and a basic group in the non-enzymatic catalysis indicates that a similar, but more efficient, assistance may be responsible for the enzymatic catalysis.

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The Mechanism of the Decompositions of *t*-Butyl 3-Phenylperpropionate and *t*-Butyl 4-Phenylperbutyrate

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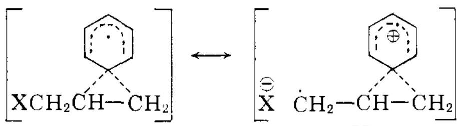
A kinetic study of the free radical decompositions of *t*-butyl 3-phenylperpropionate and 4-phenylperbutyrate has established that these peresters decompose by a two-step, non-concerted mechanism. This is evidence against the existence of bridged, "non-classical" free radicals.

Introduction

In the course of studies currently in progress relating to polar effects in free radical-forming reactions, it became essential that the question of the existence or lack of existence of bridged, "non-classical" radicals, analogous to the phenonium ions which intervene during some of the solvolytic reactions of β-phenyl-substituted benzenesulfonates and substituted benzenesulfonates,[1,2] be settled. The transition state leading to such a bridged radical formed by the addition of a free radical to allylbenzene is depicted in structure I, or, employing the polar model for the transition state of a free radical-forming reaction, suggested by Walling and Mayo,[3] and utilized by many others,[4] by structure II.



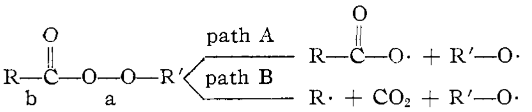
I II

To date, no evidence has been presented which requires phenyl participation in radical-forming reactions at a carbon atom beta to a benzene ring, but neither has any been presented which rigorously excludes it. In their studies on the decarbonylation of β-phenylated propionaldehydes, Curtin and Hurwitz[5] observed that for a 1,2-phenyl shift to occur, the migration origin must either be tertiary, or if secondary, both groups must be aryl. The authors recognized that no conclusions regarding the concerted or non-concerted nature of the decarbonylation could be drawn, however.

The most compelling evidence against the existence of bridged radicals was presented by Seubold,[6] who found that the degree of rearrangement of the 2-phenyl-2,2-dimethylethyl radical, generated by the decarbonylation of 3-phenyl-3,3-dimethylpropionaldehyde, depends upon the concentration of the hydrogen donor, thus implicating the simultaneous existence of at least two interconvertible radical species. However, it is still possible that the first-formed radical is bridged, and that this radical may then abstract a hydrogen atom from the hydrogen donor or rearrange to a non-bridged radical. Thus, although this work precludes a bridged radical as the product-determining species, it does not rigorously exclude bridging at the rate-determining stage of radical formation.

Overberger and Gainer[7] studied the rates of decomposition of three *p*-substituted 2-azo-bis-3-methyl-3-phenylbutanes at 255°, and found the rate to be insensitive to the electronic nature of the *p*-substituent. This result is consistent with the lack of participation by a β-phenyl group, but does not rigorously exclude it, since, as Leffler[8] has pointed out, the rates of a reaction for a series of related compounds can be relatively insensitive to changes in structure or solvent when the particular reaction is observed near the isokinetic temperature because of compensating changes in ΔH^* and ΔS^*.

Nowhere has the behavior of ΔH^* and ΔS^* been utilized so effectively in gaining an understanding of the nature of a transition state than in perester decompositions (reaction 1). In the elegant work of Bartlett's group,[9] the factors which cause a perester to decompose in a stepwise (path A) or concerted fashion (path B) are established. When



III (1)

$$\underset{\text{III}}{R-\overset{\overset{O}{\|}}{\underset{b}{C}}-O\underset{a}{-}O-R'} \begin{cases} \xrightarrow{\text{path A}} R-\overset{\overset{O}{\|}}{C}-O\cdot + R'-O\cdot \\ \xrightarrow{\text{path B}} R\cdot + CO_2 + R'-O\cdot \end{cases} \quad (1)$$

the alkyl radical R· is of a stable type (benzyl, *t*-butyl or trichloromethyl), there is simultaneous cleavage of bonds a and b, producing carbon dioxide and the alkyl radical in the rate-determining step.

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(1) D. Cram, *J. Am. Chem. Soc.*, **71**, 3863 (1949); **74**, 2129, 2137 2159 (1952).

(2) (a) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber and J. Corse, *ibid.*, **74**, 1113 (1952); (b) S. Winstein and B. K. Morse, *ibid.*, **74**, 1133 (1952); (c) S. Winstein, M. Brown, K. C. Schreiber and A. H. Schlesinger, *ibid.*, **74**, 1140 (1952); (d) S. Winstein and K. Schreiber, *ibid.*, **74**, 2165, 2171 (1952).

(3) (a) F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 191 (1950); (b) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957; (c) C. Walling and B. Miller, *J. Am. Chem. Soc.*, **79**, 4181 (1957); (d) C. Walling and B. Jacknow, *ibid.*, **82**, 1756 (1960).

(4) (a) G. A. Russell, *J. Org. Chem.*, **23**, 1407 (1958); (b) E. S. Huyser, *J. Am. Chem. Soc.*, **82**, 394 (1960); (c) P. D. Bartlett and C. Rüchardt, *ibid.*, **82**, 1756 (1960).

(5) D. Y. Curtin and M. J. Hurwitz, *ibid.*, **74**, 5381 (1952).

(6) F. H. Seubold, *ibid.*, **75**, 2532 (1953).

(7) C. G. Overberger and H. Gainer, *ibid.*, **80**, 4561 (1958).

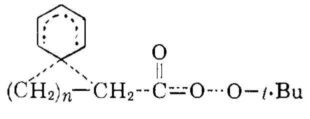
(8) (a) J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955); (b) M. G. Alder and J. E. Leffler, *J. Am. Chem. Soc.*, **76**, 1475 (1954).

(9) (a) P. D. Bartlett and R. R. Hiatt, *ibid.*, **80**, 1398 (1958); (b) P. D. Bartlett and D. M. Simon, *ibid.*, **82**, 1753 (1960); (c) P. D. Bartlett, E. P. Benzing and R. E. Pincock, *ibid.*, **82**, 1762 (1960); (d) P. D. Bartlett and R. E. Pincock, *ibid.*, **82**, 1769 (1960).

But when R· is not so stable (methyl or phenyl), only bond a cleaves in the rate-determining step and the carboxylate radical subsequently loses carbon dioxide. Bartlett and Hiatt go further to develop an interesting relationship between ΔH^* and ΔS^*. As the concerted nature of the decomposition increases, ΔH^* decreases, due to the greater stability of the transition state, but only at the expense of ΔS^*, which becomes more negative. This reflects certain rotational restrictions in the transition states of peresters leading to stable radicals by concerted loss of carbon dioxide. In the decomposition of *t*-butyl phenylperacetate, neither bonds b nor the bond from carbonyl carbon to oxygen are free to rotate in the transition state. Bond b must be "frozen" to allow resonance stabilization of the incipient benzyl radical, and the carbon–oxygen bond must be frozen because the elimination of the benzyl radical and the *t*-butoxy radical from the incipient carbon dioxide is a *trans* elimination. On the other hand, no bonds are "frozen" in the transition state for the non-concerted decomposition of *t*-butyl peracetate. The activation parameters for the phenylperacetate are ΔH^* 29 kcal./mole, ΔS^* 4 e.u.; for the peracetate, ΔH^* 38 kcal./mole, ΔS^* 17 e.u. Thus, ΔH^* and ΔS^* are sensitive and interpretable measures of transition state stability and geometry.

Making use of these principles, it should be possible to establish or preclude phenyl-bridging during the generation of a 2-phenylethyl or a 3-phenylpropyl radical by studying the decomposition of *t*-butyl 3-phenylperpropionate (III, R = $C_6H_5CH_2CH_2$) and *t*-butyl 4-phenylperbutyrate (III, R = $C_6H_5CH_2CH_2CH_2$).

If there is no participation by the phenyl group two or three carbons distant, the decompositions should proceed in a stepwise manner, through a transition state in which only bond a is perturbed, and in which no bonds are restricted in their rotation, and the activation parameters should fall in the same region of Bartlett's enthalpy–entropy diagram as those for *t*-butyl peracetate. On the other hand, if bridging is operative in free radical stabilization, then the decompositions should merge into the concerted type similar to that for *t*-butyl phenylperacetate. The transition state might be represented by IV. A decomposition proceeding through such a transition state would be characterized by activation parameters which reflect the stabilizing effect of the bridged phenyl group and the rigid geometry inherent in the formation of a ring. Thus, ΔH^* should be lower than the ΔH^* observed for *t*-butyl peracetate and ΔS^* should be a great deal more negative.



IVa, $n = 1$
b, $n = 2$

Experimental

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

***t*-Butyl 3-Phenylperpropionate.**—A solution of 5.0 g. (0.033 mole) of pyridine in 10 ml. of low boiling (30–60°) petroleum ether was added slowly to a mixture of 5.1 g. (0.03 mole) of 3-phenylpropanoyl chloride, 5.0 g. (0.055 mole) of *t*-butyl hydroperoxide and 25 ml. of low boiling petroleum ether, cooled to 0°. Stirring was continued at room temperature for 10 hours following the completion of addition. Then 25 ml. of cold water was added to the reaction mixture, the organic layer separated, washed once with 15 ml. of cold 10% sulfuric acid, twice with 15-ml. portions of cold 5% sodium bicarbonate, and finally twice with water and dried over sodium sulfate. The solution was concentrated on a rotary concentrator at room temperature, the concentrated solution passed through a short Florisil column, eluting with pentane, solvent was removed at room temperature, and the residue distilled rapidly through a short path apparatus at 0.05 mm. The yield of purified material was about 2.0 g. (30%). Material prepared and purified in this way is free of all extraneous bands in the hydroxyl and carbonyl regions of the infrared. The perester carbonyl band lies at 1784 cm.$^{-1}$.

Anal. Calcd. for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.21; H, 8.17.

***t*-Butyl 4-phenylperbutyrate** was prepared and purified in the same way; yield and purity were comparable.

Anal. Calcd. for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 71.33; H, 8.67.

Procedure for Kinetic Runs.—A weighed sample of the perester in a 5.00-ml. volumetric flask was dissolved in chlorobenzene, and aliquots of this solution were sealed in ampoules. No effort was made to conduct the reactions under a nitrogen atmosphere, since oxygen did not affect the results. A sample of this solution was considered to represent zero time. The ampoules were immersed simultaneously in an oil-bath maintained at a constant temperature ±0.05°. Ampoules were removed periodically from the oil-bath, chilled in ice-water, opened, and the solutions stored at 5° until analyzed. Points were taken until about 70% of the original perester had decomposed. One ampoule was kept in the bath until decomposition was complete. This sample was considered to represent infinite time.

Determination of Relative Concentration of Peresters by Infrared.—The analytical method was essentially the one described by Bartlett and Hiatt. The carbonyl band of the perester, at 1784 cm.$^{-1}$, was used to follow their disappearance. 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, while both increasing and decreasing frequency. The error in this measurement is of the order of 1–2%.

Treatment of Data.—Rate constants were calculated from least squares slopes of plots of log P/P_0 *vs.* time, where P is perester concentration at any given time and P_0 is initial perester 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_∞ is percentage transmission at infinite time, T_p is percentage transmission at any given time and T_0 is percentage transmission at zero time. T_∞ was less than 100%, due to the presence of carbonyl-containing decomposition products (*e.g.*, acetone), having maxima at lower frequencies, but which were beginning to absorb slightly at 1784 cm.$^{-1}$; T_∞ fell in the range 80–95%, depending upon initial perester concentration.

The plots of log P/P_0 *vs.* time were straight lines up to 70% decomposition, and first-order rate constants were determined by calculation of the slope by the method of least squares. Points lying past 70% decomposition were not included in the calculations, not because of any apparent curvature of the plot, but because random error was somewhat higher due to the greater uncertainty of log T_∞ − log T_p for dilute solutions.

The enthalpy of activation, ΔH^*, was obtained from the least squares slope of the line given by log k/T *vs.* $1/T$

at 109.38°, 115.98° and 122.44°. The entropy of activation, ΔS^*, was calculated from the expression

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

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

Results

Rate Constants.—The kinetic data for the decomposition of *t*-butyl 3-phenylperpropionate and *t*-butyl 4-phenylperbutyrate are summarized in Tables I and II, respectively. In all cases the plot of log P/P_0 *vs.* time is linear past 70% decomposition. Decompositions in chlorobenzene were carried out at three temperatures, 109.45°, 115.98° and 122.44°. At 109.45°, decompositions were carried out over a fourfold variation in initial concentration leading to rate constants which deviate from the mean by less than 2.5%. Evidence for first-order kinetics, uncomplicated by induced decompositions, thus seems convincing.

TABLE I

RATE OF DECOMPOSITION OF *t*-BUTYL 3-PHENYLPERPROPIONATE

Init. concn., *M*	T, °C. (±0.05°)	$k \times 10^5$, sec.$^{-1}$
0.0510	109.45	6.36
.1008	109.45	6.25
.1959	109.45	6.10
.1004	115.98	13.43
.1128	122.44	28.88

TABLE II

RATE OF DECOMPOSITION OF *t*-BUTYL 4-PHENYLPERBUTYRATE IN CHLOROBENZENE

Init. concn., *M*	T, °C. (±0.05°)	$k \times 10^5$, sec.$^{-1}$
0.0557	109.45	6.93
.1021	109.45	6.33
.2362	109.45	6.43
.1145	115.98	13.57
.1186	122.44	32.75

From the kinetic data of Tables I and II, it is possible to calculate the activation parameters for the two decompositions studied. These are summarized in Table III. For the perpropionate the ΔH^* is probably accurate to 0.5–1.0 kcal./mole, the ΔS^* to 1.5–3.0 e.u. For the perbutyrate, the values are slightly less precise, ΔH^* being accurate to 1.5–2.0 kcal./mole, ΔS^* to 4–6 e.u. The parameters for the two esters are then the same within experimental error.

TABLE III

ACTIVATION PARAMETERS FOR THE DECOMPOSITION OF *t*-BUTYL 3-PHENYLPERPROPIONATE AND 4-PHENYLPERBUTYRATE

Perester	ΔH^*, kcal./mole	ΔS^*, e.u.
$C_6H_5(CH_2)_2CO_3C(CH_3)_3$	35	13
$C_6H_5(CH_2)_3CO_3C(CH_3)_3$	36	16

Discussion

When the activation parameters for the decompositions of *t*-butyl 3-phenylperpropionate and *t*-butyl 4-phenylperbutyrate, summarized in Table III, are included in Bartlett's and Hiatt's enthalpy–entropy diagram, both points fall in the same region as the one for the decomposition of *t*-butyl peracetate. Consequently, all three decompositions must proceed by mechanistically similar paths. Since *t*-butyl peracetate has been shown to decompose in a stepwise, non-concerted fashion, through a transition state in which only bond a of III (R = CH_3) is stretched and in which no bond rotations are restricted, the same must be true of the two peresters studied here. Thus, *t*-butyl 3-phenylperpropionate and 4-phenylperbutyrate decompose by a two-step, non-concerted process (path A, reaction 1), and the transition states do not partake of any of the characteristics of structure IV. Since these two peresters do not undergo concerted decompositions, it must be concluded that a phenyl group is not effective in stabilizing a 2-phenylethyl or 3-phenylpropyl free radical by bridging to form "non-classical" radicals.

This same conclusion is indicated by the equality, within experimental error, of the activation parameters for the two peresters studied. Heck and Winstein[10] demonstrated that cation stabilization by phenyl participation was dependent upon the number of carbon atoms separating the cationic center from the phenyl group. When separated by two carbon atoms, as in the 2-phenylethyl cation, phenyl participation is very extensive, but when separated by three carbon atoms, as in the 3-phenylpropyl cation, it is negligible. This is apparently due to the geometric requirements of the ring of the bridged structure. Similar requirements should obtain in a bridged radical structure, if such is formed at all. Thus, it would be predicted that if bridging by phenyl were a significant feature in radical stabilization, the 3-phenylperpropionate should decompose in a more concerted fashion than the 4-phenylperbutyrate, since the former produces a 2-phenylethyl radical, the latter a 3-phenylpropyl radical. Since their activation parameters are very similar, their decompositions must proceed through similar paths, and since bridging should not be favored in the radical derived from the 4-phenylperbutyrate, and it should decompose by a non-concerted path, then both must decompose by a non-concerted path.

From this, then, it may be concluded that phenyl participation is not a significant driving force in the formation of simple 2-phenylethyl or 3-phenylpropyl free radicals.

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[10] R. Heck and S. Winstein, *J. Am. Chem. Soc.*, **79**, 3105 (1957).