The chloroether ester VII was hydrolyzed by refluxing for five minutes a mixture of 0.3 g. (0.74 mmole) of XII, 5 ml. of water, 2 drops of 10% sodium hydroxide solution and enough acetone to effect complete solution. The mixture was neutralized with dilute acid and then evaporated to dryness at reduced pressure. An impure solid which amounted to 0.26 g., m.p. 126–145°, was obtained which upon recrystallization from methanol gave 0.11 g. (41%), m.p. 150–152°. A mixture melting point with authentic α-hydroxyisobutyrophenone 3,5-dinitrobenzoate was undepressed.

Reaction of the Chloroether Ester VII with Liquid Ammonia.—A mixture of 75 ml. of liquid ammonia and 5 g. of unrecrystallized chloroether ester VII was stirred for three hours at -80°. The mixture was then stirred at room temperature for 5.5 hours after which time all the ammonia had escaped. Addition of hexane caused a solid to form which upon recrystallization from acetone–water gave 2.5 g., m.p. 160–167°. Two recrystallizations from acetone–hexane gave 0.93 g., m.p. 163° dec., of the solid compound X [5,5-dimethyl-4-phenyl-4-methoxy-2-(3,5-dinitrophenyl)-oxazolidine].

Anal. Calcd. for $C_{18}H_{19}N_3O_7$: C, 55.52; H, 4.92; N, 10.79. Found: C, 54.70, 54.66; H, 4.99, 4.69; N, 11.13, 11.01.

From the mother liquors was obtained 0.3 g., m.p. 186–187°, of a crystalline compound IX [5,5-dimethyl-4-methoxy-4-phenyl-2-(3,5-dinitrophenyl)-2-oxazoline].

Anal. Calcd. for $C_{18}H_{17}N_3O_6$: C, 58.22; H, 4.61. Found: C, 58.09; H, 4.69.

Compound IX was hydrolyzed by dissolving 0.5 g. (1.35 mmoles) in 25 ml. of acetone, 5 ml. of water and 1 ml. of concentrated hydrochloric acid and refluxing the solution for one hour. After 20 ml. of hot water was added, 0.48 g. (98%) of solid crystallized, m.p. 150–151°. A mixture melting point determination with authentic α-hydroxyisobutyrophenone 3,5-dinitrobenzoate was undepressed. The infrared spectra also were identical.

Acknowledgment.—The authors wish to thank Mr. C. Childs and associates of Parke, Davis and Co. for the analyses and Dr. J. M. Vandenbelt and associates of the same company for the spectral data.

Detroit 2, Mich.

[Contribution from the Department of Chemistry of the University of South Carolina]

Diacyl Peroxide Reactions. V. Simultaneous Rupture of Two or Three Bonds in the Initial Cleavage of δ-Phenylvaleryl Peroxide[1,2]

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Received August 20, 1958

In toluene and in carbon tetrachloride δ-phenylvaleryl peroxide gives 1.7 moles of carbon dioxide per mole of peroxide. In the presence of iodine and water the yield drops to 1.4 moles, while the rate of decomposition is essentially unchanged. This result indicates that it is possible to "trap" some of the free δ-phenylvaleryloxy radicals, and together with the previously reported detailed product study leads to the conclusion that most of the initial cleavage of the peroxide occurs by the simultaneous rupture of two or three bonds. It is significant that many reagents are suitable for "trapping" the benzoyloxy radicals from benzoyl peroxide while the iodine–water mixture was the only one of those tried that was also effective with δ-phenylvaleryl peroxide.

In the homolytic cleavage of a molecule into free radical fragments the ultimate products are often derived from units whose formation has required the cleavage of more than one bond of the original molecule. Diacyl peroxides, for example, give carbon dioxide and products derived from alkyl or aryl radicals as well as products from acyloxy radicals, and azo compounds lose nitrogen to give products arising from two alkyl free radicals. Thus these compounds must have reacted by breaking at least two bonds. There has been some speculation whether these bond cleavages occur in stepwise fashion or whether in some cases the primary break consists of the simultaneous cleavage of two or more bonds.

Some years ago Hammond and Soffer showed that the principal cleavage of benzoyl peroxide involved one bond to give two benzoyloxy fragments.[4] Accordingly the products incorporating phenyl radicals must be derived from successive reactions in one of which the benzoyloxy radical loses the carbon dioxide fragment. Recently Bartlett and his co-workers have studied the kinetics and the products of the thermal decomposition of an extensive series of peresters and have suggested that an initial two-bond cleavage occurs providing that a relatively stable alkyl radical is thereby formed, but that otherwise one-bond cleavage occurs.[5]

Because of our interest in the detailed mechanisms of diacyl peroxide reactions we have reinvestigated the Hammond and Soffer technique and have tested briefly a number of potentially useful modifications. The principle of the method is to carry out the peroxide decomposition in the presence of a "trapping" or "scavenging" agent capable of reacting rapidly with acyloxy radicals to give a product in which carbon dioxide is retained. Hammond and Soffer used an iodine and water combination for this purpose. Hammond first observed that the rate of decomposition of benzoyl peroxide in benzene or in carbon tetrachloride is not markedly affected

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[1] We wish to acknowledge with gratitude the generous support of this research by the Tennessee Eastman Co., and by the National Science Foundation (under G 4179). In addition this research was supported in part by a grant from The Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

[2] (a) IV, D. F. DeTar and R. A. J. Long, This Journal, **80**, 4742 (1958); (b) III, D. F. DeTar and C. Weis, *ibid.*, **79**, 3045 (1957).

[3] Tennessee Eastman Research Fellow, 1956–1957. This work is based on the thesis of Robert C. Lamb submitted to the Graduate School of the University of South Carolina in partial fulfillment of the requirements for the Ph.D. degree.

[4] G. S. Hammond, This Journal, **72**, 3737 (1950); G. S. Hammond and L. M. Soffer, *ibid.*, **72**, 4711 (1950).

[5] P. D. Bartlett, *Experientia, Suppl.*, **7**, 275 (1957); P. D. Bartlett and R. R. Hiatt, This Journal, **80**, 1398 (1958).

by the presence of iodine. If anything the rate is somewhat decreased. The iodine did react, however, and one of the principal products was iodobenzene. If water also was present, then a nearly quantitative yield of benzoic acid was obtained instead, and again the rate was found to be unaffected. These results were explained by the suggestion that the initial cleavage gave two benzoyloxy radicals which in the presence of iodine gave benzoyl hypoiodite. In the further presence of water the hypoiodite was hydrolyzed rapidly to benzoic acid, otherwise it decomposed to give

$$(C_6H_5COO)_2 \longrightarrow 2C_6H_5COO\cdot \qquad (1)$$

$$C_6H_5COO\cdot + I_2 \longrightarrow C_6H_5COOI + I\cdot \qquad (2)$$

$$C_6H_5COOI + H_2O \longrightarrow C_6H_5COOH + (HOI) \qquad (3)$$

iodobenzene, carbon dioxide and other products. Since this report appeared, apparently no one has looked further into the possibilities of this approach.

In the course of determining initiator efficiencies Bevington has studied the fate of benzoyl peroxide fragments in styrene polymerization using C^{14}-labeled peroxide.[6] Some 96% of the fragments attached to the polymer are benzoate groups. About 90% of the peroxide was incorporated in the polymer, and the initiation efficiency is high. At first sight this type of experiment seems to provide good evidence that benzoyloxy radicals are formed almost exclusively, but because of incompletely solved problems of induced decomposition of the peroxide the results are quantitatively less conclusive than those derived from the iodine–water scavenging.

In the present work we have compared the behavior of benzoyl peroxide and of an aliphatic peroxide, δ-phenylvaleryl peroxide, toward various potential scavenging reagents. We first carried out a survey to determine what sorts of compounds might be effective in reducing the yield of carbon dioxide. Then a preliminary check of the rate of disappearance of the peroxide in the presence of the effective compounds enabled us to reject those which were accelerating the rate and hence promoting induced decomposition of the peroxide.

The results are presented in Tables I–III. The most striking observation is the ease with which the carbon dioxide yield from benzoyl peroxide can be suppressed in comparison with the relatively small effects obtained with δ-phenylvaleryl peroxide. In fact, as shown in Table III, the only scavenger combination of those tested which reduced the carbon dioxide yield from δ-phenylvaleryl peroxide without causing extensive induced decomposition was the iodine–water mixture.

Under our conditions benzoyl peroxide gave 81% (std. dev. of avg. 2%) of carbon dioxide in carbon tetrachloride, benzene or toluene, based on a yield of two moles per mole of peroxide. With iodine and water present the average was 7% in carbon tetrachloride or in toluene. Presumably this corresponds about as well as can be expected with the "almost quantitative yield" of benzoic acid in the preliminary experiments reported by Hammond and Soffer.

TABLE I

CARBON DIOXIDE YIELDS FROM BENZOYL PEROXIDE IN THE PRESENCE OF RADICAL SCAVENGERS

Reaction conditions[a] Grams peroxide, ml. solvent, scavengers, temp., °C. time (hr.)	CO_2,[b] %
1.8, 450 CCl_4, 77, 24	87
2.1, 500 CCl_4, 77, 24	91
2.8, 600 CCl_4, 77, 24	79
2.9, 600 CCl_4, 77, 40	75
2.8, 550 CCl_4, 15 g. I_2, 15 g. H_2O, 77, 48	7
2.5, 600 CCl_4, 15 g. I_2, 40 g. H_2O, 77, 48	8
2.8, 600 CCl_4, 12 g. I_2, 40 g. H_2O, 77, 48	7
5.4, 550 CCl_4, 25 g. I_2, 20 g. H_2O, 77, 72	8
1.8, 500 C_6H_6, 80, 45	86
2.5, 500 C_6H_6, 80, 48	80
7.9, 500 C_6H_6, 20 ml. 95% C_2H_5OH, 2 g. I_2, 72, 45	6
5.9, 500 C_6H_6, 20 ml. 95% C_2H_5OH, 10 g. H_2O, 20 g. I_2, 72, 48	5
2.0, 500 dioxane, 100, 19	35[c]
2.2, 500 toluene, 110, 15	83
2.4, 500 toluene, 28 g. I_2, 20 g. H_2O, 84, 28	6[d]
2.6, 450 CCl_4, 50 g. I_2, 75 ml. allyl alc., 80, 48	1[e]
2.3, 450 CCl_4, 50 g. I_2, 75 ml. allyl alc., 80, 48	1[e]
2.0, 500 toluene, 84, 72	77[f]
2.3, 500 toluene, 84, 66	74[f]
2.2, 500 toluene, 50 ml. n-$C_{12}H_{23}SH$, 84, 48	8[f,g]
2.7, 500 toluene, 50 ml. n-$C_{12}H_{23}SH$, 84, 40	6[f,g]
2.4, 450 toluene, 125 ml. styrene, 84, 70	35[f,h]
2.1, 450 ml. α-bromonaphthalene, 84, 36	14[f,g]
2.3, 500 methylcyclohexane, 84, 60	47[f]

[a] Peroxide weighed to nearest mg., all peroxide samples were titrated and usually found to be 99–100% pure (minimum used was 95%); reaction mixtures colorless unless iodine was present or unless otherwise noted. [b] Based on two moles per mole of peroxide. [c] Reaction mixture yellow. [d] Small amount of black resin found. [e] Black resin present. [f] This superscript indicates procedure II, all others procedure I. [g] Deep yellow. [h] Viscous.

δ-Phenylvaleryl peroxide gave 86% of carbon dioxide in carbon tetrachloride or in toluene, while in toluene plus iodine and water the yield was 72% (std. dev. of avg. 2.5%). Walling reports that the carbon dioxide yield from acetyl peroxide is not depressed by iodine and water.[7] Evidently the aliphatic acyloxy radicals are formed in only low yield or else they are more difficult to trap than are aromatic acyloxy radicals.

We also attempted to determine the yield of δ-phenylvaleric acid and of the ester, δ-phenylbutyl δ-phenylvalerate, in the runs carried out in the presence of iodine and water using infrared techniques. While we observed a definite increase that could be interpreted as stoichiometric, the scatter in these preliminary attempts was quite large and the results actually have only qualitative significance.

The conditions reported in Tables I and II were all carefully chosen with some definite purpose in mind. We had a much longer list of possibilities, but due to time limitations did not test them all. The Hammond and Soffer experiment showed the high efficiency of iodine in reacting with acyloxy free radicals. However, it is also necessary to have a reagent present to remove the acyl hypoiodite

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(6) *Cf.* J. C. Bevington, J. Toole and L. Tossarelli, *Trans. Faraday Soc.*, **54**, 863 (1958).

(7) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 493.

Table II

Carbon Dioxide Yields from δ-Phenylvaleryl Peroxide in the Presence of Radical Scavengers

Reaction conditions[a] Wt. peroxide, ml. solvent, scavengers, temp., °C., time (hr.)	CO_2,[b] %
1.1, 500 CCl_4, 77, 26	86
1.2, 550 CCl_4, 40 g. I_2, 15 g. H_2O, 77, 36	80
2.3, 575 CCl_4, 35 g. I_2, 50 g. H_2O, 77, 24	82
2.7, 500 CCl_4, 31 g. I_2 50 ml. cyclohexene, 77, 36	41[e]
3.2, 500 CCl_4, 35 g. I_2, 55 ml. cyclohexene, 77, 24	44[e]
2.1, 550 CCl_4, 70 ml. styrene	76[c]
3.6, 450 CCl_4, 25 g. I_2, 50 ml. styrene, 80, 18	40[e]
3.1, 450 CCl_4, 100 g. I_2, 70 ml. $CH_2{=}CClCH_2Cl$ 77, 24	81[d]
3.2, 450 CCl_4, 50 g. I_2, 75 ml. allyl alc., 77, 40	14[e]
3.1, 450 CCl_4, 50 g. I_2, 75 ml allyl alc., 80, 36	11[e]
3.0, 350 CCl_4, 75 g. I_2, 150 ml. allyl alc., 80, 36	12[e]
3.2, 450 CCl_4, 75 g. I_2, 50 ml allyl alc., 80, 36	15[e]
3.1, 450 CCl_4, 75 ml. allyl alc., 80, 36	50
2.4, 350 CCl_4, 150 ml. allyl alc., 80, 33	52
3.3, 300 CCl_4, 200 ml. 4-vinyl-1-cyclohexene, 90, 24	88
3.1, 500 toluene, 30 g. I_2, 15 g. H_2O, 84, 17	81[d]
3.0, 500 toluene, 30 g. I_2, 15 g. H_2O, 84, 17	71[d]
3.1, 500 toluene, 30 g. I_2, 15 g. H_2O, 84, 72	68[f,d]
3.2, 500 toluene, 30 g. I_2, 15 g. H_2O, 84, 28	69[d]
3.4, 500 toluene, 30 g. I_2, 15 g. H_2O, 84, 18	72[d]
3.3, 450 toluene, 84, 36	85[f]
3.4, 450 toluene, 84, 36	86[f]
3.8, 450 toluene, 70 ml. *n*-$C_{12}H_{25}SH$, 84, 36	86[f,g]
3.3, 450 toluene, 60 ml. *n*-$C_{12}H_{25}SH$, 84, 36	74[f,g]
3.6, 420 α-bromonaphthalene, 84, 28	60[f,d]
3.0, 450 CCl_4, 100 g. I_2, 5 ml. 1-hexene, 75, 24	69[f,c]
3.5, 450 CCl_4, 100 g. I_2, 75 ml. 1-hexene, 75, 40	64[f,e]

[a] For all footnotes see Table I.

Table III

Rates and CO_2 Yields for the Decomposition of δ-Phenylvaleryl Peroxide

Reaction medium[a]	$k \times 10^5$, sec.$^{-1}$	Avg. % CO_2[b]	No. of runs[c]
CCl_4[d]	7.1	86	9
CCl_4, I_2	6.6	81[e]	2
CCl_4, allyl alc.	140	51	2
CCl_4, I_2, allyl alc.	>100	13	4
CCl_4, I_2, cyclohexene	17	42	2
Toluene	11.5	86	2
Toluene, I_2, H_2O	11	72	5

[a] Initial peroxide conc. in 0.02 *M* unless otherwise noted; concentration of scavengers similar to those used in CO_2 runs, Table II. [b] Based on 2 moles CO_2 per mole of peroxide; standard dev. of avg. is about 2% scalar. [c] No. of runs for CO_2 yield determination; the rate determinations were not usually made in duplicate. [d] Concn. in kinetics run 0.0045 *M*. [e] Water also was present in the CO_2 runs.

before it can decarboxylate, and olefins and alcohols were tested for this purpose and found unsuitable. Substances with a hydrogen atom readily susceptible to free radical attack are also potentially useful, and *n*-dodecyl mercaptan may be suitable with benzoyl peroxide. Furthermore addition of the radicals to an olefinic or aromatic system might be sufficiently rapid and quantitative, and styrene and various naphthalenes are at least partly effective with benzoyl peroxide.

Discussion.—We conclude that it is possible to trap some of the δ-phenylvaleryloxy radicals formed in the decomposition of the peroxide. This in turn indicates that the decarboxylation, eq. 4, cannot be regarded as a reaction proceeding at a rate comparable to rates of diffusion-controlled reactions.

$$C_6H_5(CH_2)_4COO\cdot \longrightarrow C_6H_5(CH_2)_4\cdot + CO_2 \quad (4)$$

This is an important conclusion, for in previous work on the mechanism of the thermal decomposition of δ-phenylvaleryl peroxide we have obtained good evidence that the ester $C_6H_5(CH_2)_4COO(CH_2)_4C_6H_5$, the dimer $C_6H_5(CH_2)_8C_6H_5$ and the tetrachloride $C_6H_5CH_2CH_2CHClCH_2CCl_3$ are all either formed in the cage, *i.e.*, in primary or secondary recombination reactions, or from a precursor ($C_6H_5CH_2CH_2CH{=}CH_2$ for the tetrachloride) which results from a cage reaction.[8] If δ-phenylbutyl free radicals are involved in a cage reaction, then they must either be formed by decarboxylation according to eq. 4 or by an initial multiple cleavage of the peroxide which involves two or three bonds and leads directly to δ-phenylbutyl radicals. Since the decarboxylation step is too slow to compete with the exceedingly rapid diffusion-controlled cage reactions, it follows that the initial bond cleavage must involve more than one bond for at least some of the molecules. Perhaps one other alternative, decarboxylative combination, should be considered. This is a remote possibility, but the only seriously proposed analogs of

$$\begin{array}{l} 2\,RCOO\cdot \longrightarrow RCOOR + CO_2 \\ \qquad \text{or } R\text{-}R + 2CO_2 \end{array} \quad (5)$$

this reaction, decarboxylative substitution, eq. 6,

$$RCOO\cdot + SX \longrightarrow RX + CO_2 + S\cdot \quad (6)$$

have been shown not to occur.[2b] We therefore regard such a reaction as unlikely.

As for quantitative results we are on less certain ground. The initially formed acyl hypoiodites are reactive and their decarboxylation is well known.[9] We are not certain that we are trapping the hypoiodites quantitatively with the water in these two-phase systems, although there are good indications that the efficiency is quite high. For example, there was sufficient variation in the experimental conditions to cause much more than the observed divergence in carbon dioxide yields if the hydrolysis were very inefficient. Furthermore, while some or possibly all of the 7% of carbon dioxide derived from the heterogeneous runs with benzoyl peroxide might be charged to incomplete trapping of the hypoiodite, homogeneous runs in the presence of aqueous ethanol gave the same yield in spite of the very much greater concentration of water. Likewise the dodecyl mercaptan runs gave the same amount of carbon dioxide. These results suggest that the benzoyl hypoiodite is being trapped essentially quantitatively in the heterogeneous runs. The fact that the carbon dioxide yield is not reduced to zero suggests that some multiple bond cleavage may be occurring in spite of the fact that phenyl radicals are perhaps the most reactive and least stabilized of all the radicals that can be formed from peroxides.

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(8) D. F. DeTar and C. Weis, This Journal, **78**, 4296 (1956); **79**, 3041 (1957).

(9) *Cf.* R. G. Johnson and R. K. Ingham, *Chem. Revs.*, **56**, 219 (1956).

The problem of evaluating the trapping efficiency achieved with δ-phenylvaleryl hypoiodite is more difficult. This hypoiodite is presumably less stable than a hypoiodite from an aromatic acid. We therefore regard the reasonably good reproducibility in carbon dioxide yields as evidence that the trapping efficiency is high. It is possible to estimate roughly how much reduction in carbon dioxide is expected if all free δ-phenylvaleryloxy radicals are trapped. As a first approximation we assume that the iodine cannot interfere with a cage reaction.[10] The yields of cage products show that some 40% of the carbon dioxide is evolved in forming these. (The 15% which is not evolved is also found in these products.) Thus the carbon dioxide yield cannot be reduced below 40%. Since it is plausible to assume that multiple bond cleavage occurs for some fixed fraction of the peroxide bonds and the resulting radicals are then partitioned between cage and non-cage products, only a fraction of the non-cage products arise from scavengeable δ-phenylvaleryloxy radicals. On the rough approximation that the probability for escaping from the cage is the same for all radicals, then the number of scavengeable δ-phenylvaleryloxy radicals is about 15%—just the amount observed. The results are at least consistent with the hypothesis that the trapping of the acyl hypoiodite is reasonably effective.

Properly speaking, of course, the calculation should be made in the reverse fashion. A detailed set of reaction steps has been presented previously.[8] The available data indicate that more than one type of cleavage of the peroxide must be occurring. In order to account for the 1,8-diphenyloctane it is necessary to postulate that at least 25% of the peroxide molecules undergo a three-bond cleavage to give δ-phenylbutyl free radicals and carbon dioxide. However, the presence of ester and acid shows that decarboxylation is not complete and that at least some of the molecules must undergo two-bond or perhaps one-bond cleavage.

We have attempted to make some estimates about the relative importance of the various steps, but there are yet too many unknowns. It is, however, possible to show that the results can be reasonably explained on the basis that there is an equal probability for one-half of a peroxide molecule to form either a phenylvaleroxy radical or a phenylbutyl radical and carbon dioxide. They can also be explained satisfactorily if the probability of forming a phenylvaleroxy radical is only 0.2. These appear to represent the limits which will permit a reasonable accounting for the products.

The picture that emerges is not so clear-cut as might have been expected. Apparently the energy and entropy factors are surprisingly comparable for these differing modes of bond cleavage. This conclusion also seems to be borne out by other data. Thus the trend in rates shown in Table IV accords quite well with the idea that the rate is faster the more stable the alkyl radical that is produced, and this in turn suggests that multiple bond cleavage becomes increasingly important with the less stable peroxides.[5]

TABLE IV

RATES OF DECOMPOSITION OF DIACYL PEROXIDES

Peroxide	Conditions	10^5k, sec.$^{-1}$
$(C_6H_5COO)_2$[a]	0.07 M in CCl_4, at 79°, 0.06 M I_2 also present	1.7
$(CH_3COO)_2$[b]	0.5 M in CCl_4 at 77°	5.2
$[C_6H_5(CH_2)_4COO]_2$[c]	0.12 M in CCl_4 at 77.1°	8.1
$(C_6H_5CH_2CH(CH_3)COO)_2$[c]	0.1 M in CCl_4 at 40.2°	17.4
$(C_6H_5CH_2COO)_2$[d]	Inf. diln. in toluene at 0°	2.5

[a] Ref. 4. [b] Ref. 11, interpolated. [c] This work. [d] Ref. 12.

However, our results with δ-phenylvaleryl peroxide suggest a rather indecisive cleavage but with a considerable amount of two- and three-bond rupture. Yet there does not seem to be very much of a rate enhancement. Along the same line Bartlett's product results indicate that the carbon dioxide yield is not quantitative in the perester series even with compounds which show a great deal of rate enhancement.[5] It may even turn out that benzoyl peroxide shows a few per cent. of the multiple bond cleavage.

Rate Studies.—Product studies indicate that very little induced decomposition accompanies the reaction of δ-phenylvaleryl peroxide in carbon tetrachloride solution. We have carried out preliminary kinetic experiments to ascertain the extent of departure from first-order kinetics. The results are presented in Table V.

TABLE V

RATE OF DECOMPOSITION OF δ-PHENYLVALERYL PEROXIDE IN CCl_4 AT 77.1°

Initial concn., 10^3 M	$k_{obs} \times 10^5$, sec.$^{-1}$	$k_{calcd} \times 10^5$,[a] sec.$^{-1}$
4.53	7.05	7.21
5.0[b]	7.27	7.22
10.2	7.48	7.32
120	8.08	8.10

[a] From $10^5\ k_{calcd} = 7.00 + 3.21\ (P)_0^{1/2}$. [b] Average of three runs; (a) a titrimetric run under nitrogen, (b) and (c) two runs followed spectrophotometrically, one under nitrogen and one in the presence of air.

Assuming that the induced decomposition step is given by eq. 6 and that the termination step is the

$$CCl_3\cdot + [C_6H_5(CH_2)_4COO]_2 \longrightarrow C_6H_5(CH_2)_4COOCCl_3 + C_6H_5(CH_2)_4COO\cdot \quad (6)$$

combination of two trichloromethyl free radicals, then the induced decomposition involves a term in the three-halves power of the peroxide concentration.[13] The amount of induced decomposition is too small to cause detectable deviation from the first-order kinetics within a run. However by varying the initial concentration over a sufficient range, the increase in rate with increasing concentration can be computed as due to this three-halves order term. In the product studies, seven of the nine runs at 77° were carried out at concentrations of 0.086 M or less.[8] Initially some 12% of the peroxide decomposes by the induced step, but the average amount of induced decomposition throughout the run is about 8%. Since no allowance is made for the possible accelerating medium effect often

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[10] *Cf.* R. M. Noyes, THIS JOURNAL, **78**, 5486 (1956).

[11] F. G. Edwards and F. R. Mayo, *ibid.*, **72**, 1265 (1950).

[12] P. D. Bartlett and J. E. Leffler, *ibid.*, **72**, 3030 (1950).

[13] K. Nozaki and P. D. Bartlett, *ibid.*, **68**, 1686 (1946); C. G. Swain, W. H. Stockmayer and J. T. Clarke, *ibid.*, **72**, 5426. (1950).

observed on going from carbon tetrachloride to aromatic solvents[14] this may be an overestimate. The product studies suggest that induced decomposition is a bit less important, perhaps only half as great as the kinetics imply. The agreement, however, is quite reasonable.

We found that the titrimetric rate is somewhat slower and erratic in the presence of oxygen than under nitrogen. However, oxygen had no effect on the rate followed by observing the rate of disappearance of the peroxide peak at 5.59 μ. We conclude that the oxygen yields substances that release iodine from iodide solutions, and the apparent effect on the titrimetric rate is an artifact. We would not expect to find oxygen inhibition for a reaction which involves very little induced decomposition.

Experimental

Reagents.—The carbon tetrachloride, benzene and toluene were reagent grade solvents, redistilled through a 4-foot helices-packed column. The iodine was Baker and Adamson reagent grade. Commercial dioxane was refluxed for 4 hours over sodium hydroxide pellets, distilled, allowed to stand over sodium, and then distilled through the column. The 1-hexene was the "Pure" grade of Phillips Petroleum Co. stated to be 99 mole % and used without purification. The styrene was distilled through an 18-inch column at 13 mm. Allyl alcohol was dried by azeotropic distillation with benzene. The *n*-dodecyl mercaptan was a commercial sample from the Wateree Chemical Co. 1-Bromonaphthalene was prepared by brominating naphthalene, b.p. 133–145° at 12 mm. (yield 55%).[16] The preparation of δ-phenylvaleryl peroxide already has been described.[8] The material, m.p. 33–34°, was stable for long periods of time when stored in a desiccator in a refrigerator. The benzoyl peroxide was purified by solution in chloroform followed by precipitation with methanol.

Peroxide Assay.—The acetone method of Swain, Stockmayer and Clarke[13] gave somewhat low results in our hands, and we preferred a modification of the isopropyl alcohol method of Wagner, Smith and Peters, adapted also for assaying solutions of the peroxide in solvents such as carbon tetrachloride.[17] An aliquot containing up to 30 mg. of the peroxide and up to 15 ml. of carbon tetrachloride was placed in a 250-ml. iodine flask. Isopropyl alcohol was used for rinsing, and enough was added to give a final volume of about 70 ml. All of the isopropyl alcohol had to be freshly distilled in order to give a zero blank. To the solution were added: (a) 2 ml. of glacial acetic acid, (b) small pieces of solid carbon dioxide until ice began to form on the outside of the flask, then (c) 10 ml. of a solution of sodium iodide (1 g.) in 30–40 ml. of isopropyl alcohol which had been flushed with CO_2. The flask was attached to a condenser, a small piece of solid carbon dioxide added, the condenser stoppered loosely with a cork with a small hole, and the solution heated at a very slow reflux for 3–5 minutes. The flask was cooled in an ice-bath, the condenser removed and rinsed with a little isopropyl alcohol, and a special head attached. This head had an inlet and outlet for carbon dioxide, an inlet for thiosulfate solution, and two platinum electrodes connected to a dead-stop end-point apparatus (consisting of 10 mv. source, and a galvanometer in series with the electrodes).[18] With magnetic stirring the liberated iodine was titrated with 0.01 *N* sodium thiosulfate solution, a very slow stream of carbon dioxide being used to prevent iodine loss.

In the kinetic runs agreement between the observed peroxide titer and that calculated from the appropriate first order kinetic expression agreed within 2.4% relative (30 D. F.) for some half-dozen different runs. This is a more rigorous test than is customarily applied to kinetic data.

Determination of Evolved Carbon Dioxide. Procedure I.—The apparatus consisted of a 1-liter flask with a sealed in gas inlet tube and a sealed on Allihn condenser. This arrangement obviated hot joints which might lead to contamination or leaks. With ball joint connections the condenser was attached to a cold trap, a small di-*n*-butyl phthalate trap (used only in the iodine runs), two more cold traps, a phosphorus pentoxide tube and two Ascarite tubes in series. High purity nitrogen was introduced through a bubbler and a phosphorus pentoxide tube. The peroxide was introduced in solution, and the apparatus and solution swept for 15 minutes before connecting the Ascarite tubes or placing the solid carbon dioxide containers around the cold traps. The solution was then heated while a slow stream of nitrogen was passed through; this required some 30–50 hours. At the end of this period the cold traps were allowed to warm to room temperature to sweep out any carbon dioxide dissolved in the small amounts of liquid carried over by the lengthy sweeping.

Procedure II.—The reaction flask was modified by sealing a high-vacuum stopcock on the inlet tube and one on the exit tube from the condenser. It was also necessary to provide a side arm through which the peroxide and solvent could be introduced. After the solution had been made up, the flask and contents were cooled to −80°, the side arm sealed off, and the contents degassed twice by evacuation and by introduction of high purity nitrogen. The flask was again evacuated, the stopcocks closed, tied on with twine, and the reaction mixture heated in a constant temperature bath at 83–85° for 36–72 hr. The flask now was attached to the gas train described above (which had been flushed with nitrogen) and, after admitting nitrogen, the evolved carbon dioxide was swept onto the Ascarite. In the runs in carbon tetrachloride a quinoline trap also was used in the gas train to remove acidic gases such as HCl.

Spectroscopic Assay.—Sample tubes were heated for appropriate times and then were stored at −80° (solid carbon dioxide). The following spectra were determined in the 5–6 μ region in 3-mm. cells using a Perkin-Elmer model 21 infrared spectrophotometer: (a) solvent *vs.* solvent, (b) each of five unknown samples and (c) solvent *vs.* air. The peroxide peak at 5.59 μ (1791 cm.$^{-1}$) was used; zero per cent. transmission was determined from the strong solvent (CCl_4) peak—scattered radiation can cause this to differ from the machine zero by up to 2%; 100% transmittance was assumed for the sample which had been allowed to react for 8 half-lives. The concentrations in the other samples was computed from their absorbance, assuming the validity of the Beer–Lambert relationship, and using known peroxide samples for calibration.

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[14] See Table IV for CCl_4 data. For benzoyl peroxide the corresponding rate in benzene is 50% larger,[6] and likewise for acetyl peroxide allowing a factor of 2 for the 5° temperature difference.[15]

[15] M. Levy, M. Steinberg and M. Szwarc, This Journal, **76**, 5978 (1954).

[16] A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1951, p. 519.

[17] C. D. Wagner, R. H. Smith and E. D. Peters, *Anal. Chem.*, **19**, 976 (1947).

[18] E. W. Abrahamson and H. Linschitz, *Anal. Chem.*, **24**, 1355 (1952).