Another sample of the same composition as that above was allowed to stand at room temperature for 1 month. The reaction mixture was added to saturated sodium chloride solution, filtered, added to aqueous sodium hydroxide to make the solution slightly alkaline, and extracted with benzene. From this benzene extract, the most of the solvent was evaporated on a steam-bath. The remaining liquid was analyzed by vapor phase chromatography. Propylene glycol diacetate was the only product detected. The aqueous solution after benzene extraction was neutralized by nitric acid. Analysis by periodic acid indicated that 6.4 millimoles of glycol was contained in the solution.

Rate Measurements of the Decompositions of II and III.—Required reaction mixtures were obtained by mixing 80% acetic acid solutions of II or III and perchloric acid in a constant temperature bath. Aliquots (10 or 20 ml.) were withdrawn and added into slightly excess sodium hydroxide solutions to precipitate the mercurous salt formed as mercurous oxide. The oxides were filtered, washed with cold water (with cold ethanol in the case of styrene), acidified with hydrochloric acid and analyzed by iodometry.

Rate Measurements of the Reaction of I, II and III with Aromatics.—The previously described method[2] was applied without modifications.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF GEORGIA, ATHENS, GA.]

Organic Peroxides. I. The Intramolecular Reaction between the Olefinic Double Bond and the Peroxide Linkage in the Decomposition of *trans*-γ-Benzylidenebutyryl Peroxide[1]

BY ROBERT C. LAMB,[2] FULTON F. ROGERS, JR., GEORGE D. DEAN, JR., AND FRED W. VOIGHT, JR.

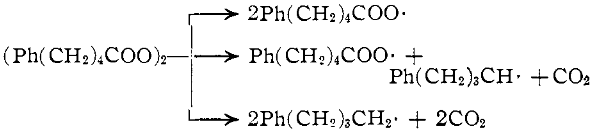
RECEIVED SEPTEMBER 20, 1961

The unsaturated diacyl peroxide *trans*-γ-benzylidenebutyryl peroxide (I) decomposes more rapidly than its saturated relative δ-phenylvaleryl peroxide (II). In most solvents, the decomposition of I is accurately first order through at least three half-lives. The rate is markedly higher in solvents of high dielectric constant. However, I causes the polymerization of styrene, and it decolorizes 1,1-diphenyl-2-picrylhydrazyl. The results are interpreted as an intramolecular reaction between the olefinic double bond and the peroxide linkage, *via* a rather polar transition state, forming radicals. A new modification of the method of determining the kinetics of initiator decomposition with a colored free radical has been developed which allows the simultaneous determination of the first-order rate constant and the efficiency of radical formation for the initiator.

Introduction

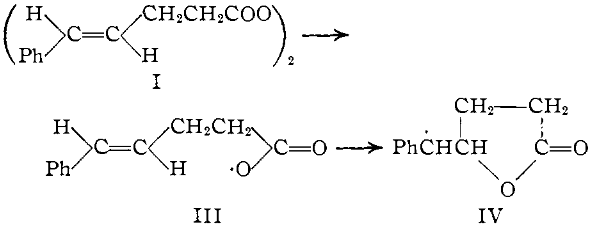
While syntheses of many unsaturated aliphatic diacyl peroxides have been described in several publications[3] and patents,[4] very little work has been reported on their decomposition, although Cooper measured the rates of initiation of styrene polymerization by several unsaturated peroxides.[3d]

This problem was originally undertaken in an attempt to obtain information about the mode of initial cleavage of aliphatic diacyl peroxides. DeTar and Lamb have shown that in the decomposition of δ-phenylvaleryl peroxide in toluene, a small reduction of the carbon dioxide yield is effected by the addition of iodine and water, although the latter reagents have no effect on the rate of decomposition.[5a,b] This was interpreted to mean that some δ-phenylvaleryloxy radicals are formed in the decomposition of II in toluene, and are "trapped" by the inhibitor system.[6] However, since the reduction in the carbon dioxide yield was small, it was postulated that much of the peroxide undergoes multiple initial cleavage to form alkyl radicals directly



$$(Ph(CH_2)_4COO)_2 \rightarrow \begin{cases} 2Ph(CH_2)_4COO\cdot \\ Ph(CH_2)_4COO\cdot + Ph(CH_2)_3CH\cdot + CO_2 \\ 2Ph(CH_2)_3CH_2\cdot + 2CO_2 \end{cases}$$

The γ-benzylidenebutyryloxy radicals (III) from the thermal decomposition of I might be trapped by an intramolecular cyclization reaction



I

III

IV

The present paper reports on the kinetics of the reaction. The product study is incomplete, although strong absorptions at 5.7μ in the infrared spectra of products indicates the presence of γ-lactones in the reaction mixtures.

During the course of this work, Martin and Drew reported that acetyl peroxide undergoes a direct attack by cyclohexene, forming free radicals.[7]

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[1] This work was supported for the most part by the Research Corporation, and also by the National Science Foundation. That portion of the work which involves the use of stable free radicals was supported by the Petroleum Research Fund of the American Chemical Society. Part of this work was presented at the Southeastern Regional Meeting of the American Chemical Society, Birmingham, Ala., Nov. 3, 1960. This paper is taken for the most part from the theses of Fulton F. Rogers, Jr., and of George C. Dean, Jr., presented in partial fulfillment of Master of Science degrees, August, 1960, and August, 1961, respectively.

[2] To whom correspondence should be addressed.

[3] (a) H. Erlenmeyer and W. Schoenaur, *Helv. Chim. Acta*, **20**, 1008 (1937); (b) A. Wacek and R. Fiedler, *Monatsh.*, **80**, 170 (1949); (c) L. F. Fieser, *et al.*, *J. Am. Chem. Soc.*, **64**, 2060 (1942); **70**, 3195 (1948); (d) W. Cooper, *J. Chem. Soc.*, 3106 (1951); 2408 (1952).

[4] (a) U. S. Patent 2,593,399, April 22, 1952 (Monsanto Chem. Co.); (b) U. S. Patent 2,793,201, May 21, 1957 (Hooker Electrochem. Co.).

[5] (a) D. F. DeTar and R. C. Lamb, *J. Am. Chem. Soc.*, **81**, 122 (1959); (b) D. F. DeTar and C. Weis, *ibid.*, **79**, 3041 (1957); **78**, 4296 (1956).

[6] G. S. Hammond and L. M. Soffer, *ibid.*, **72**, 4711 (1950).

[7] J. C. Martin and E. H. Drew, *ibid.*, **83**, 1232 (1961). We are indebted to Prof. Martin for furnishing us with some of the results

TABLE I

KINETICS OF DECOMPOSITION OF γ-BENZYLIDENEBUTYRYL PEROXIDE[a]

Solvent[b]	T,[c] °C.	$(P)_0$[d]	No. samples	$t_{1/2}$, min.	10^5k, sec.$^{-1}$	E_a, A[e]	(Ml.)$_0$ and s.d.
Carbon tetrachloride[g]	70	0.0258	10	77			
	60	.0348	9	230			
Carbon tetrachloride-0.06 M products	70	.0274	9	110	10.6		8.61, ±0.12
Carbon tetrachloride-10% styrene	70	.0274	9	110	10.6	26.9	21.40, 0.03
	60	.0257	9	330	3.47	1.42×10^{13}	13.75, .01
Toluene	70	.0337	9	60	16.4		25.25, .13
Acetophenone	65	.0166	3	28	41.3	23.8	14.54, .20
	55	.0280	7	80	14.5	1.07×10^{12}	19.33, .07
	50	.0246	9	146	7.92		17.24, .19
Acetophenone-2% styrene	65	.0316	4	29	40.2	23.6	21.02, .23
	55	.0316	5	84	13.8	7.14×10^{11}	21.02, .09
Nitrobenzene	60	.0325	6	34	33.8		22.52, .09
Propylene carbonate	50	.0249	10	54	21.3	21.4	21.58, .16
	40	.0262	11	157	7.36	5.93×10^{10}	24.76, .14
Propylene carbonate-10% styrene	50	.0244	8	56	20.8		21.93, .09
Propylene carbonate-10% toluene	50	.0242	4	57	20.4		25.40, .13
Chloroform[g]	65	.0270	4	<20			
	40	.0256	9	138			

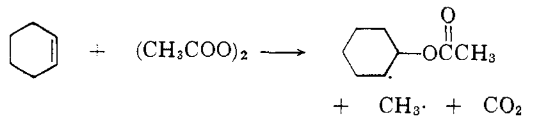
[a] Kinetics followed through 3 half-lives in all runs except that in propylene carbonate-10% toluene, which was followed through 2 half-lives. [b] Mixed solvents expressed in % by volume of minor component. [c] Bath temperature measured with NBS standardized 0.1° thermometer, the bath temperature was controlled to ±0.04°. [d] Initial concentration of peroxide, based on iodometric assay, and assuming the solution density was the same as the density of the solvent or solvent mixture at 20°. [e] Calculated from Arrhenius equation; E_a in kcal./mole and A in sec.$^{-1}$. [f] Standard deviation expressed in ml. of approximately 0.01 N sodium thiosulfate solution; the data were adjusted to the expression log (ml. thiosulfate solution required)/(wt. stock solution in sample vial) = $(k/2.303)t$ + const., and all error was placed in the numerator of log term; (ml.)$_0$ refers to the ml. of 0.01 N sodium thiosulfate required for the initial sample (all samples within a run were generally of nearly the same weight). [g] Kinetics in carbon tetrachloride and chloroform are between first and second order; the first half-life of each run is reported.

TABLE II

KINETICS OF DECOMPOSITION OF δ-PHENYLVALERYL PEROXIDE[a]

Solvent[b]	T,[c] °C.	$(P)_0$[d]	No. samples	$t_{1/2}$, min.	10^5k, sec.$^{-1}$	E_a, A[e]	(Ml.)$_0$ and s.d.[f]
Carbon tetrachloride[g]	77	0.0102	6	154	7.48		
Carbon tetrachloride-10% styrene	70	.0257	8	418	2.76	31.1	26.54, 0.21
	77	.0259	11	161	7.19	1.76×10^{15}	13.03, .08
	85	.0279	11	62	18.7		28.71, .23
Acetophenone	77	.0291	8	49	23.7		21.65, .26
Propylene carbonate	60	.0281	9	262	4.41		22.90, .14
Propylene carbonate-10% styrene[a]	60	.0281	5	412	2.80		23.52, .11
Propylene carbonate-10% cyclohexene[a]	60	.0285	7	364	3.18		23.60, .14

[a] Last two runs followed through 43% and 78% reaction, respectively. All others followed through more than three half-lives. [b,c,d,e,f] See Table I. [g] Taken from ref. 5a in text.



Thus acetyl peroxide, labeled with oxygen-18 in the carbonyl group, when heated in cyclohexene containing 0.3 M hydroquinone, gave cyclohexyl acetate which contained 65% of the O^{18} in the carbonyl group. This result requires that a significant portion of the cyclohexyl acetate be formed *via* a path which does not involve acetoxy radicals, and hence the direct attack mechanism is implicated.

Results and Discussion

The kinetics data for the decomposition of γ-benzylidenebutyryl peroxide are given in Table I; those for the decomposition of δ-phenylvaleryl peroxide are given in Table II. A list of relative rates is presented in Table III.

There are three main differences in the kinetics of the decomposition of γ-benzylidenebutyryl peroxide (I) and of its saturated relative δ-phenylvaleryl peroxide (II): (a) I decomposes more rapidly than II in all solvents for which comparisons are available; (b) in solvents in which the decompositions of both peroxides are first order, the rate constants for I increase more rapidly with the dielectric constant of the medium than do the rate constants of II; and (c) I undergoes much more induced decomposition than II in carbon tetrachloride, while the reverse is true in propylene carbonate.

The activation energy for the decomposition of the unsaturated peroxide in carbon tetrachloride–10% styrene is lower by 4 kcal./mole than that for the saturated peroxide in the same solvent. The activation energy for the decomposition of the un-

reported in this reference by personal communication prior to its publication. A more recent report on olefin–diaroyl peroxide reactions in which radicals are formed is that of F. D. Greene, W. Adam and J. E. Cantrill, *ibid.*, **83**, 3461 (1961).

TABLE III

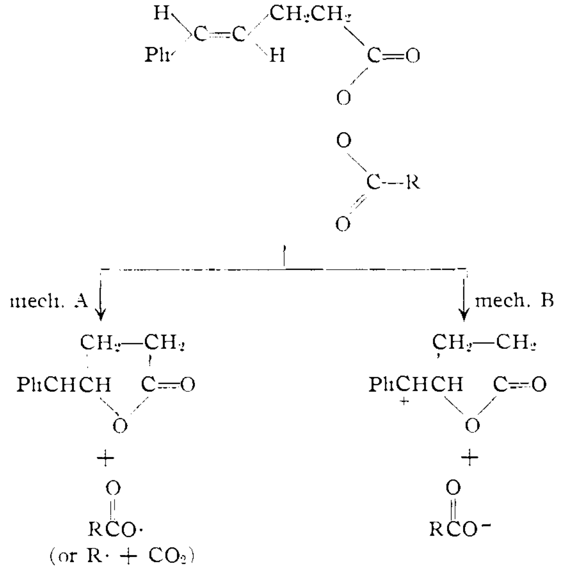
RELATIVE RATES OF DECOMPOSITION OF γ-BENZYLIDENEBUTYRYL PEROXIDE (I) AND δ-PHENYLVALERYL PEROXIDE (II) AT 60°

Solvent	$k_{\text{I}}/k_{\text{II}_0}$[a]	$k_{\text{II}}/k_{\text{II}_0}$[a]
Carbon tetrachloride–10% styrene	4.9[b]	1[a]
Acetophenone	34.3[c]	(3.3)[d]
Acetophenone–2% styrene	33.2[e]	
Nitrobenzene	47.2[b]	
Propylene carbonate–10% toluene	77.6[f]	
Propylene carbonate–10% styrene	79.1[f]	3.9[b]
Propylene carbonate–10% cyclohexene		4.4[b]
Propylene carbonate	81.0[g]	6.2[b]

[a] k_{I} and k_{II} are the first-order rate constants for the decomposition of peroxides I and II, respectively. k_{II_0} is the rate constant for decomposition of II at 60°, 7.15×10^{-6} sec.$^{-1}$, obtained by extrapolation of data at 70, 77, and 85° [b] Rate measured at 60°. [c] Obtained by interpolation of data determined at 50, 55 and 65°. [d] k_{II} and k_{II_0} both determined at 77°. [e] Obtained by interpolation of data determined at 65° and 55°. [f] Obtained from 50° run, assuming E_a = 21.4 kcal./mole, as in pure propylene carbonate. [g] Extrapolated from 40 and 50°.

saturated peroxide is lowered still further in going from non-polar to polar solvents, the frequency factors simultaneously decreasing. (The values of $\Delta S^{\ddagger}$ in carbon tetrachloride–10% styrene, in acetophenone and in propylene ccarbonate are −0.3, −5.7 and −11.3 e.u., respectively).

There is thus a significant difference in the modes of initial cleavage of the two peroxides. γ-Benzylidenebutyryl peroxide does not undergo single and multiple cleavages to give acyloxy and alkyl radicals as does δ-phenylvaleryl peroxide. A neighboring group effect of the double bond in the decomposition of γ-benzylidenebutyryl peroxide seems more likely, and scale models indicate that the γ-carbon atom can be placed in close juxtaposition to the ether oxygen of the peroxide linkage for such reaction to occur. The molecule may undergo either homolysis (mechanism A), or heterolysis (mechanism B), or both



To evaluate the relative importance of these two mechanisms the peroxide was decomposed in the presence of the stable free radical 1,1-diphenyl-2-picrylhydrazyl (DPPH). A new modification has been developed which permits evaluation of both the rate of peroxide decomposition and the efficiency of "free" radical production.[8]

Equations 1 and 2 may be expected to apply when a free radical initiator is decomposed in the presence of a completely dissociated, stable free radical

$$\text{In} \longrightarrow (2\text{R}\cdot)_c \begin{cases} \xrightarrow{k_1} 2\text{R}\cdot \\ \xrightarrow{k_1'} \text{cage products} \end{cases} \qquad (1)$$

$$\text{R}\cdot + \text{Z}\cdot \xrightarrow{k_2} \text{stable product} \qquad (2)$$

where In = initiator, R· = reactive free radical, $(2\text{R}\cdot)_c$ = two reactive radicals in solvent cage, Z· = stable free radical.

Assuming a steady state in $(2\text{R}\cdot)_c$ and R·, it can be shown that:

$$-\text{d}(\text{Z}\cdot)/\text{d}t = 2k_d f(\text{In}) \qquad (3)$$

where $f = k_1/(k_1' + k_1)$, the free radical efficiency of the peroxide.[9] The new modification of this kinetics method is to use the stable free radical in excess. The amount remaining provides a new boundary value which allows the simultaneous determination of k_d, the first-order rate constant for the decomposition of the initiator, and f, the free radical efficiency of the latter

$$k_d = (-1/t)\ln[(\text{Z}\cdot) - (\text{Z}\cdot)_\infty]/[(\text{Z}\cdot)_0 - (\text{Z}\cdot)_\infty] = (-1/t)\ln(D - D_\infty)/(D_0 - D_\infty) \qquad (4)$$

$$f = [(\text{Z})_0 - (\text{Z}\cdot)_\infty]/2(\text{In})_0 \qquad (5)$$

where D = the absorbance of Z· at λ_{max}; the subscripts have their usual significance.

Equation 3 requires that the reaction be zero order in stable free radical, *i.e.*, that the rate of fading of the stable free radical be governed only by the rate of decomposition of the initiator. Previous work has shown that solutions of DPPH are unstable, and it was necessary to work out techniques for eliminating spontaneous fading before the method could be applied. It was found that if solutions of DPPH in carbon tetrachloride are degassed, and intermittently flushed with helium during the degassing process, and if the solutions are also protected from laboratory light, then they resist spontaneous fading for 20 hr. or more at 70°. Solutions exposed to light, or strangely, flushed with commercial high purity nitrogen rather than helium, underwent rapid fading. Two runs, reported in Table IV, show excellent agreement with theory. The f-values obtained for γ-benzylidenebutyryl peroxide were 0.42 and 0.45.[10] The average value for the first-order rate constant for

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[8] Recent papers on this general method give the pertinent literature: C. E. H. Bawn and D. Verdin, *Trans. Faraday Soc.*, **56**, 815 (1960); D. Verdin, *ibid.*, **56**, 823 (1960). Some definitive recent work on cage reactions has heen reported by L. Herk, M. Field and M. Szwarc, *J. Am. Chem. Soc.*, **83**, 2998 (1961).

[9] G. S. Hammond, J. N. Sen and C. E. Boozer, *ibid.*, **77**, 3244 (1955). The same equation is also given by Bawn and Verdin, ref. 8.

[10] It can be shown that if any products formed in reaction 1 and 2 absorb at λ_{max} for the stable radical, there will be no effect on the value of k_d obtained. However, since in this instance the values of f were calculated using the expression $f = (D_0 - D_\infty)/2\epsilon(\text{In})_0$, where D is the absorbance of DPPH at 518 mμ and ε is the extinction coefficient thereof at the same wave length, absorption of products at this wave length would yield values of f which are low. Hence the values of f reported here should be regarded as minimum.

TABLE IV

DECOMPOSITION OF γ-BENZYLIDENEBUTYRYL PEROXIDE IN THE PRESENCE OF DIPHENYLPICRYLHYDRAZYL AT 70° IN CARBON TETRACHLORIDE

Time, min.	Absorbance at 518mμ		
	Control[a]	Sample I[a,b,c]	Sample II[a,b,d]
0	1.42	1.37	1.39
60	1.42	1.12	1.13
120	1.41	0.96	0.96
180	1.41	.85	.83
240	1.42	.76	.74
300	1.38	.70	.68
420	1.40	.65	.62
500	1.36	.61	.58
1200	1.38	.55	.51
1260	1.39	.55	.51

[a] $(\mathrm{DPPH})_0 = 1.06 \times 10^{-4}$ M. [b] $(\mathrm{Peroxide})_0 = 7.43 \times 10^{-5}$ M, corrected for 98.7% purity, based on iodometric assay. [c] Data from sample I (through 300 min.) fit expression $\log (D - D_\infty) = -(k_d/2.303)t + C$, with $10^5 k_d$ (sec.$^{-1}$) = 9.37 and $C = 1.909$ with a standard deviation in $D = \pm 0.008$ absorbance unit; the f-value is 0.42. [d] Data from sample II fit expression in (c) with $10^5 k_d = 9.16$ and $C = 1.939$ with s.d. in $D = \pm 0.006$ abs. unit. The f-value is 0.45. The data from both runs at 420 and 500 minutes deviate from the respective lines by 0.02 and 0.01 abs. unit, respectively, but because these small errors constitute large percentage errors in $D - D_\infty$, they are not included in the statistical analyses.

the decomposition in carbon tetrachloride at 70° obtained by this method is about 12% lower than the value obtained in carbon tetrachloride–10% styrene. Part of this difference is probably due to the difference in solvent; perhaps part is also due to the fact that the styrene does not get rid of all the induced decomposition, which is very pronounced in pure carbon tetrachloride. There should, of course, be no induced decomposition in the presence of DPPH, for not only is the stable free radical a most effective inhibitor but, also, the peroxide is present in very low concentration (7.43×10^{-5} M).

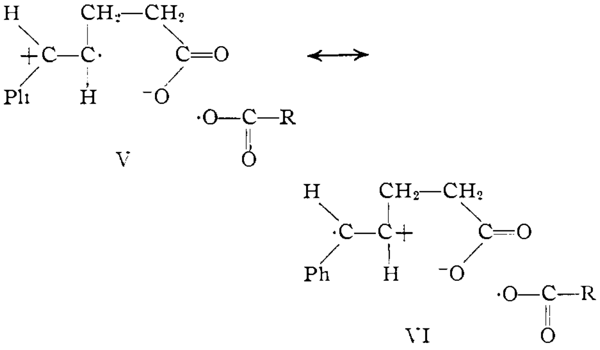
By a very thorough series of product studies, DeTar and Weis have shown that, in the decomposition of δ-phenylvaleryl peroxide in carbon tetrachloride, the only product containing the δ-phenylbutyl group which is derived from radicals which escape cage reactions is δ-phenylbutyl chloride.[5b] The yield of δ-phenylbutyl chloride is essentially independent of temperature, and is about 0.8 mole per mole of peroxide decomposed. Since the theoretical yield is 2 moles/mole peroxide, it follows that the free radical efficiency of δ-phenylvaleryl peroxide in carbon tetrachloride, as measured by the yield of δ-phenylbutyl chloride is 0.8/2, or 0.4.

The fact, in conjunction with the experiment reported here on the decomposition of the unsaturated peroxide in the presence of DPPH, leads to an important conclusion: While the rates of decomposition of the two peroxides differ significantly, since the f factors are essentially the same, *the initial cleavage of γ-benzylidenebutyryl peroxide is no less a homolysis than is the initial cleavage of δ-phenylvaleryl peroxide in carbon tetrachloride.* Since the considerable information which has been compiled on the decomposition of the saturated peroxide in carbon tetrachloride indicates that the decomposition is all homolytic, the same conclusion can be applied to the initial cleavage of the unsaturated peroxide I in the same solvent. Mechanism B is therefore unimportant in the decomposition of γ-benzylidenebutyryl peroxide in carbon tetrachloride.

Attempts to perform an experiment of this type in more polar solvents have encountered the complication that the stable radicals react with solvent. Galvinoxyl[11] fades rapidly in propylene carbonate; DPPH fades rapidly in nitrobenzene and acetophenone, but somewhat more slowly in propylene carbonate.

Since the spontaneous fading of DPPH was found to be slow in propylene carbonate, an experiment was performed to determine the rate of radical production from γ-benzylidenebutyryl peroxide in that solvent at 60°. To do this, the extent of fading in a solution of the peroxide plus DPPH was compared to that in a control sample at low conversion.[12] It was found that the rate of formation of radicals is roughly six times as great in propylene carbonate as in carbon tetrachloride at 50°. While this result does show that the rate of radical production from γ-benzylidenebutyryl peroxide is considerably higher in the more polar solvent than in carbon tetrachloride, the ratio of rates of radical production is less than half the ratio of the total rates of decomposition of the unsaturated peroxide in propylene carbonate and carbon tetrachloride. Thus the efficiency of radical production, f, is lower in propylene carbonate than in carbon tetrachloride, either because of a contribution of a polar decomposition (mechanism B) to the total reaction, or because of more cage recombination of radicals in propylene carbonate. Since propylene carbonate is considerably more viscous than carbon tetrachloride, we believe that the latter explanation is more likely, although our data will not refute mechanism B entirely.

It is clear, however, that the transition state for the homolysis is more polar than the ground state, and we propose the contribution of such structures as V and VI to the transition state.[13]



V

VI

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(11) (a) G. M. Coppinger, *J. Am. Chem. Soc.*, **79**, 501 (1957); (b) M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, **22**, 1435 (1957).

(12) An experiment performed in this fashion does not yield k_d and f separately, but only the rate of formation of radicals, $2k_d f(\Delta P)$.

(13) Another example of a homolysis which proceeds *via* a polar transition state has been reported recently. Honsberg and Leffler have found that the rate of decomposition of o-iodo-p'-nitrobenzoyl peroxide (which involves a neighboring group participation of the iodine atom) is very dependent upon the polarity of the medium; W. Honsberg and J. E. Leffler, *J. Org. Chem.*, **26**, 733 (1961).

One would suspect that if polar solvents accelerate the intramolecular reaction between the olefinic double bond and the peroxide linkage in the decomposition of γ-benzylidenebutyryl peroxide, it may follow that a direct *intermolecular* reaction between an olefin and a saturated diacyl peroxide would be kinetically discernible in a solvent of high polarity. However, the last three entries in the right column of Table III do not support this prediction. Thus, the rates of decomposition of δ-phenylvaleryl peroxide in propylene carbonate–10% styrene and propylene carbonate–10% cyclohexene are considerably slower than is the rate in propylene carbonate alone. Therefore the added olefins do not undergo a direct reaction with the saturated peroxide, and apparently serve only to inhibit a radical induced decomposition of the peroxide which takes place in propylene carbonate (despite the fact that the decomposition of II in the latter solvent is first order).

On the other hand, the unsaturated peroxide I does not appear to undergo radical induced decomposition in propylene carbonate, since the rates of its decomposition are about the same in propylene carbonate, propylene carbonate–10% styrene and propylene carbonate–10% toluene. (The two mixed solvents have roughly the same dielectric constant.) In carbon tetrachloride and chloroform, however, the γ-benzylidenebutyryl peroxide undergoes a great deal of radical induced decomposition, as evidenced by the fact that the kinetics are higher than first order in both solvents. The kinetics in pure carbon tetrachloride are complicated not only by considerable induced decomposition, but also by the fact that the induced decomposition is inhibited by products. Thus a run in the presence of 0.06 M products is first order, and the rate is essentially the same as the rate of decomposition of the unsaturated peroxide in carbon tetrachloride–10% styrene. Infrared spectra of the products of the decomposition of γ-benzylidenebutyryl peroxide in carbon tetrachloride indicate that some of the products contain the *trans* double bond originally present in the peroxide, and are therefore styrene derivatives. It is not surprising that such products effect inhibition of the radical chain decomposition of the peroxide.

The kinetics experiments reported here have provided a general outline of the rather complex chemistry of the thermal decomposition of γ-benzylidenebutyryl peroxide. Definitive product studies are obviously needed to fill in the details of the mechanisms of its decomposition. Such studies are in progress in this Laboratory.

Acknowledgments.—The authors are indebted to the Research Corporation for a Frederick Gardner Cottrell Grant for F.F.R., and also to the National Science Foundation and the Petroleum Research Fund of the American Chemical Society for additional support. In addition, acknowledgment is made to the Statistics Institute of the University of Georgia for help in the statistical adjustment of data.

Experimental[14]

Cinnamyl Chloride.—The method of Gilman and Harris was used to convert cinnamyl alcohol, m.p. 31–33°, to cinnamyl chloride.[15]

γ-Benzylidenebutyric acid was prepared from cinnamyl chloride *via* the malonic ester synthesis, using the method for preparation of pelargonic acid as a guide, as reported by Reid and Ruhoff.[16]

After decarboxylation of the dicarboxylic acid, the resulting impure γ-benzylidenebutyric acid was distilled directly from one flask into an ice-cooled flask using aspirator vacuum (about 25 mm.). Under these conditions the acid came over in the range 235–250°. The γ-benzylidenebutyric acid, which in some cases was too impure to be recrystallized before this distillation, always solidified in the ice-cooled flask used as a receiver in fairly pure form, and left a substantial quantity (10–15%) of a higher boiling acidic material as residue.

The white crystalline γ-benzylidenebutyric acid obtained from this distillation was recrystallized from a benzene–petroleum ether mixture. The over-all yields of the acid from cinnamyl chloride in the several runs were between 50–60%. The neutralization equivalent on two batches was determined to be 174.7, 176.3; and 175.3, 176.3 (calcd. 176.2). The melting points of various samples were 89.2°–91° (reported[17] 90°). The presence of a strong peak at 10.35μ, and the absence of absorptions which can be ascribed to the *cis* isomer in the infrared spectrum of γ-benzylidenebutyric acid indicates that this acid is the pure *trans* isomer. *Anal.* Calcd. for $C_{11}H_{12}O_2$: C, 75.0; H, 6.9. Found: C, 74.9; H, 6.7.

γ-Benzylidenebutyryl chloride was prepared by treating the acid with excess phosphorus pentachloride. Difficulty was encountered, however, in purification by distillation, since even *in vacuo* considerable resin formation occurred. It was found that a better over-all yield of the γ-benzylidenebutyryl peroxide could be obtained from γ-benzylidenebutyric acid if the intermediate acid chloride was not distilled.

γ-Benzylidenebutyryl peroxide was prepared by the standard method of adding the ether solution of the acid chloride to an ice–water mixture containing sodium peroxide. The peroxide was recrystallized first from a chloroform–methanol mixture, to which a few drops of distilled water was added to promote crystallization, then from benzene–petroleum ether, and dried in a vacuum desiccator. The peroxide samples were stored below 0° in a refrigerator.

The γ-benzylidenebutyryl peroxide, previously unreported, melts sharply at 60°. Its infrared spectrum exhibits a doublet at 5.53 and 5.63μ, which is characteristic of diacyl peroxides, as well as a strong absorption at 10.39μ, indicating a *trans*-RCH=CHR$'$ group. An absorption at 6.30μ indicates that the double bond is conjugated to the ring.[18] γ-Benzylidenebutyric acid can be obtained in near quantitative yield (as sodium salt), by reduction with sodium iodide.

Although the peroxide melts sharply, it was most difficult to raise the purity above 98%, based on iodometric assay. The kinetics experiments reported here on peroxide I were therefore performed on samples which were between 94 and 98% pure; two exceptions to this were the runs in propylene carbonate–10% styrene and propylene carbonate–10% cyclohexene, which were run with peroxide samples which were 88% pure.

The δ-phenylvaleric acid, its acid chloride and δ-phenylvaleryl peroxide were prepared by methods which have been described.[5b] All kinetics experiments reported here were done on δ-phenylvaleryl peroxide samples which assayed above 99% pure.

Solvents.—The solvents used were reagent grade commercially available solvents which were redistilled in a 2-ft. column packed with glass helices. The propylene carbonate was of technical grade, which was dried over anhydrous sodium sulfate and distilled through a 4-ft. vacuum jacketed column, packed with helices, b.p. 70–72° at 1 mm.

Kinetics Runs.—Stock solutions were prepared by dissolving a weighed quantity of peroxide in the appropriate

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(14) Melting points are uncorrected. Microanalyses are by Geller Laboratories, Bardonia, N. Y. Infrared spectra obtained with Perkin–Elmer Infracord spectrophotomer; visible spectra of DPPH determined with a line-operated Beckman DU spectrophotometer.

(15) H. Gilman and S. A. Harris, *Rec. trav. chim.*, **50**, 1052 (1931).

(16) E. E. Reid and J. R. Ruhoff, "Organic Syntheses," **Coll. Vol. II** John Wiley and Sons, Inc., New York, N. Y., p. 474.

(17) E. Erlenmeyer, Jr., and A. Kreutz, *Ber.*, **38**, 3503 (1905).

(18) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, pp. 31, 36, 111.

solvent and diluting to a measured volume in a volumetric flask. The stock solutions were distributed by hypodermic syringe between sample vials which were equipped with 10/30 ₮ joints at the neck, and the quantity of sample was determined by weight. The samples were doubly degassed, that is, frozen in a Dry Ice–trichloro-ethylene slurry, degassed, melted, re-frozen, and degassed again. The vials were then sealed while under vacuum.

The runs were carried out in an oil-bath thermostated to the proper temperature ±0.04 degree. The bath temperatures were determined by an NBS standardized 0.1° thermometer.

Iodometric assay methods were used, using acetone as the assay solvent for all runs except for the runs in acetophenone.[19] We found it difficult to obtain reproducible results in the acetophenone runs using the acetone method, but the method using isopropyl alcohol as the solvent for iodometric assay gave good results.[20]

It was determined that double bonds of the type such as are to be expected in the products of the decompositions of γ-benzylidenebutyryl peroxide do not interfere with the iodometric assay. Thus in test experiments it was shown that addition of more than an equivalent of γ-benzylidenebutyric acid to solutions of iodine in isopropyl alcohol and acetone did not alter the observed titer of the iodine solution with standard sodium thiosulfate solution.

The kinetics run on the decomposition of γ-benzylidenebutyryl peroxide in carbon tetrachloride in the presence of products (Table I) was performed as follows: 100 ml. of a stock solution of 0.091 *M* peroxide in carbon tetrachloride was placed in a flask with a previously constricted neck. The flask was degassed and sealed under vacuum. The flask was then placed on the bath thermostated at 70°, where it remained until the concentration of peroxide was 0.026 *M*, whereupon the flask was broken, the contents distributed between 9 vials, and a kinetics run performed.

1,1-Diphenyl-2-picrylhydrazyl.—Commercial 1,1-diphenyl-2-picrylhydrazine (5.1 g., 0.013 mole), 5.1 g. of anhydrous sodium sulfate and 31.4 g. (0.13 mole) of lead peroxide were mixed together in 100 ml. of reagent grade benzene. After stirring the mixture for 2 hours at room temperature, the solids were removed from the dense violet colored solution by repeated suction filtration. The solution was evaporated to dryness in a stream of dry nitrogen, and the impure DPPH was recrystallized three times from benzene–petroleum ether mixtures. The lustrous needles which resulted (the 1:1 benzene complex) were then heated *in vacuo* at 80° for 20 hours.[21] The pure DPPH obtained (3.0 g., 0.008 mole) corresponds to a 59% yield, based on the hydrazine; m.p. 134° (reported[22] 137°). *Anal.* Calcd. for $C_{18}H_{12}N_5O_6$: C, 54.8; H, 3.1. Found: C, 54.8; H. 3.3.

Kinetics Run Reported in Table IV.—1,1-Diphenyl-2-picrylhydrazine (20.9 mg.) DPPH was weighed out and dissolved in 100 ml. of carbon tetrachloride solution, designated E-44 1; 10 ml. of E-44 1 was diluted to 50 ml., giving E-44 2, with (DPPH) = 1.06×10^{-4} *M*. The control vial contained E-44 2. E-44 3 was prepared by dissolving 26.4 mg. of γ-benzylidenebutyryl peroxide (98.7% pure by duplicate iodometric assays) in 100 ml. of carbon tetrachloride. E-44 4 (samples I and II) was prepared by mixing 10 ml. of E-44 1 and 5 ml. of E-44 3, and diluting with carbon tetrachloride to 50 ml.

The reagent grade carbon tetrachloride used in this experiment had been previously distilled twice on a 4-ft. glass helices-packed column from (1) phosphorus pentoxide and (2) sufficient DPPH to give the solution a deep purple color.

The sample vials used were constructed of 1 cm. (i.d.) square Pyrex tubing, which was sealed off at the bottom, and connected at the top, *via* a constricted neck, to a short length of regular Pyrex tubing which was terminated by a 10/30 male joint (for attachment to vacuum manifold).[22] square Pyrex tubing, which was wealed off at the bottom, The degassing procedure used was identical to that used in the iodometric runs, except that the vials were wrapped with aluminum foil prior to degassing, and the manifold was flooded with helium twice during the degassing process.

Four vials were used in the experiment: two samples containing E-44 4, one containing E-44 2 (control) and one containing carbon tetrachloride (blank for spectrophotometer as does a regular cuvette.

The run in which propylene carbonate was used as solvent was performed in an analogous way.

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(19) A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954, pp. 52–53.

(20) A. T. Blomquist and A. J. Buselli, *J. Am. Chem. Soc.*, **73**, 3883 (1951), obtained best results when the acetone method of assay was used for kinetics experiments in which benzoyl peroxide was decomposed in acetophenone. The reason for our difficulty is not clear.

(21) J. A. Lyons and W. F. Watson, *J. Polymer Sci.*, **18**, 141 (1955).

(22) The precision bore square tubing was obtained from the Fisher and Porter Co., Warminster, Pa.

[CONTRIBUTION FROM THE SHELL DEVELOPMENT CO., EMERYVILLE, CALIF.]

Catalytic Free Radical Rearrangement of Alkylbenzenes

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Catalytic free radical rearrangements (*via* 1,2-phenyl shifts) of several alkylbenzenes have been achieved in good yields by heating the latter in the presence of halogen- or sulfur-containing promoters. A free radical chain mechanism is proposed for these reactions depicting the important function of chain transfer agents produced from the promoters.

Introduction

Free radicals capable of undergoing rearrangement, *via* a 1,2-phenyl migration, such as the neophyl radical, have been obtained in high yields only by the decarbonylation of aldehydes[1] and other stoichiometric reactions.[2] Also, these radicals have been prepared in low yields by a free radical-initiated pyrolysis of alkylbenzenes[3] and more recently by the decomposition of peroxides in alkylbenzenes.[4] We have been able to produce these free radicals in high yields from alkylbenzenes by the use of an effective free radical chain transfer agent (TH) in the presence of a free radical initiator (In·)

$$\mathrm{In}\cdot + \mathrm{HT} \rightleftharpoons \mathrm{InH} + \mathrm{T}\cdot$$

$$\mathrm{RH} + \mathrm{T}\cdot \rightleftharpoons \mathrm{R}\cdot + \mathrm{TH}$$

The incipient phenylalkyl radicals rearrange *via* a 1,2-phenyl migration. Consequently, free radical-catalyzed isomerizations of alkylbenzenes have been obtained.[5]

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(1) S. Winstein and F. H. Seubold, *J. Am. Chem. Soc.*, **69**, 2916 (1947); D. Y. Curtin and M. J. Hurwitz, *ibid.*, **74**, 5381 (1952); F. H. Seubold, *ibid.*, **75**, 2532 (1953); L. H. Slaugh, *ibid.*, **81**, 2262 (1959).

(2) W. H. Urry and M. S. Kharasch, *ibid.*, **66**, 1438 (1944); W. H. Urry and N. Nicolaides, *ibid.*, **74**, 5163 (1952); C. G. Overberger and H. Gainer, *ibid.*, **80**, 4561 (1958).

(3) H. Pines and C. N. Pillai, *ibid.*, **81**, 3629 (1959), and references cited therein.

(4) H. Pines and C. N. Pillai, *ibid.*, **82**, 2921 (1960).

(5) For a preliminary report of the work see L. H. Slaugh and J. H. Raley, *ibid.*, **82**, 1259 (1960).