

camera of 17.19 cm. effective diameter and rotated during the exposure. It was next mounted in a pin-hole type of camera and the patterns made with specimen-to-film distance of 10 cm. and 24.35 cm.^{8,9,10}

The observed short-spacing diffraction data are given in Table I, and the observed long-spacing data, together with the calculated long-spacing values, are given in Table II. The observed values given in both tables are the composite data obtained from the patterns made with both types of cameras.

Discussion

It will be observed that the side-spacing data in Table I correspond to the diffraction data typical for the *beta* form of 1-monoglycerides.

TABLE I
INTERPLANAR SPACINGS AND RELATIVE INTENSITIES OF
THE β -FORM OF 1-MONOARACHIDIN

$d \times 10^{-8}$ cm.	I/I_0	$d \times 10^{-8}$ cm.	I/I_0
18.2	M ⁺	3.34	W
15.7	VW	3.11	W ⁺
13.6	M	2.99	VW
9.03	M	2.90	VW
7.96	VW	2.78	W
6.98	W	2.54	VW
6.00	W	2.45	M ⁺
5.55	VW	2.29	VW
5.08	W	2.24	W
4.60	VS	2.15	W
4.42	VS	2.08	M
4.17	W	1.95	VW
3.92	VS	1.91	VW
3.83	VS	1.80	M
3.55	VW	1.75	VW
3.42	W	1.68	W
3.40	VW	1.64	W

(8) Filer, Sidhu, Daubert and Longenecker, *THIS JOURNAL*, **66**, 1333 (1944).

(9) Filer, Sidhu, Chen and Daubert, *ibid.*, **67**, 2085 (1945).

(10) Filer, Sidhu, Daubert and Longenecker, *ibid.*, **68**, 167 (1946).

TABLE II
LONG-SPACING VALUES AND MELTING POINTS OF
1-MONOGLYCERIDES

Number of carbons in fatty acid chain	Long Spacing		M. p., °C.
	Obs.	Calcd.	
10	32.6	32.7	53.0
12	36.9	37.0	63.0
14	41.6	41.4	70.5
16	45.7	45.7	77.0
18	49.9	50.1	81.5
20	54.4	54.4	84.0

* Repeated from an earlier paper for comparison (ref. 8).

The long-spacing value in Table II represents the average weighted value obtained from a very strong first order line of 54.0 Å., a weak second order of 27.3 Å., a strong third order of 18.2 Å., a medium fourth order of 13.6 Å., and a medium sixth order of 9.03 Å.

The average increment in long-spacing value for the C₁₀₋₂₀ series of saturated 1-monoglycerides is 4.36 Å. The calculated long-spacing value for the 1-monoarachidin was based upon an empirical relation between long-spacing values and the effective number of carbon atoms in a double monoglyceride molecule, as derived in a previous paper.⁸

Acknowledgment.—The assistance of Gretta L. Scott in obtaining the X-ray diffraction patterns is gratefully acknowledged. Acknowledgment is also made of the generous financial assistance of the Buhl Foundation which made this investigation possible.

Summary

X-Ray diffraction and melting point data for the solvent-crystallized *beta* form of 1-monoarachidin are reported.

PITTSBURGH, PENNA.

RECEIVED JUNE 8, 1946

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.]

Kinetics of the Decomposition of Benzoyl Peroxide in Various Solvents

By W. E. CASS

Previous studies of the rate of decomposition of benzoyl peroxide have indicated approximately first order kinetics for the reactions in toluene,¹ nitrobenzene,¹ benzene,^{2,3,4} styrene-benzene,⁵ vinyl acetate-benzene,³ and allyl acetate.⁶ However, in certain cases,^{5,6} the first order constants were found to increase with higher initial peroxide concentrations. Furthermore, the rates of de-

(1) Bartlett and Altschul, *THIS JOURNAL*, **67**, 812 (1945).

(2) McClure, Robertson and Cuthbertson, *Can. J. Research*, **20B**, 103 (1942).

(3) Medvedev and Kamenskaya, *Acta. Physicochim. U. R. S. S.*, **13**, 365 (1940).

(4) Brown, *THIS JOURNAL*, **62**, 2657 (1940). In this case the order determined for the reaction was approximately 1.3.

(5) Cohen, *ibid.*, **67**, 17 (1945).

(6) Bartlett and Altschul, *ibid.*, **67**, 816 (1945).

composition of benzoyl peroxide in vinyl acetate-benzene³ and in styrene-toluene⁷ and of 3,4,5-tribromobenzoyl peroxide in styrene-benzene⁸ were increased several times over those in the non-polymerizing solvents alone. The possibility of recombination of benzoyloxy radicals has been suggested^{9,10} in explanation of the latter observation.

In the present work the rates of decomposition of benzoyl peroxide in a number of solvents were measured in the absence of air at 30±0.2°. It was found that not only the rates but also the

(7) Breitenbach and Taglieber, *Ber.*, **76**, 272 (1943).

(8) Price and Tate, *THIS JOURNAL*, **65**, 517 (1943).

(9) Price, *Ann. N. Y. Acad. Sci.*, **44**, 365 (1943).

(10) Matheson, *J. Chem. Phys.*, **13**, 584 (1945).

orders of reaction varied considerably among these solvents. The results obtained are summarized in Table I. In each case, the initial concentration of peroxide was approximately 0.2 molar and, following the initial peroxide determination, five or six peroxide determinations were made over the indicated period of time. From the data thus obtained, zero, first, second or third order plots were made; in each case, the order which most nearly gave a straight line was selected. The rate constants given in Table I represent the slopes of the "best" straight lines drawn through the points and the inhibition periods represent the intersection of these lines with the time axis. The term, x , in Table I is the amount of peroxide decomposed during the indicated period of time; H/x is the ratio of the total amount of acidity produced during the reaction to the amount of peroxide decomposed. Concentrations are expressed in moles per liter and time, in hours. The graphs for certain of the solvents in Table I are presented in Fig. 1.

TABLE I

SUMMARY OF DATA FOR THE DECOMPOSITION OF $\sim 0.2 M$ BENZOYL PEROXIDE SOLUTIONS AT $30 \pm 0.2^\circ$

Solvent	Total time, hr.	x	H/x	Inhib., hr.	k (graph) ^a
Benzene	435	0.0145	1.0	24	k_1 0.000173
Toluene	366	.0120	0.9	24	k_1 .000178
Ethylbenzene	312	.0065	1.1	30	k_1 .000130
Cumene	379	.0175	1.0	35	k_1 .000263
Chlorobenzene	355	.0075	1.3	30 ^c	Autocatalytic
Nitrobenzene	387	.0150	1.4	58	k_1 0.000238
Anisole	305	.0245	1.1	48	k_1 .000512
Phenetole ^b	339	.0490	1.0	50 ^c	Autocatalytic
Carbon tetrachloride	393	.0125	1.6	90 ^c	Autocatalytic
Chloroform	400	.0130	2.2	56	k_1 0.000197
Ethylene chloride	401	.0340	1.2	40	k_3 .0161
Acetone	479	.0468	1.0	10	k_2 .00326
Acetic acid ^b	281	.0537	...	60	k_3 .0429
Ethyl acetate ^b	353	.0720	1.0	44	k_3 .0545
Butyraldehyde ^c	187	.0600	^d	0	k_2 .0116

^a The units for the constants are as follows: first order (k_1), hr.⁻¹; second order (k_2), hr.⁻¹ (moles/liter)⁻¹; third order (k_3), hr.⁻¹ (moles/liter)⁻². ^b Experiment repeated with similar results. ^c Approximately same rate observed in sample exposed to air. ^d Alkali apparently caused oxidation of aldehyde by peroxide resulting in rapid fading of end-point. ^e Value estimated from zero order plot.

It should be emphasized that the data in Table I merely summarize observed rates at one concentration and are not intended to imply any particular mechanism of reaction. This is particularly true for the solvents exhibiting kinetics other than first order, as will be shown below in the case of certain ethers, higher order reactions may involve rather complex kinetic expressions. The apparent autocatalysis observed in the case of three solvents may be due to the presence of retarding impurities which were gradually con-

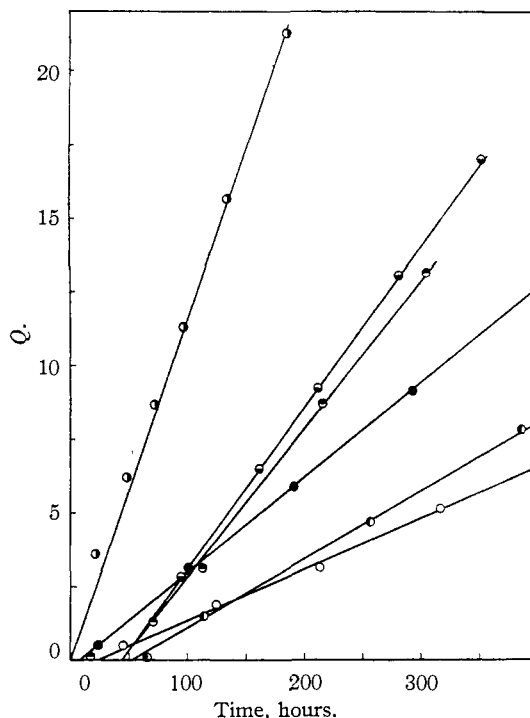


Fig. 1.—Rate of decomposition of $\sim 0.2 M$ benzoyl peroxide in various solvents at $30 \pm 0.2^\circ$: [$(Q = 2.3 \log a/(a-x))$ (first order); $Q = x/a(a-x)$ (second order); $Q = x(2a-x)/2a^2(a-x)^2$ (third order)]. For purposes of plotting Q has been multiplied by the indicated factors. \circ , benzene (1st order, $10^2 Q$); \bullet , acetone (2nd order, $10 Q$); \odot , ethyl acetate (3rd order, $1 Q$); \ominus , anisole (1st order, $10^2 Q$); $\omin�$, nitrobenzene (1st order, $10^2 Q$); $\omin�$, butyraldehyde (2nd order, $10 Q$).

sumed; however, in the case of phenetole, it may represent a real effect, *i.e.*, the products of the primary reaction induce a more rapid decomposition of the peroxide.

From the rate constants at 30° listed in Table I and the published constants for benzene² at 66° , toluene¹ at 100° and nitrobenzene¹ at 100° , energies of activation for the reactions in these solvents were calculated to be 28.7, 28.8 and 28.1 kcal., respectively. These values are somewhat lower than the value of 31 kcal. reported² for the reaction in benzene at $66-78^\circ$.

The rates of decomposition of benzoyl peroxide in dioxane, diethyl Cellosolve ("ethylene glycol diethyl ether") and diethyl ether were found to be considerably more rapid than in the solvents listed in Table I. Accordingly, a more thorough study was made of the kinetics of the reactions in these ethers. It was found that the orders of reaction were complex, that the rapid decomposition could be inhibited by air (oxygen), by hydroquinone or quinone and by monomers (methyl methacrylate and styrene) and that the decomposition was retarded by aromatic compounds (benzoic acid, ethyl benzoate and benzene). These observations are believed to indicate the

existence of a chain reaction in which radicals derived from the solvent attack undissociated benzoyl peroxide molecules or the postulated benzoyl peroxide-benzoyloxy radical complex.¹⁰

In the calculation of the rate constants for the reactions, the approximate expressions given below were employed. In these equations, a is the initial peroxide concentration; x , the amount of peroxide decomposed at time, t ; b , the concentration of added retarder (benzoic acid, ethyl benzoate or benzene); and f , a "reactivity factor" to be discussed later. Concentrations are expressed in moles per liter and time, in hours.

Dioxane

$$(1) \quad \frac{dx}{dt} = k \frac{(a-x)^2}{(2x+fb)}$$

or

$$k = \frac{1}{t} \left[\frac{2a}{a-x} - 4.6 \log \frac{a}{a-x} + \frac{fb}{a-x} - \frac{fb}{a} - 2 \right]$$

Diethyl Cellosolve

$$(2) \quad \frac{dx}{dt} = k \frac{(a-x)^{3/2}}{(2x+fb)^{1/2}}$$

or

$$k = \frac{1}{t} \left[\frac{2(2x+fb)^{1/2}}{(a-x)^{1/2}} + \sqrt{2} \sin^{-1} \left(\frac{2a-4x-fb}{2a+fb} \right) - \frac{2(fb)^{1/2}}{a^{1/2}} - \sqrt{2} \sin^{-1} \left(\frac{2a-fb}{2a+fb} \right) \right]$$

Diethyl ether

$$(3) \quad \frac{dx}{dt} = k \frac{(a-x)^{3/2}}{(a+fb)^{1/2}}$$

or

$$k = \frac{2(a+fb)^{1/2}}{t} \left[\frac{1}{(a-x)^{1/2}} - \frac{1}{a^{1/2}} \right]$$

Data from a number of experiments with dioxane, diethyl Cellosolve and diethyl ether are summarized in Tables II, III and IV. In each case, the experimental data were substituted in the integrated form of the appropriate kinetic equation and the results plotted; the over-all

TABLE II
DECOMPOSITION OF BENZOYL PEROXIDE IN DIOXANE

Total time, hr.	a	$a-x$	b	H/x	Inhib., hr.	k , hr. ⁻¹
30 = 0.2°						
118	0.1980	0.1072	0.0	1.1	17	0.00460
119	.0407	.0233	.0	...	35	.00457
114	.3960	.2210	.0	1.1	13	.00413
93	.1998	.1385	.1 ^a	1.1	11	.00458
121	.1998	.1290	.1 ^b	1.1	11	.00427
112	.1990	.1120	.2 ^c	1.1	14	.00453
114.5	.1965	.1278	1.11 ^c	1.2	13	.00362
115	.1975	.1503	2.81 ^c	1.2	7	.00288
135	.2020	.1705	5.6 ^c	1.1	14	.00237
40 = 0.1°						
59	0.1990	0.0748	0.0	1.1	6.5	0.0258
50 = 0.1°						
27	0.2000	0.0498	0.0	1.0	3	0.131

^a Benzoic acid. ^b Ethyl benzoate. ^c Benzene.

TABLE III
DECOMPOSITION OF BENZOYL PEROXIDE IN DIETHYL CELLOSOLVE

Total time, hr.	a	$a-x$	b	H/x	Inhib., hr.	k , hr. ⁻¹
30 = 0.2°						
94.5	0.1990	0.0320	0.0	0.87	10	0.0375
149.5	.0995	.0112	.0	.87	15	.0332
187.5	.3680	.0269	.0	.89	7	.0349
90	.1990	.0452	.2 ^a	.87	5	.0368
112	.1980	.0420	.2 ^b	.89	16	.0343
112.8	.1975	.0326	.55 ^c	.87	10	.0367
111.3	.1975	.0397	1.11 ^c	.88	10	.0361
163	.1990	.0430	2.8 ^c	.85	10	.0292
141.5	.2000	.1050	5.6 ^c	.84	5	.0140
40 = 0.1°						
37	0.1990	0.0204	0.0	0.81	3.4	0.136
50 = 0.1°						
8.4	0.2000	0.0312	0.0	0.79	1	0.426

^a Benzoic acid. ^b Ethyl benzoate. ^c Benzene.

TABLE IV
DECOMPOSITION OF BENZOYL PEROXIDE IN DIETHYL ETHER

Total time, hr.	a	$a-x$	b	H/x	Inhib., hr.	k , hr. ⁻¹
30 = 0.2°						
88.5	0.1492	0.0136	0.0	0.84	4	0.0550
90.7	.1010	.0086	.0	.80	5	.0553
94.5	.0501	.0054	.0	.88	12	.0489
89.7	.1510	.0230	.2 ^a	.85	4	.0553
113.8	.1485	.0210	.2 ^b	.85	18.5	.0527
96	.1480	.0131	.2 ^c	.82	5	.0545
93.3	.1480	.0270	1.11 ^c	.84	5	.0397
112.3	.1482	.0454	2.8 ^c	.83	8	.0263
138	.1513	.0812	5.0 ^c	..	13	.0126
40 = 0.1°						
23	0.1490	0.0146	0.0	0.79	1	0.200
50 = 0.1°						
6	0.1480	0.0184	0.0	0.77	0.3	0.624

^a Benzoic acid. ^b Ethyl benzoate. ^c Benzene.

rate constant and the inhibition period were obtained from the slope and intersection of the straight line most nearly describing each curve. The reactivity factor, f , was assumed to be unity in all cases for benzoic acid and ethyl benzoate. For benzene, the value of f was taken as 0.05 in dioxane, 0.2 in diethyl Cellosolve and 0.1 in diethyl ether. The graphs for the first four experiments in Tables II, III and IV are presented in Figs. 2, 3 and 4.

From the rate constants at 30° for the first experiment in Tables II, III and IV and from the constants at 40 and 50°, the following over-all energies of activation were calculated: for dioxane: 32.4 (30-40°) and 32.4 kcal. (40-50°); for diethyl Cellosolve: 24.1 (30-40°) and 22.9 kcal. (40-50°); for diethyl ether: 24.3 (30-40°) and 22.8 kcal. (40-50°).

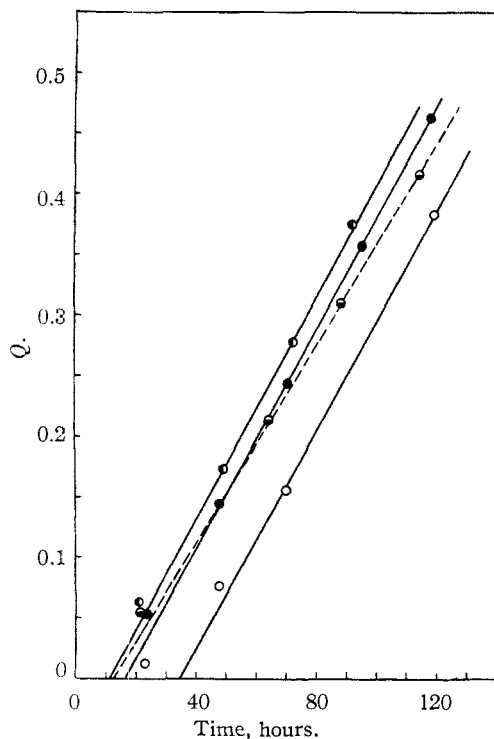
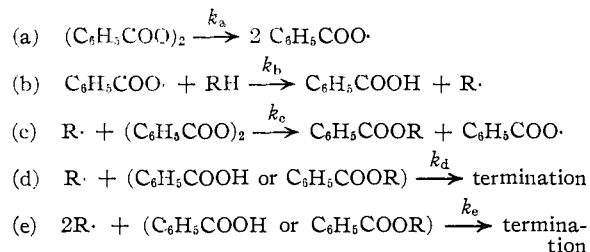


Fig. 2.—Rate of decomposition of benzoyl peroxide at $30 \pm 0.2^\circ$ in dioxane: $[Q = 2a/(a-x) - 4.6 \log a/(a-x) + fb/(a-x) - fb/a - 2]$. \circ , $a = 0.0407$; \bullet , $a = 0.1980$; \bullet , $a = 0.3960$; \bullet , $a = 0.1998$, $b = 0.1$ (benzoic acid).

Discussion

In general, this work indicates that the decomposition of benzoyl peroxide in non-polymerizing solvents is not necessarily a simple unimolecular process. Of the solvents listed in Table I, it will be noted that most of the aromatic solvents and also carbon tetrachloride and chloroform do not lead to an acceleration of the decomposition of the peroxide. This is believed to indicate that the free radicals derived from these solvents do not interact appreciably with the peroxide.

In the derivation of the kinetic expressions used for dioxane and diethyl cellosolve (eq. (1) and (2)) the following reaction chains were assumed (RH is solvent):



With the assumption that most of the peroxide is decomposed via the chain reaction (steps (b) and (c)), a steady state approximation¹¹ applied

(11) In this derivation it is assumed that the aromatic free radicals produced in step (d) disappear by mutual interaction. If these

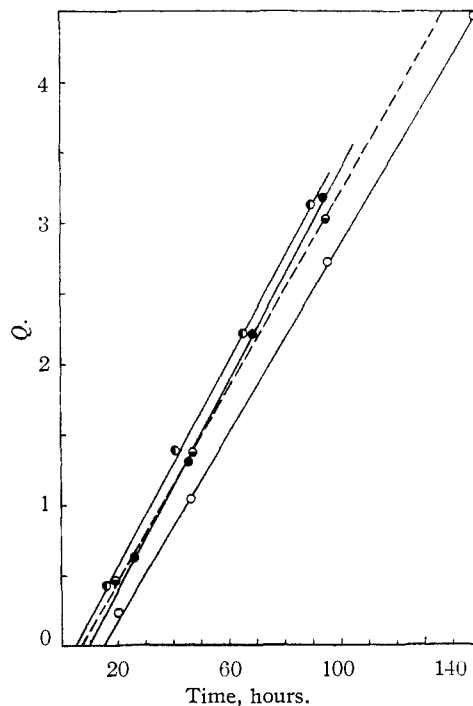


Fig. 3.—Rate of decomposition of benzoyl peroxide at $30 \pm 0.2^\circ$ in diethyl Cellosolve: $[Q = 2(2x + fb)^{1/2}/(a-x)^{1/2} + \sqrt{2} \sin^{-1}(2a - 4x - fb)/(2a + fb) - 2(fb)^{1/2}/a^{1/2} - \sqrt{2} \sin^{-1}(2a - fb)/(2a + fb)]$. \circ , $a = 0.0995$; \bullet , $a = 0.1990$; \bullet , $a = 0.3680$; \bullet , $a = 0.1990$, $b = 0.2$ (benzoic acid).

to steps (a), (b), (c) and (d) yields eq. (1a), which has the same form as eq. (1).

$$\text{(1a)} \quad -\frac{d[(\text{C}_6\text{H}_5\text{COO})_2]}{dt} = \frac{k_a k_c [(\text{C}_6\text{H}_5\text{COO})_2]^2}{k_d [(\text{C}_6\text{H}_5\text{COOH} + \text{C}_6\text{H}_5\text{COOR})]}$$

Similarly, a steady state approximation applied to steps (a), (b), (c) and (e) yields eq. (2a) from which eq. (2) was derived.

$$\text{(2a)} \quad -\frac{d[(\text{C}_6\text{H}_5\text{COO})_2]}{dt} = k_c \left(\frac{k_a}{k_e}\right)^{1/2} \frac{[(\text{C}_6\text{H}_5\text{COO})_2]^{3/2}}{[(\text{C}_6\text{H}_5\text{COOH} + \text{C}_6\text{H}_5\text{COOR})]^{1/2}}$$

Equation (3) for diethyl ether was established empirically and no simple kinetic derivation has been found to apply.¹²

$$\text{(3a)} \quad -\frac{d[(\text{C}_6\text{H}_5\text{COO})_2]}{dt} = k_c \left(\frac{k_a}{k_e}\right)^{1/2} \frac{[(\text{C}_6\text{H}_5\text{COO})_2]^{3/2}}{a^{1/2}}$$

It is improbable that the above expressions completely describe the reactions occurring in these ethers. For example, in the case of dioxane the graphical points showed a tendency to curve upward, possibly indicating a lower-order reaction. It is probable that aromatic radicals actually react with solvent radicals, a factor of one-half must be included in the constants of eq. (1a).

(12) If it be assumed that termination according to step (e) can occur with undissociated benzoyl peroxide as well as with the aromatic products and if it be further assumed that the peroxide molecule is as effective in the termination reaction as both aromatic product molecules, then eq. (3a) results, where a is the initial peroxide concentration.

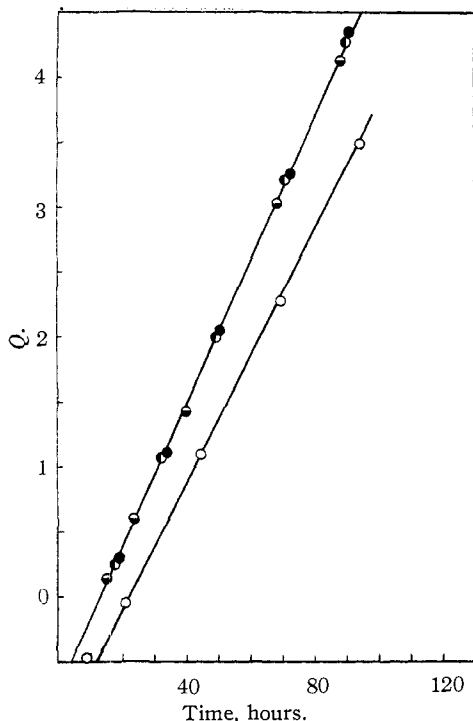


Fig. 4.—Rate of decomposition of benzoyl peroxide at $30 \pm 0.2^\circ$ in diethyl ether: [$Q = 2(a + fb)^{1/2}(1/(a - x)^{1/2} - 1/a^{1/2})$]. ○, $a = 0.0501$; ●, $a = 0.1010$; ◐, $a = 0.1492$; ◑, $a = 0.1510$, $b = 0.2$ (benzoic acid).

tion concurrent with the main chain reaction. However, using the present equations,¹³ the rate constants agree fairly well, even in the presence of added benzoic acid and ethyl benzoate which exert a definite retarding action on the reaction velocity.

The fact that no elimination of carbon dioxide is provided for in the above reaction scheme was generally borne out by experiment. Actually, of the three rapid solvents, only diethyl ether showed appreciable gas evolution at 30° when the sample tubes were opened.¹⁴ Saponification experiments on the ether solutions indicated that decarboxylation at 30° did not exceed about 0.2 mole of carbon dioxide per mole of peroxide decomposed.

The inhibition periods are believed to represent a suppression of the chain mechanism by oxygen dissolved in the solutions.¹⁵ Experi-

(13) In this connection it should be noted that ordinary rate equations definitely do not apply. For example, the experiments with dioxane at three different concentrations yielded "straight" lines when plotted as third order reactions, but the resulting rate constants differed by a factor of one-hundred. Actually more than fifteen rate expressions, both conventional and complex, were applied to the data from the reactions in dioxane, diethyl Cellosolve and diethyl ether; from these expressions, eqs. (1), (2) and (3) were selected as being most nearly in agreement with the observed kinetics.

(14) Of the solvents in Table I, acetic acid and butyraldehyde evolved appreciable amounts of gas and phenetole and ethyl acetate, small amounts of gas.

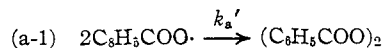
(15) In this process, oxygen is believed to combine readily with a primary radical, R' , to form a peroxy radical, $R'OO\cdot$. The peroxy

radical then either combines with another primary radical to form a peroxide, $R'OO R'$, or captures a hydrogen from the solvent to form a hydroperoxide, $R'OOH$, and a new free radical. The latter process should result in an initial increase in peroxide concentration; actually such an increase was observed in several instances.

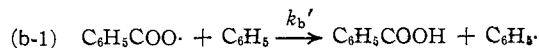
ments in which the solutions were deliberately exposed to air indicated that the rapid decomposition of the peroxide was thereby effectively suppressed. The fact that the decomposition of benzoyl peroxide in butyraldehyde was not inhibited by air may indicate a different decomposition process for this reaction.

Inhibition of the rapid decomposition of peroxide by quinone and hydroquinone might be predicted. However, the strong retardation of the decomposition by methyl methacrylate and styrene was unexpected. An obvious explanation is that the monomers have a high affinity for free radicals and that the resulting monomer radicals do not interact with the undissociated peroxide.

It will be noted that eq. (1), (2) and (3) do not involve solvent concentration. It was hoped that the experiments in which benzene was added would illustrate this point. Actually, however, the rate constants did fall off as the concentration of benzene was increased to 5.6 M (50% benzene). Solvent dependence could be introduced by assuming a primary recombination (step (a-1)) as suggested by Matheson.¹⁰



The decrease in rate constants could also be explained by a "wastage" of benzoyloxy radicals through interaction with benzene (step (b-1)).



However, none of the expressions derived from these assumptions gave results in uniform agreement with the experimental results. The difficulty here may rest in an error in the establishment of the values for the reactivity factor, f ,¹⁶ which was obtained empirically in each case from the experiment in which benzene was present in the lowest concentration.

A point not explained by the above kinetic picture is the variance of the H/x ratios for the three ethers. This is concerned with the actual chemical nature of the reactions and work on this phase of the problem is now in progress. In this work, benzoic acid and 1-ethoxyethyl benzoate (b.p. $57-58^\circ$ at 0.2 mm., n_D^{25} 1.4868) have been isolated as main products of the reaction of benzoyl peroxide with diethyl ether at 37° . The isolation of these compounds is considered chemical evidence for the general chain mechanism proposed.

Acknowledgment.—The author is indebted to Dr. D. W. Scott for much helpful discussion.

radical then either combines with another primary radical to form a peroxide, $R'OO R'$, or captures a hydrogen from the solvent to form a hydroperoxide, $R'OOH$, and a new free radical. The latter process should result in an initial increase in peroxide concentration; actually such an increase was observed in several instances.

(16) As here employed, f represents the approximate ratio of the reactivity of benzene to the reactivity of the "aromatic products" toward solvent radicals. When f was taken as unity for benzene, the resulting rate constants were, in some cases, actually higher than those in the absence of benzene.

Experimental

Purification of Materials.—Commercial benzoyl peroxide was purified by dissolving about 75 g. in 1 liter of acetone at room temperature, precipitating by the addition of 2 liters of distilled water with stirring, filtering and thoroughly drying the product in an air stream. The purified material assayed 99.5–99.7% by iodometric titration.

Benzoic acid was an analytical standard grade. Ethyl benzoate was purified by vacuum distillation.

Commercial samples of methyl methacrylate and styrene were washed several times with 10% sodium hydroxide solution and then with water, dried over anhydrous potassium carbonate or calcium chloride, and then distilled under reduced pressure (30 and 13 mm., respectively), collecting the middle fraction in each case. Prior to some experiments, the substances were redistilled under reduced pressure.

Solvents used for the rate studies were tested for peroxide content by the iodometric method to be described below. Except where otherwise noted, the solvents as used were "peroxide-free," *i. e.*, $< 3 \times 10^{-5}$ equiv. active oxygen per liter, determined on a 30-ml. sample using 0.01 *N* (sodium) thiosulfate.

Reagent (c. p.) grades of benzene, acetone, acetic acid and ethyl acetate were used as received. Toluene was purified by sulfuric acid treatment in the usual manner.

Except where otherwise noted, distillations were conducted through a 25-cm. unpacked column to minimize entrainment. In all cases only the middle fractions were collected. Generally, a slow stream of hydrogen was bubbled through the mixture during distillation, the hydrogen flow being interrupted during boiling point determinations. Solvents found initially to be peroxidized were first boiled under reflux over considerable amounts of sodium, a hydrogen atmosphere being maintained above the refluxing mixture. All-glass apparatus was used.

Ethylbenzene: refluxed over sodium five hours; b. p. 136°. Cumene: refluxed over sodium sixteen hours; b. p. 153°. Chlorobenzene: b. p. 132°. Nitrobenzene: b. p. 209–211°. Anisole: refluxed over sodium thirty hours; b. p. 154°. Phenetole: refluxed over sodium sixteen hours; b. p. 170–171°. Carbon tetrachloride: b. p. 76–77°.

Ethylene chloride (b. p. 82.9 at 745 mm.) and chloroform (b. p. 60.7° at 743 mm.) were both distilled through an efficient 50-cm. packed fractionating column.

The purification of butyraldehyde offered considerable difficulty and the final product obtained was still relatively impure. Technical butyraldehyde was distilled through the 50-cm. fractionating column with the head and receiver vented into nitrogen. The fraction used had the following properties: b. p. 74.8–74.9° at 757 mm.; acidity, 0.03 equiv./liter ($\sim 0.26\%$ butyric acid); peroxide, 2.4×10^{-3} equiv./liter.

Dioxane was generally purified by refluxing for at least thirty hours over much sodium, b. p. 101°. Dioxane was also purified by a preliminary treatment with hydrochloric acid followed by sodium treatment¹⁷; no change in the rate constant was observed with this more rigorously purified solvent.

Diethyl Cellosolve was purified similarly to dioxane, b. p. 121°; peroxide, $3-8 \times 10^{-5}$ equiv./liter.

Reagent grade anhydrous diethyl ether was used as received in preliminary experiments. It was found that ether from two sources gave reproducibly different rate constants for the decomposition of 0.15 *M* benzoyl peroxide, 0.043 for one and 0.055 for the other. These constants were unchanged following simple distillation with or without a preliminary sodium treatment. Fractionation through an efficient 50-cm. column did not change the constant for the "faster" ether but raised the constant for the "slower" ether to 0.048. It was concluded that the slower ether contained traces of difficultly removable retarding impurities. The data summarized in Table IV were based on experiments with the faster ether; in most

cases this ether was refluxed over sodium and distilled before use.

Rate Studies.—Ampules of about 9-ml. capacity were prepared by drawing out 12-cm. soft-glass test-tubes which had been cleaned with Calgonite and carefully rinsed with distilled water. Several check experiments in which the tubes were also cleaned with sulfuric acid–dichromate showed no significant changes in the rate constants. In each experiment 4–6 ampules were filled with benzoyl peroxide solution and sealed. Before sealing, air was displaced by flushing with nitrogen. The filling and sealing were so conducted that the free gas space above the liquid when the samples were in the thermostat was 0.1–0.4 ml., generally 0.2–0.3 ml. The tubes were placed in a well-stirred water thermostat kept in dim light. In opening the ampules, the neck was broken below the meniscus so that any pressure resulting from evolved gases could be observed.

Peroxide Analyses.—The procedure used was that of Bartlett and Altschul⁶ with minor changes. The sample (generally 5 ml.) was pipetted into the reaction mixture which consisted of 20 ml. of glacial acetic acid, 1 ml. of freshly prepared, saturated aqueous potassium iodide solution and a few lumps of Dry Ice. After five minutes, 20–30 ml. of water was added and the mixture titrated with standard thiosulfate to the disappearance of the iodine color. The use of a starch indicator was found unnecessary except in the case of nitrobenzene; 50 ml. of water was added in this case. Below 0.05 *M* peroxide, 0.01 *N* thiosulfate was used; otherwise, 0.1 *N* thiosulfate was employed. In thirty-eight cases duplicate peroxide determinations were made on initial samples (5-ml. samples of approx. 0.2 *M* peroxide solutions titrated with 0.1 *N* thiosulfate). The average difference in the titration values in these thirty-eight cases was 0.04 ml. thiosulfate and the maximum difference (four cases) was 0.10 ml.

The use of acetone as a solvent in peroxide determinations may lead to error. It was found that acetone apparently reacted slowly with iodine, particularly after the addition of water. This is illustrated by the following experiment: an approximately 0.1 *M* solution of benzoyl peroxide in acetic acid was prepared and 5-ml. samples were analyzed according to the above method, 20 ml. of acetone being added initially to certain of the reaction mixtures. The data are presented in Table V.

TABLE V
EFFECT OF ACETONE ON BENZOYL PEROXIDE
DETERMINATION

(CH ₃) ₂ CO, ml.	Approx. time, min.—		0.1013 <i>N</i> Na ₂ S ₂ O ₄ , ml.
	For reaction	After water added, before titration	
0	5	2	10.10
0	5	15	10.08
20	5	3	9.95 ^a
20	15	1	10.00
20	5	6	9.80 ^a
20	5	12	9.55 ^a
20	5	24	9.10 ^a

^a Iodine color gradually reappeared after colorless endpoint was reached.

Determination of Acidity.—Titration of peroxide samples (3 ml.) for acidity was done in acetone solution using 0.1 *N* sodium hydroxide and phenol red indicator. The endpoint faded rapidly (more rapidly with phenolphthalein) and a standard blank of 0.05 ml. of 0.1 *N* alkali was applied to all samples.

Saponification Experiments. (a) **Dioxane.**—A dioxane solution of benzoyl peroxide (initially 0.396 *M*) was sealed under nitrogen in a large ampule and kept in the dark for one hundred hours at 30°, fifty hours at 40° and about three months at room temperature (20–30°). At the end of this time analysis gave the following results: 0.061 *M* peroxide; 0.385 *N* acid. Saponification of 10

(17) Hess and Frahm, *Ber.*, **71**, 2627 (1938).

ml. at 80° for one hour with 0.5 *N* alcoholic potassium hydroxide, indicated a total acidity (ester plus acid) of 0.882 equiv./liter. This figure is high compared with the calculated acidity to be produced by the benzoyl peroxide alone (0.792 equiv./liter). However, reaction of benzoyl peroxide with alcohol in the presence of excess alkali (see below) gives 2.5 equiv. acid per mole of peroxide. Thus, a correction factor of 0.031 added to the calculated value gives 0.823 equiv./liter for the total acidity, a figure in better agreement with experiment. Moreover, if an aldehyde were present in the dioxane solution which was saponified, the correction factor would be 0.061, giving a calculated value for the total acidity of 0.853 equiv./liter, a figure in still better agreement with experiment.

The solution from the above saponification was made slightly basic and evaporated to dryness at 80°. The residue was dissolved in 20 ml. of water (nearly clear solution) and the acid precipitated with hydrochloric acid. The yield of dried acid was 0.885 g. (calcd. for benzoic acid 0.966 g.), m. p. 100–110°. A mixed melting point (112–117°) with pure benzoic acid (m. p. 121.5–122°) indicated that the product was impure benzoic acid.

The fact that benzoyl peroxide reacts almost quantitatively with alcohol during saponification to give 2.5 equiv. acid per mole of peroxide was proved by the following experiments. A 0.198 *M* solution of the peroxide in dioxane, saponified as above with alcoholic potassium hydroxide, indicated 0.485 equiv. total acidity per liter (calcd. 0.396 (no oxidation of alcohol), 0.495 (oxidation of alcohol to acid)). A 0.198 *M* solution of the peroxide in dioxane saponified with 0.5 *N* aqueous sodium hydroxide indicated 0.415 equiv. total acidity per liter.

(b) **Diethyl Cellosolve.**—A diethyl Cellosolve solution of benzoyl peroxide (initially 0.368 *M*) was sealed under nitrogen and kept at 30° for about one hundred ninety hours. At this time analysis gave the following results: 0.0269 *M* peroxide; 0.3033 *N* acid. A sample (20 ml.) saponified with 0.5 *N* alcoholic potassium hydroxide as before (aldehyde gum produced during saponification in this case) indicated 0.758 equiv. total acidity per liter (calcd. 0.736 (no oxidation), 0.7495 (alcohol oxidized), 0.763 (aldehyde oxidized)).

The acid from the above saponification was recovered as before; yield 1.59 g. (calcd. for benzoic acid 1.80 g.); m. p. 117–119°; mixed m. p. 119.5–121°.

(c) **Ether.** A solution of benzoyl peroxide in ether (initially 0.1485 *M*) after twenty-seven days at 30° gave the following analysis: $< 7 \times 10^{-4}$ *M* peroxide; 0.124 *N* acid. Saponification of a 20-ml. sample as before (aldehyde gum produced) indicated 0.2985 equiv. total acidity per liter (calcd. 0.297). There was recovered 0.610 g. (calcd. 0.725 g.) of fairly pure benzoic acid, m. p. 119–121°; mixed m. p. 120–122°; equiv. wt. 127.

Inhibition Experiments. (a) **By Oxygen.** (1) **Dioxane.**—Forty ml. of a 0.1990 *M* solution of benzoyl peroxide in dioxane was placed in a 125 ml. g.s. Erlenmeyer flask (greased stopper) in the 30° thermostat. The flask was opened daily for peroxide determinations; this procedure permitted the air atmosphere to be renewed. The peroxide content gradually increased and at the end of ninety-five hours was 0.2240 *M*. (During this time the peroxide content of samples under nitrogen decreased to < 60% of the initial value.) A 10-ml. sample was pipetted into 100 ml. of distilled water. After cooling, the precipitate was filtered and dried; yield 0.460 g. (calcd. for benzoyl peroxide 0.482 g.); m. p. 101–103° (dec.). This material was identified as fairly pure benzoyl peroxide by iodometric assay (97%) and mixed m. p. 104–105° (dec.) with a sample of purified benzoyl peroxide (m. p. 106–107° (dec.)).

(2) **Diethyl Cellosolve.**—A solution of benzoyl peroxide (0.1990 *M*) in diethyl Cellosolve was kept under air at 30° as above for sixty-eight hours. At this time the peroxide content had increased to 0.2405 *M*. (The peroxide concentration of the same solution sealed under nitrogen decreased to 0.0446 *M* during this time.) Benzoyl peroxide (assay 97%) was recovered in nearly quantitative yield; m. p. 104–106° (dec.); mixed m. p. 105–106° (dec.).

(3) **Diethyl Ether.**—Similar results were obtained with a 0.1515 *M* solution of the peroxide in ether sealed under much air in a large ampule. After thirty-one hours at 30° (during which time the peroxide concentration of a sample under nitrogen decreased to less than one-half its initial value) there was practically quantitative recovery of peroxide: assay 99%; 0.5° depression observed in mixed m. p.

(b) **By Quinone and Hydroquinone.**—A solution of benzoyl peroxide (0.2015 *M*) and *p*-quinone (0.002 *M*) in dioxane was sealed under nitrogen and kept at 30° for eighty-eight hours. The peroxide concentration at this point was 0.195 *M*. Worked up as described previously, benzoyl peroxide (assay 96.6%) was recovered in 94% yield; 1° depression in mixed melting point. A repetition of this experiment using hydroquinone in place of quinone gave similar results.

(c) **By Methyl Methacrylate and Styrene.** (1) **Dioxane.**—A solution of benzoyl peroxide¹⁸ (initially 0.1930 mole/kg.) and methyl methacrylate (1.0 *M*) in dioxane was sealed under nitrogen and kept at 30 ± 0.2° for eighty-seven hours. At this point the peroxide concentration in the viscous solution was 0.1920 mole/kg. A 5.11-g. sample was added to 110 ml. of methyl alcohol. The precipitated polymer was filtered and dried; yield 86%. The filtrate was added to 200 ml. distilled water and the precipitate was filtered and dried. There was thus obtained benzoyl peroxide somewhat contaminated with polymer; yield > 100%; assay 88%; 1.5° depression in mixed melting point.

A similar experiment was conducted using styrene (1.0 *M*) in place of methyl methacrylate. After one hundred fourteen hours at 30° the peroxide concentration had decreased from 0.1980 mole/kg. to 0.1925 mole/kg.; yield of polymer 33%; yield of recovered benzoyl peroxide 92.5%; assay 97%; 0.5° depression in mixed m. p.

(2) **Diethyl Cellosolve.**—A solution of benzoyl peroxide (0.233 mole/kg.) and methyl methacrylate (1.0 *M*) in diethyl Cellosolve was kept at 30° under nitrogen. After ninety hours the peroxide concentration was 0.234 mole/kg. Benzoyl peroxide was not recovered but the yield of dried polymer was 88%.

In a similar experiment using styrene in place of methyl methacrylate, the peroxide concentration decreased from 0.238 mole/kg. to 0.235 mole/kg. during one hundred sixty hours at 30°; yield polymer 30%. Yield of recovered benzoyl peroxide was 88%; assay 97.7%; no depression in mixed melting point.

Summary

1. In the decomposition of ~0.2 *M* benzoyl peroxide in a number of solvents at 30 ± 0.2° in the absence of air, both the reaction rates and the kinetic dependence have been found to vary considerably. In general, aromatic hydrocarbons give the lowest rates and exhibit first order kinetics.

2. In dioxane, diethyl Cellosolve and diethyl ether, the rates of decomposition of benzoyl peroxide at 30 ± 0.2° in the absence of air are markedly accelerated in comparison with the rates in aromatic solvents. This rapid decomposition has been shown to be susceptible to inhibition. On the basis that a chain mechanism is involved, kinetic expressions for the derivation of rate constants have been derived and applied. In these solvents at 30°, decomposing benzoyl peroxide evolves considerably less than one mole of carbon dioxide per mole of peroxide.

SCHENECTADY, N. Y.

RECEIVED MAY 8, 1946

(18) By expressing the concentration of peroxide on a weight basis in experiments with polymerizing monomers, errors due to the pipetting of viscous solutions were minimized.