquot was considered to represent infinite time.

**Determination of Relative Concentration of Di-*t*-butyl Diperoxycarbonate by Infrared.**—The analytical procedure was basically the one described by Bartlett and Hiatt.<sup>1</sup> The analyses were carried out in matched 0.1-mm. cells on a Perkin-Elmer model 21 infrared spectrophotometer. All samples of a given run were allowed to warm to room temperature, and the transmission in the carbonyl region of each was measured in turn. Di-*t*-butyl diperoxycarbonate possesses a split carbonyl band, having a high intensity peak at  $1825\text{ cm.}^{-1}$  and a somewhat less intense peak at  $1796\text{ cm.}^{-1}$ . The  $1825\text{ cm.}^{-1}$  peak was used for quantitative analysis. The percentage transmission at  $1825\text{ cm.}^{-1}$  was measured several times, while both increasing and decreasing frequency, and an average value taken. The maximum error in this measurement is 1%.

**Treatment of Data.**—Rate constants were calculated from least squares slopes of plots of  $\log P/P_0$  vs. time, where  $P$  is percarbonate concentration and  $P_0$  is initial percarbonate concentration. The ratio,  $P/P_0$ , was calculated from the expression

$$P/P_0 = \frac{\log T_\infty - \log T_P}{\log T_\infty - \log T_0}$$

where  $T_\infty$  is percentage transmission at infinite time,  $T_P$  is percentage transmission of any given sample, and  $T_0$  is percentage transmission at zero time. Except for those decompositions conducted in the presence of *t*-stilbene,  $T_\infty = 100\%$ . When *t*-stilbene was present, a product of the reaction absorbed about  $1804\text{ cm.}^{-1}$ , and the side of the peak was rising at  $1825\text{ cm.}^{-1}$ , lending a bit of uncertainty to the magnitude of  $T_\infty$ .  $T_\infty$  was between 90 and 95%.

The graphs of  $\log P/P_0$  vs. time were straight lines up to 80% decomposition, and first-order rate constants were determined by calculation of the slope by the method of least squares. Points lying past 80% reaction were not included in the calculations, not because of any apparent curvature of the plot, but because random scatter was somewhat higher due to the greater error in the measurement of percentage transmission in the very dilute solutions.

The enthalpy of activation,  $\Delta H^*$ , was obtained from the least squares slope of the line given by  $\log k$  vs.  $1/T$  for runs at  $100^\circ$ ,  $110^\circ$  and  $120^\circ$ . The entropy of activation,  $\Delta S^*$ , was calculated by substituting into the equation

$$k = \frac{k'T}{h} e^{\frac{\Delta S^*}{R}} e^{-\frac{\Delta H^*}{RT}}$$

where  $k$  is a first-order rate constant at temperature  $T$ ,  $k'$  is the Boltzmann constant,  $h$  is the Planck constant, and  $R$  is the gas constant.

**Study of Carbon Dioxide Yield.**—The amount of carbon dioxide evolved during the decomposition of di-*t*-butyl diperoxycarbonate was determined gravimetrically by observing the increase in weight of a tube filled with Ascarite. A sample of the perester was weighed into the reaction flask, weighed quantities of any other materials were added, and solvent was introduced from a pipet. Prepurified nitrogen from a tank was then passed through a tube filled with Ascarite and Dehydrite into the reaction flask to a point a few cm. above the surface. The top of the condenser was connected to a trap cooled in a Dry Ice-acetone-bath, then to a tube filled with Dehydrite, then two tubes filled with Ascarite, and finally to a bubbler. The system was purged with nitrogen, maintaining the reaction flask at room temperature, until the Ascarite tube nearest the reaction mixture reached a constant weight. The increase in weight during this purging process rarely exceeded 0.5–1.0 mg. Then the reaction flask was immersed in the oil-bath, maintained at a constant temperature, and the weight of the Ascarite tube nearest the reaction flask was periodically checked by stopping the nitrogen flow at the tank, clamping off rubber tubing, and removing the Ascarite tube. The second Ascarite tube did not increase in weight, and simply protected the first one from atmospheric carbon dioxide.

The reaction was allowed to proceed until the Ascarite tube reached constant weight. In several instances (see Results) it was found to be advantageous to run the decomposition to partial completion, in which case the procedure was to remove the reaction flask from the bath at the specified time, immerse it in an ice-water-bath to stop the reaction, and purge the system at room temperature with nitrogen until the Ascarite tube reached a constant weight.

**Detection of *t*-Butyl Hydroperoxide as a Decomposition Product in Cumene.**—A solution of 1.1750 g. (0.0057 mole) of di-*t*-butyl diperoxycarbonate in 12 ml. of cumene was heated at  $100^\circ$  for 3 hours, then cooled. The mixture was distilled through a semimicro column. The boiling point was quite constant at  $38^\circ$  (18 mm.) and 1-ml. fractions were arbitrarily taken until 6 ml. had been distilled. Infrared analysis indicated the presence of hydroxyl-containing constituents in the first two fractions. The remaining fractions appeared to be pure cumene, and the distillation residue was a solution of undecomposed di-*t*-butyl diperoxycarbonate in cumene. The first two fractions, containing all of the *t*-butyl hydroperoxide and *t*-butyl alcohol from the decomposition and none of the unreacted perester, were combined.

To the fraction containing hydroperoxide was added 5 ml. of methylene chloride, 0.15 g. (0.027 mole) of potassium hydroxide in 3 ml. of water and 0.25 g. (0.0015 mole) of *p*-nitrobenzoyl chloride. The mixture was stirred at room temperature for 4 hours, 5 ml. of methylene chloride added, the organic layer separated and washed once with 5 ml. of dilute sodium carbonate, twice with 10-ml. portions of water, dried over sodium sulfate, and concentrated to dryness at room temperature and 1 mm. pressure. The solid residue was recrystallized from petroleum ether ( $60\text{--}75^\circ$ ); m.p.  $77.5\text{--}78^\circ$ . Authentic *t*-butyl *p*-nitroperbenzoate melts at  $77\text{--}78^\circ$  (lit.<sup>11</sup>  $79^\circ$ ). A mixed melting point was undepressed.

## Results

**Rate Constants.**—The kinetic results are shown in Table I. In all twelve runs, the graph of  $\log P/P_0$  vs. time is linear past 80% reaction. Beyond 80% reaction the experimental scatter becomes somewhat greater due to lesser accuracy of the analytical technique, but no curvature in the plots is apparent.

Decompositions in chlorobenzene were carried out at three temperatures,  $99.95^\circ$ ,  $110.10^\circ$  and  $120.10^\circ$ . At  $99.95^\circ$ , four decompositions were conducted over an eightfold variation in the initial percarbonate concentration, leading to rate constants which deviate from the mean by only 1.5%. Evidence for first-order kinetics thus seems convincing.

The rate constants in *o*-dichlorobenzene, toluene and cumene are the same as the rate constants in chlorobenzene at the same temperature. Thus it would appear that free radicals which could be derived by interaction of an initial percarbonate cleavage product with solvent, such as benzyl or cumyl radicals, do not induce decomposition of the percarbonate. However, in diisopropyl ether at  $99.95^\circ$ , the rate constant is 4.1 times as large as in chlorobenzene. This acceleration is indicative of an induced decomposition involving radical derived from the solvent. Decomposition in styrene resulted in polymerization.

The results in solutions of *t*-stilbene (runs 11 and 12) are of considerable importance. The presence of *t*-stilbene is found to alter the yield of carbon dioxide (*vide infra*) without changing the rate of decomposition. The magnitude of the error in the rate constants in mixtures containing stilbene is

(11) A. T. Blomquist and I. H. Berstein, *J. Am. Chem. Soc.*, **73**, 5346 (1951).

TABLE I

RATES OF DECOMPOSITION OF DI-*t*-BUTYL DIPEROXYCARBONATE

Run	Solvent	Initial concn., <i>M</i>	<i>T</i> , °C.	<i>k</i> , sec. <sup>-1</sup> × 10 <sup>5</sup>
1	Chlorobenzene	0.0295	99.95 ± 0.05	6.58
2	Chlorobenzene	.0534	99.95 ± .05	6.76
3	Chlorobenzene	.1035	99.95 ± .05	6.90
4	Chlorobenzene	.2423	99.95 ± .05	6.65
5	Chlorobenzene	.0570	110.1 ± .05	21.3
6	Chlorobenzene	.0610	120.1 ± .05	60.5
7	<i>o</i> -Dichlorobenzene	.1736	120.1 ± .05	59.8
8	Toluene	.0494	99.95 ± .05	6.83
9	Cumene	.0881	99.95 ± .05	6.72
10	Diisopropyl ether	.0752	99.95 ± .05	27.6
11	0.560 <i>M t</i> -Stilbene in chlorobenzene	.0652	99.95 ± .05	5.8-6.6
12	0.560 <i>M t</i> -Stilbene in <i>o</i> -dichlorobenzene	.1893	120.1 ± .05	50-60

somewhat larger than the others due to an uncertainty in the percentage transmission at 1825 cm.<sup>-1</sup> of a sample in which decomposition of the percarbonate had proceeded to completion. This uncertainty arises from the fact that a product of this decomposition has a peak at 1804 cm.<sup>-1</sup>, and the pen is rising at 1825 cm.<sup>-1</sup>. In spite of this difficulty, however, the rate constants in the presence of *t*-stilbene seem to be the same, within experimental error, as the rate constants in pure chlorobenzene (compare runs 1-4 and 11) at 99.95° and in pure *o*-dichlorobenzene (compare runs 7 and 12) at 120.10°. Thus, we can conclude that the rate-determining step of the decomposition is the same and involves only the di-*t*-butyl diperoxy-carbonate in the presence or absence of *t*-stilbene.

**Activation Parameters.**—From the kinetic information summarized in Table I, runs 1-6, it is possible to calculate that the enthalpy of activation,  $\Delta H^*$ , is 31.8 kcal., and the entropy of activation,  $\Delta S^*$ , is 7.1 e.u.

**Carbon Dioxide Yield.**—The effect upon carbon dioxide yield of several materials present during the decomposition of di-*t*-butyl diperoxy-carbonate is indicated in Table II. The percentage yields probably are accurate to about 5%. The yield of carbon dioxide is seen to be quantitative in pure chlorobenzene, *o*-dichlorobenzene and cumene, and in chlorobenzene in the presence of anthracene. However, when *t*-stilbene is present, the yield of carbon dioxide is less than quantitative. Interestingly enough, the yield of carbon dioxide in *o*-dichlorobenzene plus *t*-stilbene decreases with increasing temperature (runs 16, 17 and 18). The effect of *t*-stilbene seems to be the same, within experimental limits, in cumene as in *o*-dichlorobenzene (compare 17 with 20 and 18 with 21). In both cases the yield is somewhat less in cumene, but the figures are the same within the limits of experimental error.

**Organic Products.**—No great effort was made to characterize rigorously all of the organic products of the decomposition of di-*t*-butyl diperoxy-carbon-

TABLE II

EFFECT OF VARIOUS MATERIALS ON YIELD OF CARBON DIOXIDE FROM DECOMPOSITION OF DI-*t*-BUTYL DIPEROXY-CARBONATE

Run	Solvent	Material added	<i>T</i> , °C.	Yield CO <sub>2</sub> , % <sup>b</sup>
13	Chlorobenzene	None	110.1	95
14	Chlorobenzene	Anthracene	110.1	99
15	<i>o</i> -Dichlorobenzene <sup>a</sup>	None	110.1	100
16	<i>o</i> -Dichlorobenzene	<i>t</i> -Stilbene <sup>a</sup>	100.0	102
17	<i>o</i> -Dichlorobenzene	<i>t</i> -Stilbene	110.1	79
18	<i>o</i> -Dichlorobenzene	<i>t</i> -Stilbene	120.1	72
19	Cumene <sup>a</sup>	None	110.1	100
20	Cumene	<i>t</i> -Stilbene	110.1	73
21	Cumene	<i>t</i> -Stilbene	120.1	67

<sup>a</sup> In runs 15-21, 2.38 mmoles of di-*t*-butyl diperoxy-carbonate and 25.00 ml. of solvent were employed. In runs in which *t*-stilbene was present, 27.8 mmoles were used. Thus mmoles *t*-stilbene/mmoles perester = 11.7. <sup>b</sup> Those runs in which *t*-stilbene was present were not carried out to complete decomposition. A reaction time greater than the half-life was selected, and at a given temperature the yields of carbon dioxide in pure *o*-dichlorobenzene, in *o*-dichlorobenzene plus *t*-stilbene, and in cumene plus *t*-stilbene were compared after the same reaction time. Since runs 15 and 19 demonstrate that the yield of carbon dioxide in either pure solvent is quantitative, the percentage yield in the stilbene-containing samples was calculated from the ratios of yields after the same reaction time. This procedure was followed in order to avoid errors in carbon dioxide yield which might arise from a gradual decarboxylation of any of the possible products of the reaction of *t*-stilbene with radicals derived from di-*t*-butyl diperoxy-carbonate.

ate in chlorobenzene. It certainly has been established that the free radical decomposition of *t*-butyl peresters generates the *t*-butoxy radical, and the chemistry of the *t*-butoxy radical has been studied extensively. Although the presence of acetone and *t*-butyl alcohol was indicated by the infrared spectra of the decomposition mixtures, calculation of their relative yields would contribute nothing to this study. However, one important organic product was detected when the decomposition was conducted in cumene. It was demonstrated that *t*-butyl hydroperoxide was a product of the decomposition in this solvent.

### Discussion

The wealth of information on other peroxide decompositions<sup>12,13</sup> certainly points to a free radical reaction as the mode of thermal decomposition of di-*t*-butyl diperoxy-carbonate. The clean first-order kinetics and the constancy of the rate constant in *o*-dichlorobenzene, chlorobenzene, toluene and cumene are consistent with this notion. Likewise, the greater rate of decomposition in diisopropyl ether is typical of a free radical reaction in which radicals derived from the solvent bring about an induced decomposition of the perester. The facile polymerization of styrene and the formation of acetone, a product of decomposition of the *t*-butoxy radical, are also signs of the free radical nature of the thermal decomposition of di-*t*-butyl diperoxy-carbonate.

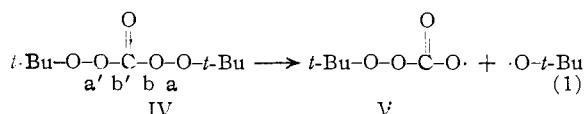
The activation parameters,  $\Delta H^*$ , 31.8 kcal., and  $\Delta S^*$ , 7.1 e.u., provide further insight into the

(12) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, Chapt. 10.

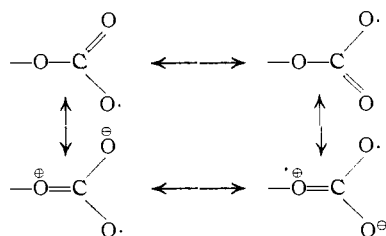
(13) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, pp. 710-720.

details of the process. When included in Bartlett and Hiatt's enthalpy-entropy correlation,<sup>1</sup> the parameters fall in the same range as those for the decomposition of *t*-butyl perbenzoate and *t*-butyl trichloroperacetate. Bartlett has characterized these two peresters as ones that decompose through a transition state in which the rotation about one bond is restricted. In the case of the perbenzoate, a perester which undergoes a stepwise decomposition to lose carbon dioxide, the bond from the ring to the carboxyl group is frozen at the transition state due to the requirement of coplanarity of the benzene ring and the carboxyl group for overlap of  $\pi$ -orbitals to occur. In the case of the trichloroperacetate, which loses carbon dioxide in a one-step, concerted manner, the frozen bond is the alkyl carbon-oxygen bond. This bond, which is to become a double bond in the incipient carbon dioxide, is restricted such that the *t*-butoxy group and the trichloromethyl group are *trans* to each other during the decomposition.

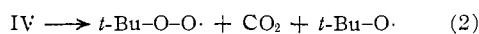
The activation parameters for the decomposition of di-*t*-butyl diperoxy carbonate indicate that the rotation of one bond is restricted at the transition state, but which bond depends upon the mechanism.



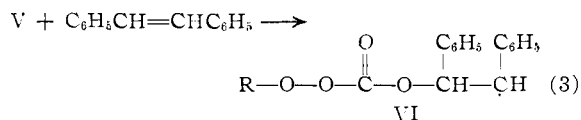
If reaction 1 represents the first step of a non-concerted decomposition, then bond b' must be restricted for the same reason that the bond from the ring to the carboxyl group of the benzoate radical is restricted during the decomposition of *t*-butyl perbenzoate. Resonance of the type indicated requires that the carboxyl group of radical V be perpendicular to the *p*-orbital of the oxygen atom.



However, if the decomposition is a concerted, one-step process (reaction 2), then bond b must be restricted because of the requirements of a *trans* elimination.



That reaction 1 actually is followed was established readily by trapping the intermediate *t*-butyl peroxy carbonate radical V before it decarboxylates. When the decomposition is conducted in the presence of *t*-stilbene, the rate of decomposition is the same, indicating that no change in mechanism occurs, but the yield of carbon dioxide is decreased from 100% to about 72% at 120°. Under these conditions, some of the intermediate radicals V add to the *t*-stilbene (reaction 3) before they are able to decarboxylate. Radical VI then could couple with another free radical in the system or



undergo an internal induced decomposition to give stilbenediol carbonate. The absorption at 1804  $\text{cm}^{-1}$  in the infrared spectrum of decompositions conducted in the presence of *t*-stilbene doubtless arises from such products.

It is interesting to note that the yield of carbon dioxide in the presence of stilbene decreases as the temperature increases. This is contrary to the behavior exhibited by the benzoate radical, although the temperature effect in this case is small.<sup>14</sup> In other words, reaction 3 competes with decarboxylation more effectively at higher temperatures. This means that the activation energy for reaction 3 is higher than for decarboxylation, which would indicate that the *t*-butyl peroxy carbonate radical V is not a very stable one, the energy of activation for further decomposition being quite low.

One objection might be raised to the above-stated conclusion that the decomposition proceeds in a stepwise fashion. Might it not be possible that the 72% yield of carbon dioxide obtained from the decomposition in *o*-dichlorobenzene in the presence of *t*-stilbene at 120° indicates that 72% of the decompositions are concerted, giving carbon dioxide in one step, and 28% are stepwise, giving the intermediate radical V which is intercepted by the stilbene? This possibility can be rejected through the following argument.

If it is assumed that reactions 1 and 2 are competing processes, then a ratio of rate constants may be obtained from the Arrhenius equations corresponding to the two reactions

$$k_1 = Z_1 e^{-E_1/RT} \text{ and } k_2 = Z_2 e^{-E_2/RT}$$

Hence

$$\frac{k_1}{k_2} = \frac{Z_1}{Z_2} e^{(E_2 - E_1)/RT}$$

Now, if it is assumed that radical V is effectively scavenged by the *t*-stilbene, so that the carbon dioxide formed is all formed from reaction 2, then the ratio (100 - yield of carbon dioxide)/(yield of carbon dioxide) is equal to  $k_1/k_2$ . From the data in Table II it is then possible to substitute values for  $k_1/k_2$  at three different temperatures, 373°K., 383°K. and 393°K. Thus, with three equations it is possible to solve for the two variables,  $E_2 - E_1$  and  $Z_1/Z_2$ . Assuming an accuracy of 5% for the carbon dioxide yields, it is thus possible to calculate that  $E_1$  must exceed  $E_2$  by 10 to 50 kcal./mole while  $Z_1/Z_2$  ranges correspondingly from 1 to over 100. Now, if the measured rate,  $k_m$ , is in fact a sum of  $k_1 + k_2$ , that is then an Arrhenius plot of

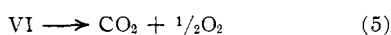
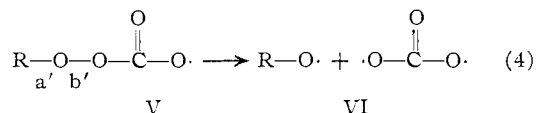
$$k_m = Z_1 e^{-E_1/RT} + Z_2 e^{-E_2/RT}$$

In  $k_m$  vs.  $1/T$  could not possibly be linear. Consequently, since it is linear, then the original assumption that reactions 1 and 2 were competing must be in error. Having ruled out a competition

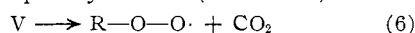
(14) P. D. Bartlett and S. G. Cohen, *J. Am. Chem. Soc.*, **65**, 543 (1943).

between reaction 1 and 2, it then can be concluded that the first step of the decomposition is represented by reaction 1, and that the radical V is only partially scavenged by the *t*-stilbene.

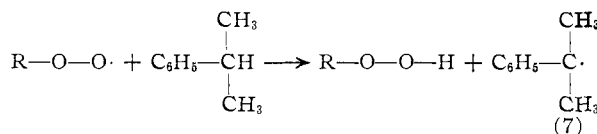
Having established that the first step of the reaction involves the cleavage of one bond, the peroxidic bond a, it remains to ascertain which bond cleaves in the second step. Cleavage of the other peroxidic bond, a', would lead to the *t*-butoxy radical and the species CO<sub>3</sub>, which might then decompose into carbon dioxide and oxygen (reactions 4 and 5). Cleavage of bond b', on the



other hand, would lead directly to carbon dioxide and the *t*-butyl peroxy radical (reaction 6).



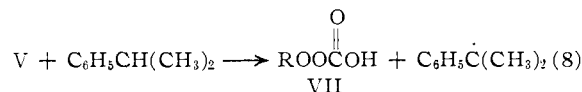
Experiments conducted in cumene establish the latter to be the case. In cumene, the rate is unchanged, indicating no change in mechanism, but it is possible to trap the *t*-butyl peroxy radical, which abstracts a hydrogen atom from the cumene to give *t*-butyl hydroperoxide. The *t*-butyl hydroperoxide was isolated and characterized as its



*p*-nitroperbenzoate derivative. The isolation of *t*-butyl hydroperoxide demonstrates that the peroxidic bond, a', remains intact during the decomposition.

One further possibility had to be ruled out to establish the validity of this conclusion. It is

conceivable that the *t*-butyl peroxy carbonate radical V might abstract a hydrogen atom from the cumene to give the unstable acid VII and this acid might then decompose to carbon dioxide and *t*-butyl hydroperoxide. In other words, the pathway



by which carbon dioxide is evolved may have been altered by the cumene without affecting the rate of the first step. This can be excluded, however. It was shown that the yield of carbon dioxide from the decomposition in cumene is quantitative. Thus, the acid VII, if formed, must decarboxylate completely. Furthermore, it was found that the effectiveness of stilbene at lowering the carbon dioxide yield was the same in cumene as in *o*-dichlorobenzene. This rules out the acid VII as a carbon dioxide source when cumene is the solvent because, had it been involved, some of the radicals V which in *o*-dichlorobenzene would have added to stilbene and had their subsequent decarboxylation prevented, would have been intercepted by cumene before being scavenged. In short, the stilbene would have been less effective at lowering the yield of carbon dioxide in cumene than in *o*-dichlorobenzene.

It may be concluded that the thermal, free radical decomposition of di-*t*-butyl diperoxy carbonate is a two-step process, in which reaction 1 is followed by reaction 6.

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## The Salt Effect in the Aromatic Nucleophilic Substitution Reaction of 2,4-Dinitrochlorobenzene and Methoxide in Methanol-Benzene

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The effect of added salts on the rate of reaction of 2,4-dinitrochlorobenzene and alkali metal methoxides in 50% methanol-benzene has been investigated. The rate of reaction follows the order LiOCH<sub>3</sub> < NaOCH<sub>3</sub> < KOCH<sub>3</sub>. Potassium salts increase the rate of reaction with all methoxides and lithium salts decrease the reaction rate constant. Sodium salts decrease the rate of reaction with KOCH<sub>3</sub>, increase the rate with LiOCH<sub>3</sub> and have little effect with NaOCH<sub>3</sub>; NaI does not have the same effect as other sodium salts.

In the previous paper,<sup>2</sup> the effect of added salts on the rate of reaction of 2,4-dinitrochlorobenzene, hereinafter abbreviated as 2,4-DNCB, and MOCH<sub>3</sub> in methanol was investigated. The salt effects observed were attributed to ion pairing of the

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(2) J. D. Reinheimer, W. F. Kieffer, S. W. Frey, J. C. Cochran and E. W. Barr, *J. Am. Chem. Soc.*, **80**, 164 (1958).

methoxide ion and alkali metal cation. The hypothesis was not regarded as complete, for the accelerating effect of K<sup>+</sup> salts on KOCH<sub>3</sub> was not explained. A change in dielectric constant of the medium to a lower value should enhance the ion pairing and thus verify or disprove the original hypothesis. A mixture of methanol and benzene was deemed to be a suitable solvent in which to pursue the further investigation of salt effects