Treatment of Data.—Since this study was primarily a survey of reactions under a variety of conditions, rate constants were calculated from single experiments (*e.g.*, one point) for each pressure in each solvent, a procedure which appeared justified, since the first-order kinetics of Claisen and Cope rearrangements at atmospheric pressure are well established, and since the plots of rate *vs.* pressure (Figs. 1 and 2) give reasonably smooth curves. Original data for two sets of runs are listed in Tables V and VI. The values of $\Delta V^{\neq}$'s listed in Tables I and II were obtained from the slope of lines obtained by the method of least squares, and experimental errors given are standard deviations. No experimental errors are assigned to the Benson-Berson extrapolations, which involve plots of $(\log k/k_0)/P$ *vs.* $P^{0.523}$, since points often scattered badly and extrapolation seemed to involve a good deal of subjective judgment.

[Contribution from the Institute for Chemical Research, Kyoto University, Yoshida, Kyoto, Japan]

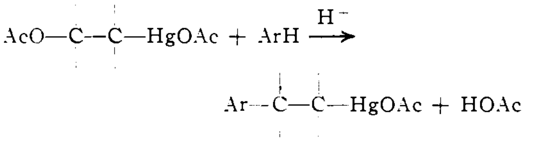
The Kinetics of the Reactions of β-Acetoxyethylmercuric, β-Acetoxypropylmercuric and β-Acetoxy-β-phenylethylmercuric Acetate with Aromatic Substances

By Katsuhiko Ichikawa, Koichi Fujita and Osamu Itoh

Received September 5, 1961

The reaction rates of β-acetoxyethylmercuric, β-acetoxypropylmercuric and β-acetoxy-β-phenylethylmercuric acetate with aromatic substances have been studied in acetic acid–perchloric acid–water systems. The results showed that the reactivity order of various aromatics is the same with those in the usual electrophilic aromatic substitutions. The relative rates of the three mercurials mentioned above with anisole were 1.0, 1.3 and 710, respectively, under the same conditions. From these results, the mechanism is discussed as an electrophilic aromatic substitution. As a preliminary experiment for the rate study above, the stabilities of the mercurials in acetic acid containing perchloric acid have been studied and the stoichiometry, rates and mechanism of the decompositions are reported.

In previous papers,[1] it has been shown that β-acetoxyalkylmercuric acetates (obtained by the addition of mercuric acetate to olefins in acetic acid) react with aromatics by eq. 1. The kinetics and



$$\mathrm{AcO{-}C{-}C{-}HgOAc} + \mathrm{ArH} \xrightarrow{\mathrm{H}^+} \mathrm{Ar{-}C{-}C{-}HgOAc} + \mathrm{HOAc} \quad (1)$$

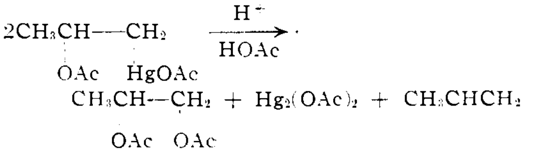
mechanism of this reaction between β-acetoxyethylmercuric acetate and anisole have been reported also.[2] It is desired, however, that the kinetic studies are extended to other mercurials and aromatics more extensively as a new type of aromatic substitution. In this paper, the results of the rate studies of the reactions of β-acetoxyethylmercuric (I), β-acetoxypropylmercuric (II) and β-acetoxy-β-phenylethylmercuric acetate (III) (prepared by the addition of mercuric acetate to ethylene, propylene and styrene in acetic acid) with various aromatic substances are reported.

Unfortunately, these mercurials are not always stable enough for the kinetic measurements of reaction 1 in the presence of perchloric acid which is one of the typical catalysts. As a preliminary study, therefore, the decompositions have been studied.

Stabilities of I, II and III in Acetic Acid Containing Perchloric Acid.—In 80% acetic acid containing perchloric acid up to 2 molar, I is stable indefinitely. At room temperature, no appreciable decomposition was observed even after 5 days. With II and III, however, a reaction to form mercurous salt was observed, while their acetic acid solutions containing no perchloric acid are much more stable.

Many examples of this type of reaction can be found in terpene chemistry, since the oxidation of terpene with mercuric acetate to form the corresponding diacetate and mercurous salt proceeds apparently through the formation of the addition compounds, *i.e.*, β-acetoxy mercuric compounds. The stoichiometry of this reaction, however, is not yet established, because these oxidations have been carried out in the presence of excess mercuric acetate usually. With the addition compounds of lower olefins, such as II, no detailed results have been reported.[3] Therefore, the product analysis and kinetics have been studied.

At room temperature, the solution (50 ml.) which contained 48.1 millimoles of II and 1.03 molar perchloric acid in 80% acetic acid gave 5.6 ml. (at N.T.P.) of gaseous product (5.1 millimoles as propylene). This gas was identified to be propylene by vapor phase chromatograph. The analysis of the liquid mixture showed that 5.1 millimoles of mercurous acetate was formed. Although the quantitative analysis of the liquid organic products was difficult, propylene glycol diacetate and its hydrolyzed product glycol were found to be formed which were expected from the results in terpene chemistry mentioned above (no acrolein was detected). These results show that the reaction of II in the presence of perchloric acid can be expressed by eq. 2. The results described above were obtained in the range of less than about 20% reaction. At higher reaction percentages, the situation is much more complicated. The mercurous acetate produced may disproportionate to give metallic mercury and mercuric acetate which reacts with propylene to give II again. The reaction equation in this case might be expressed by the equation



$$2\mathrm{CH_3}\underset{\mathrm{OAc}}{\mathrm{CH}}{-}\underset{\mathrm{HgOAc}}{\mathrm{CH_2}} \xrightarrow[\mathrm{HOAc}]{\mathrm{H}^+} \mathrm{CH_3}\underset{\mathrm{OAc}}{\mathrm{CH}}{-}\underset{\mathrm{OAc}}{\mathrm{CH_2}} + \mathrm{Hg_2(OAc)_2} + \mathrm{CH_3CHCH_2} \quad (2)$$

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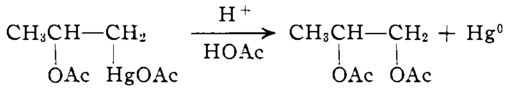
[1] K. Ichikawa, S. Fukushima, H. Ouchi and M. Tsuchida, *J. Am. Chem. Soc.*, **80**, 6005 (1958); **81**, 3401 (1959).

[2] K. Ichikawa, K. Fujita and H. Ouchi, *ibid.*, **81**, 5316 (1959).

[3] The formation of acrolein by the reaction of propylene with mercuric sulfate in aqueous sulfuric acid (du Pont, U. S. Patent 2,197,258) appears to belong to a different type of reaction.



$$\underset{\text{OAc}}{\text{CH}_3\text{CH}}-\underset{\text{HgOAc}}{\text{CH}_2}\xrightarrow[\text{HOAc}]{\text{H}^+}\underset{\text{OAc}}{\text{CH}_3\text{CH}}-\underset{\text{OAc}}{\text{CH}_2}+\text{Hg}^0$$

Actually, in the case of perchloric acid more than 2 *M*, the formation of metallic mercury was observed. Therefore, eq. 2 is correct only in the lower reaction percentages where the disproportionation of mercurous salt does not proceed.

Recently, it has been reported that the alkylmercuric ions solvolyze to give alkyl acetate and metallic mercury in acetic acid.[4] It appears, however, that this scheme is not applicable to reactions where the formation of mercurinium ions is possible as the reaction intermediates, which occurs in the cases of II and III.

The rates of reaction 2 were followed by determining the concentrations of mercurous salt formed. With both II and III, the best rate equation was $dx/dt = k_1(a - x)$, where a is the initial concentration of II or III and x is the amount of the product at time t. The plots of the values of log $a/a\text{-}x$ against time t gave straight lines passing through the origin up to about 20% reaction. The changes in the initial concentrations showed no effects on the first-order rate constants. In the ranges of higher reaction percentages, however, the points deviated from the lines. The results obtained are shown in Table I.

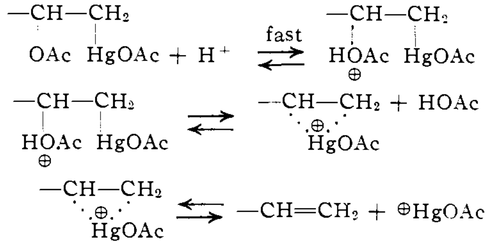
TABLE I

FIRST-ORDER RATE CONSTANTS OF THE DECOMPOSITIONS OF II AND III IN 80% ACETIC ACID CONTAINING PERCHLORIC ACID

Init. concn. of II or III, mole/l.		Perchloric acid concn., mole/l.	Temp., °C.	$k_1 \times 10^5$,[a] sec.$^{-1}$
II	0.1949	1.03	25.15	0.096
	.0968	1.03		.091
	.0968	1.65		.317[b]
	.1948	2.07		1.28
	.0968	2.40		2.78
	.1000	1.65	35.15	1.38[b]
III	0.1059	0.527	25.15	3.07
	.1880	0.527		2.7
	.0955	1.04		16.5[c]
	.0955	1.37		32.5
	.0955	1.65		48.3
	.0955	1.04	15.15	3.68[c]

[a] The plots of log k_1 against acidity function H_0 gave straight lines with the slopes of 0.85 and 1.1 for the cases of II and III, respectively. [b] $\Delta H^* = 26.1 \pm 0.2$ kcal./mole, $\Delta S^* = 3.6 \pm 0.7$ e.u. [c] $\Delta H^* = 22.6 \pm 0.3$ kcal./mole, $\Delta S^* = 0.6 \pm 1.0$ e.u.

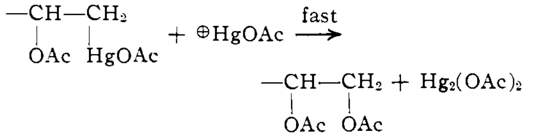
The most probable mechanism to explain these results is proposed as



$$-\underset{\text{OAc}}{\text{CH}}-\underset{\text{HgOAc}}{\text{CH}_2}+\text{H}^+\underset{}{\overset{\text{fast}}{\rightleftarrows}}-\underset{\underset{\oplus}{\text{HOAc}}}{\text{CH}}-\underset{\text{HgOAc}}{\text{CH}_2}\quad(3)$$

$$-\underset{\underset{\oplus}{\text{HOAc}}}{\text{CH}}-\underset{\text{HgOAc}}{\text{CH}_2}\rightleftarrows-\underset{\underset{\text{HgOAc}}{\cdot\cdot\oplus\cdot\cdot}}{\text{CH}-\text{CH}_2}+\text{HOAc}\quad(4)$$

$$-\underset{\underset{\text{HgOAc}}{\cdot\cdot\oplus\cdot\cdot}}{\text{CH}-\text{CH}_2}\rightleftarrows-\text{CH}=\text{CH}_2+{}^{\oplus}\text{HgOAc}\quad(5)$$



$$-\underset{\text{OAc}}{\text{CH}}-\underset{\text{HgOAc}}{\text{CH}_2}+{}^{\oplus}\text{HgOAc}\xrightarrow{\text{fast}}-\underset{\text{OAc}}{\text{CH}}-\underset{\text{OAc}}{\text{CH}_2}+\text{Hg}_2(\text{OAc})_2\quad(6)$$

Equation 3 and 4 have been established already in the case of the decomposition of I with hydrochloric acid.[5] From the results given here, it can not be determined whether step 4 or 5 is rate determining. The previously proposed mechanism for the demercuration of benzyl- and β-(*p*-methoxyphenyl)-ethylmercuric acetate with mercuric acetate in the presence of perchloric acid[6] appears to be applicable to reaction 6. To derive the first-order rate equation from this mechanism, it must be assumed that reaction 6 proceeds faster than reaction 5. This necessary assumption has been demonstrated to be correct by the following experiments. For example, in 80% acetic acid containing 1.03 *M* perchloric acid and at a initial concentration of 0.0968 molar II, it took about 65 hr. to reach 25% reaction at 25.15°, while the same reaction percentage was attained only after 2.5 hr. in the presence of 1.00 molar mercuric acetate which produces additional $\text{HgOAc}^{\oplus}$. Since reaction 5 is reversible, it is not surprising that the rate equation for the decomposition mentioned above could not be applied in the range of higher reaction percents. The values given in Table I, therefore, were calculated from the data obtained in the ranges within 20% reaction.

In connection with eq. 6, the second-order rate constants of the reaction between II and mercuric acetate have been determined and given in Table II.

TABLE II

SECOND-ORDER RATE CONSTANTS FOR THE REACTION OF II WITH MERCURIC ACETATES IN 80% ACETIC ACID CONTAINING PERCHLORIC ACID AT 25.15°

Perchloric acid, moles/l.	Initial concn., mole/l. II	Initial concn., mole/l. Hg(OAc)_2	$k_2 \times 10^4$, l./mole. sec.
1.03	0.0968	0.1000	0.76
	.0935	.0503	.78
	.0935	.0935	.77
1.36	.0935	.042	1.33
1.65	.0935	.0503	2.06
	.0935	.0935	2.03

The Rates of the Reactions of I, II and III with Aromatics.—The preliminary experiments mentioned above show that the rate studies of the reactions of II and III with aromatics are not always possible because of the decompositions of the former. With II and III, the experiments are limited to the cases of reactive aromatics such as anisole, while extensive studies are possible with I. Tables III and IV show the results of the rate studies.

The results given in Table III show clearly that the reactivity order of aromatic substances in the reactions with I is the same as those observed in the usual electrophilic aromatic substitutions. This supports also the previously proposed mechanism that the reacting species are the mercurinium

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(4) F. R. Jensen and R. J. Ouellette, *J. Am. Chem. Soc.*, **83**, 4477 (1961).

(5) K. Ichikawa, H. Ouchi and S. Araki, *ibid.*, **82**, 3880 (1960).

(6) K. Ichikawa and H. Ouchi, *ibid.*, **82**, 3876 (1960).

TABLE III

RATE DATA FOR THE REACTION OF I WITH VARIOUS AROMATICS IN 80% ACETIC ACID CONTAINING 2.0 *M* PERCHLORIC ACID

Aromatics	Temp., °C.	$k_2 \times 10^6$, l./mole. sec.	Rel. rate at 25.2°	ΔH^*, kcal./mole	ΔS^*, e.u.
Phenol	0.0	10.9		19.7 ± 0.2	−9.1 ± 0.7
	15.2	78			
	25.2	257	95		
Anisole	0.0	5.37		19.5 ± .2	−10.2 ± .7
	15.2	56.2			
	25.2	190	70		
Naphthalene	15.2	3.06		22.1 ± .3	−7.1 ± .9
	25.2	11.7	4.3		
	35.2	40.5			
Tetralin	25.2	24.2	9.0	23.5 ± .3	−0.9 ± .9
	35.2	90.5			
o-Xylene	25.2	13.0	4.8	23.2 ± .3	−3.2 ± 1.0
	35.2	48			
m-Xylene	25.2	89	33	21.0 ± .2	−6.5 ± 0.7
	35.2	293			
p-Xylene	25.2	12.8	4.7	24.9 ± .3	2.5 ± 1.0
	35.2	52.0			
Toluene	25.2	2.7	1.00	25.6 ± .3	1.9 ± 1.0
	35.2	11.5			
	45.2	43			
Benzene	25.2	0.128	0.047	28.5 ± .4	5.5 ± 1.3
	35.2	0.63			
Ethyl-	25.2	2.15	.80	27.6 ± .3	7.9 ± 1.0
	35.2	9.95			
i-Propyl-	25.2	1.75	.65	29.1 ± .4	12.6 ± 1.3
	35.2	9.0			
t-Butyt-	25.2	1.15	.43	29.4 ± .4	12.7 ± 1.3
	35.2	6.0			

TABLE IV

RATE DATA FOR THE REACTION OF II AND III WITH ANISOLE IN ACETIC ACID CONTAINING PERCHLORIC ACID

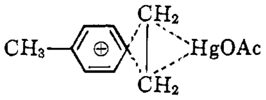
	HOAc, %	Perchloric acid concn., moles/l.	Temp., °C.	$k_2 \times 10^5$, l./mole. sec.	
II[a]	75	1.03	25.15	0.408	[b]
		1.36	25.3	1.44	
		1.65	25.3	3.55	
		2.07	25.3	10.4	[c]
		2.07	15.2	2.98	
		2.07	35.2	38.4	
	80	2.07	15.2	6.64	[d]
		2.07	25.2	24.2	
III[e]	75	0.507	5.0	4.60	[f]
		1.03		29.8	
		1.32		89	
		1.65		240	
		1.03	−4.0	9.55	[g]
		1.03	5.0	29.8	
		1.03	10.0	51.2	
		1.03	25.2	270 (calcd.)	
		1.32	−4.0	31.7	[h]
		1.32	5.0	98	
		1.32	10.0	152	

[a] Initial concentrations of II and anisole were 0.1 and 0.5 *M* respectively. [b] The plot of log k_2 against acidity function H_0 gave a straight line with a slope of 1.38. [c] ΔH^* = 21.8 kcal./mole, ΔS^* = −3.4 e.u. [d] ΔH^* = 21.1 kcal./mole, ΔS^* = −4.3 e.u. [e] Initial concentrations of III and anisole were 0.1 and 0.3 *M*, respectively. [f] The plot of log k_2 against H_0 gave a straight line with a slope of 1.42. [g] ΔH^* = 18.1 kcal./mole, ΔS^* = −8.5 e.u. [h] ΔH^* = 16.9 kcal./mole, ΔS^* = −11.4 e.u.

ions formed from I in the presence of strong acids.[2] Both inductive and resonance effects are important for the aromatic reactivities. In the series of toluene, ethylbenzene, isopropylbenzene and *t*-butylbenzene, the hyperconjugation effect is predominant.

Brown proposed[7] that the reactivity of electrophilic reagents in aromatic substitutions can be expressed by the reactivity ratio $k_{\text{toluene}}/k_{\text{benzene}}$. According to this proposal, the ratio of 21 obtained in this reaction suggests that the reactivity of the mercurinium ion from I is about the same as that of nitronium ion ($k_{\text{toluene}}/k_{\text{benzene}}$ = 27 in the case of $AcONO_2$ at 0° in Ac_2O; 21, HNO_3 in CH_3NO_2 at 30°) and is much more stable than the reacting species in isopropylation (2.1, *i*-PrCl with $AlCl_3$ in CH_3NO_3), acylation (13, AcCl with $AlCl_3$) and mercuration (5.9–7.9, $Hg(OAc)_2$ in HOAc with $HClO_4$).

The effects of the structures of the mercurials on the rates are interesting. The relative rates of I, II and III in the reactions with anisole in 75% acetic acid containing 1.03 *M* perchloric acid at 25.15° are 1.0, 1.3 and 710, respectively. The difference in the first two cases is very small, in contrast to the large reactivity difference observed in usual reactions. There must be, therefore, a special type of stabilization for the activated complexes in the reaction between mercurinium ions and aromatics. In the case of I, the supposed complex A (the positive charge is supposed to be distributed in the whole molecule) has a symmetrical structure which is suitable for the resonance stabilizations and this appears to be the reason why the rates of I are much faster than those expected from the usual reaction series. The phenonium ion participation appears to increase the stability of the activated complex and results in the greater rates in the case of III.


(A)

Experimental

β-Acetoxyethylmercuric (I), β-Acetoxypropylmercuric (II) and β-Acetoxy-β-phenylethylmercuric Acetate (III).—Compound I was prepared by the same method reported previously.[2] With propylene and styrene, this method gave no crystalline products. From the acetic acid solutions of II and III prepared by the same method, therefore, the solvent was pumped out at below 50°. The results of the analyses by the thiocyanate titration method and amalgam method[2] both showed that the liquids II and III obtained above were more than 98% pure, respectively.

Analysis of the Decomposition Products of II in Acetic Acid Containing Perchloric Acid.—Compound II (48.1 millimoles) was dissolved in 50 ml. of 80% acetic acid containing 1.03 *M* perchloric acid. The solution was placed in a 100-ml. flask which was connected to a gas buret. At room temperature and after 49 hr., 5.7 ml. of gas (at 30°) was evolved. This gas was analyzed to be propylene by vapor phase chromatograph and by the absorption method by concentrated sulfuric acid. The liquid reaction mixture was made slightly alkaline with aqueous sodium hydroxide and the mercurous oxide formed was filtered, washed with cold water, acidified with hydrochloric acid and analyzed by iodometry. The result showed that 5.1 millimoles of mercurous salt was contained in the liquid product. It was concluded, therefore, that propylene and mercurous acetate, $Hg_2(OAc)_2$, were formed in a ratio of 1 mole to 1 mole.

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(7) B. T. Brooks, C. E. Boord, S. S. Kurtz, Jr., and L. Schmerling, "The Chemistry of Petroleum Hydrocarbons," Vol. 3, Reinhold Publishing Corporation, New York, N. Y., 1955, p. 505.

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.

Acknowledgment.—The authors express their thanks for support partially by the Grant in Aid provided by the Ministry of Education and partially by Sumitomo Chemical Co.

[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.

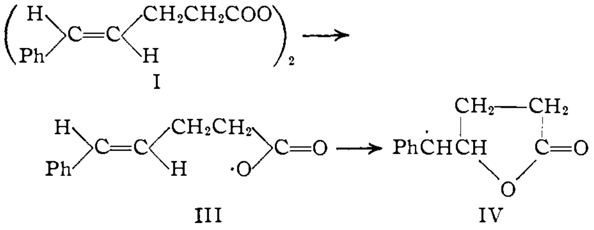
Introduction

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

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

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