Summary

1. A mechanism for the polymerization of urea–formaldehyde resins, based on the view that urea is an amino acid amide has been suggested. The polymerization is postulated as proceeding in two stages: first, the formation of trimethylenetriamine rings from methylene urea or the monomeric methylene methylol urea, and then the formation of methylene-bis-amide links to tie the rings together to form a cross-linked molecule.

2. As support for this theory, resins have been prepared from the reaction of glycinamide and ϵ-aminocaproamide with formaldehyde. The composition of these resins indicates that they are composed of trimethylenetriamine rings linked by methylene bridges between amide groups on different rings.

3. The trimers of the methylene-imine derivative of glycine methylamide and urethan have been prepared.

4. Sarcosinamide appears to react with formaldehyde to give a low molecular weight linear polymer.

URBANA, ILLINOIS RECEIVED MAY 22, 1946

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Kinetics of Decomposition of Benzoyl Peroxide in Solvents. I

BY KENZIE NOZAKI[1] AND PAUL D. BARTLETT

Introduction.—Despite a considerable amount of able investigation of the thermal decomposition of acyl peroxides,[2] one encounters many unanswered questions in the attempt to deal kinetically with peroxide-induced polymerization. Perhaps the simplest of these questions concerns the kinetic order of the decomposition. This decomposition is so nearly unimolecular that it is usually treated as such,[2,3,4] but its rate definitely varies with concentration.[4,5] Brown[5] showed that this variation could be accounted for on the basis of concurrent first- and second-order decompositions, and he assigned velocity constants to these processes.

In view of our observation[6] that the decomposition of benzoyl peroxide can be strongly induced by free radicals, it seems likely that such decomposition is induced in part by the radicals normally present in a solution of decomposing benzoyl peroxide. The result of this would be a reaction of higher order accompanying the unimolecular decomposition. All the observed decomposition products of benzoyl peroxide can be fitted into this scheme, the following example showing how one of these products, phenyl benzoate, might be formed as a product of the chain reaction. Every other product of the decomposition can be formulated as arising in a more or less similar fashion.

$$C_6H_5COO{-}OOCC_6H_5 \longrightarrow 2C_6H_5COO{-} \qquad (1)$$

$$2C_6H_5COO{-} \longrightarrow CO_2 + C_6H_5COOC_6H_5 \qquad (2)$$

$$C_6H_5COO{-} + C_6H_5COO{-}OOCC_6H_5 \longrightarrow CO_2 + C_6H_5COOC_6H_5 + C_6H_5COO{-} \qquad (3)$$

In general the benzoate radicals will also attack the solvent, as they are known to do in the case of benzene.[7] If such attack (chain transfer to the solvent) results in new free radicals which are more stable and less reactive than the benzoate radicals, the effect of the solvent should be to suppress the chain decomposition shown in equation 3. If, on the other hand, chain transfer to the solvent yields new radicals comparable in activity to the old, this process will affect only the products and not the kinetics of the over-all reaction. The special case in which chain transfer to the solvent results in a change in the chain-terminating reaction will be dealt with in a forthcoming paper.

In order to test the reality of this picture of the decomposition of benzoyl peroxide, we have first established that a part of the decomposition of benzoyl peroxide in common solvents is of chain character (a) by showing that it responds to inhibitors, and (b) by inducing it with known free radicals. Next a survey has been made of the over-all rates of decomposition of benzoyl peroxide in a series of solvents. Finally, a kinetic equation derived from the chain mechanism has been rigorously tested in a number of solvents and velocity constants determined for the spontaneous and induced parts of the decomposition.

The Effect of Inhibitors on Benzoyl Peroxide Decomposition.—If the decomposition of benzoyl peroxide can be induced by free radicals, the addition of inhibitors for radical chain reactions to benzoyl peroxide solutions should result in a decreased rate of decomposition. It is evident from Table I that such is the case.

Oxygen, hydroquinone, *p-t*-butylcatechol, *m*-dinitrobenzene and picric acid are all inhibitors for the reaction. This evidence not only supports induced decomposition but also renders unlikely Price's suggestion[8b] that the recombination of two benzoate radicals to reform benzoyl peroxide is

---

(1) Pittsburgh Plate Glass Fellow.

(2) For historical references see McClure, Robertson and Cuthbertson, *Can. J. Research*, **20B**, 103–113 (1942).

(3) Kamenskaya and Medvedev, *Acta Physicochim., U. R. S. S.*, **13**, 565 (1941).

(4) Bartlett and Altschul, THIS JOURNAL, **67**, 816 (1945).

(5) D. J. Brown, *ibid.*, **62**, 2657 (1940).

(6) Bartlett and Nozaki, *ibid.*, **68**, in press (1946).

(7) Gelissen and Hermans, *Ber.*, **59**, 662 (1926); Wieland, Popper and Seefried, *ibid.*, **55**, 1816 (1922); Hey, *J. Chem. Soc.*, 1966 (1934).

(8) (a) Price, *Ann. N. Y. Acad. Sci.*, **44**, 351 (1943); (b) *ibid.*, p. 365; (c) Matheson, *J. Chem. Phys.*, **13**, 584 (1945).

TABLE I

THE EFFECT OF INHIBITORS ON THE DECOMPOSITION OF BENZOYL PEROXIDE IN ACETIC ANHYDRIDE AT 79.8°
$((Bz_2O_2)_0 = 0.20\ M)$

Inhibitor	Concn., m./l.	% Dec. after 6.25 hr.
None	..	92.7
Air	..	89.8
Oxygen	..	82.5
Hydroquinone	0.21	79.0
p-*t*-Butylcatechol	.21	67.5
m-Dinitrobenzene	.21	58.8
Picric acid	.21	48.0

an important reaction in non-reactive solvents. It also becomes probable that the interaction of the two benzoate radicals as a result of the "cage effect"[8c] leads chiefly to decomposition products rather than to regeneration of peroxide.

The Effect of Added Free Radicals on Benzoyl Peroxide Decomposition.—When hexaphenylethane, pentaphenylethane or tetraphenylhydrazine was added to reaction mixtures, the rate of benzoyl peroxide decomposition was increased considerably (Table II). The great efficiency of tetraphenylhydrazine as a decomposition accelerator may be related to its being an amine, and not due entirely to free radicals (see Table III).

TABLE II

THE DECOMPOSITION OF BENZOYL PEROXIDE AT 79.8° IN BENZENE $((Bz_2O_2)_0 = 0.197\ M)$

Added substances	Concn. m./l.	% Dec. of Bz_2O_2 10 Min.	1 Hr.	4 Hr.
None			15.5	50.4
$(C_6H_5)_3CC(C_6H_5)_3$	0.206		58.8	84.5
$(C_6H_5)_3CCH(C_6H_5)_2$	.206		32.1	68.7
$(C_6H_5)_2NN(C_6H_5)_2$	.208	47.6	94.0	

The Decomposition of Benzoyl Peroxide in Different Solvents at 79.8°.—The rate of decomposition has been measured in over thirty different solvents and the data are summarized in Table III. The results are listed as percentage decomposition of a 0.197 *M* solution of benzoyl peroxide after heating at 79.8° for the given time interval. All solvents were freshly distilled before use and the measurements were made under oxygen-free conditions.

By way of a rough generalization, the order of increasing rates of decomposition appears to be as follows: highly halogenated solvents < most aromatics < most aliphatics < ethers, alcohols, monohydric phenols < amines. In this paper studies on the decomposition of benzoyl peroxide in only the first three groups will be reported. Despite the high position of phenols as accelerating solvents, dihydric phenols such as hydroquinone and *t*-butylcatechol, which can lose a hydrogen atom to yield a stabilized semiquinone radical, are inhibitory, as is the highly nitrated picric acid.

TABLE III

THE DECOMPOSITION OF BENZOYL PEROXIDE AT 79.8°

Solvent	Per cent. decomposition 10 Min.	30 Min.	1 Hr.	2 Hr.	4 Hr.
Tetrachloroethylene			13.0		35.0
Carbon tetrachloride			13.5		40.0
Cyclohexene			14.0		39.5
Methyl benzoate			14.5		41.4
Anisole			14.0		43.0
Chloroform			14.5		43.7
Ethylbenzene			15.0		45.5
Chlorobenzene			18.0		48.5
Nitrobenzene			15.5		49.0
Benzene			15.5		50.4
Toluene			17.4		49.5
Allyl acetate			17.0		52.3
Styrene			19.0		..
Cumene			20.0		53.3
Iodobenzene			18.0		55.8
Carbon disulfide			19.0	32.6	..
Ethyl iodide			23.4		61.2
Methylene chloride			24.5		62.2
Ethyl chloride			26.0		64.7
Bromobenzene			26.3		69.0
t-Butylbenzene			28.5		69.5
Acetone			28.5	43.0	
Maleic anhydride		20.3			
Ethyl bromide			33.6		71.8
Allyl bromide			37.2	69.0	
Acetic anhydride		32.5	48.5	64.0	
Cyclohexane		34.0	51.0		84.3
Ethyl acetate			53.5		85.2
Acetic acid			59.3		87.4
Pyridine		57.0	77.3		
Dioxane		67.6	82.4		
Diethyl ether	75.2				
Ethyl alcohol	82.2				
m-Cresol	87.7				
Aniline, triethylamine, etc.		Explosive reaction			

Derivation of the Kinetic Equations.—The simplest kinetic equations for induced decomposition of benzoyl peroxide are those which may be derived by assuming equations 1–3 or their equivalent. Equations 1–3 may be written

$$P \xrightarrow{k_1} 2R$$

$$2R \xrightarrow{k_3} RR$$

$$R + P \xrightarrow{k_4} X + R$$

where *P* denotes peroxide, *R* any free radical and *X* the product or products of the chain decomposition. There is no k_2 in this scheme because we reserve this constant for the chain-propagating step in olefin polymerization. The concentration of free radicals at the steady state is expressed by making the usual approximation

$$\mathrm{d}R/\mathrm{d}t = k_1P - k_3R^2 \cong 0$$

$$R = \sqrt{k_1P/k_3}$$

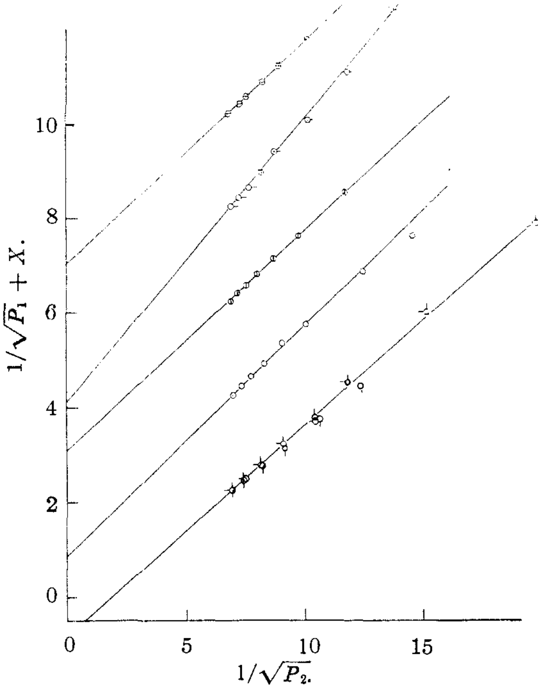

Fig. 1.—Benzoyl peroxide decomposition in solvents at 79.8°: ⊖, carbon tetrachloride ($X = 8$); ⊙-, *t*-butyl benzene ($X = 6$): ⦶, ethyl iodide ($X = 4$); ⊙, cyclohexene ($X = 2$); ⊙̇, benzene ($X = 0$): ·⊙. toluene ($X = 0$); and ♀, nitrobenzene ($X = 0$).

The rate of decomposition of peroxide is then

$$\frac{-\mathrm{d}P}{\mathrm{d}t} = k_1P + k_4PR = k_1P + k_4\sqrt{\frac{k_1}{k_3}}\,P^{3/2}$$

$$= k_1P + k_iP^{3/2} \quad \text{where } k_i \equiv k_4\sqrt{\frac{k_1}{k_3}}$$

This equation may be integrated to give

$$\ln\frac{a + \sqrt{P}}{\sqrt{P}} - \ln\frac{a + \sqrt{P_0}}{\sqrt{P_0}} = \frac{k_1t}{2} \qquad (4)$$

where $a = k_1/k_i$.

The same equation can be derived on the assumption that every radical from the peroxide attacks the solvent, yielding a new radical by chain transfer which in turn may induce the decomposition of a peroxide molecule. Certain intermediate cases lead to more complicated kinetic equations.

A description of the peroxide decomposition in terms of the "cage effect"[8c] introduces further details of mechanism, but leads to a differential equation of the same form under certain assumptions. Thus, if all the benzoate radicals formed by dissociation of benzoyl peroxide either (a) react together as the original pairs with rate constant k_x or (b) become separated by chain transfer to the solvent (with rate constant k_t) then the peroxide disappears by the equation

$$-\mathrm{d}P/\mathrm{d}t = k_1P + k_iP^{3/2}$$

where $k_i = k_3\sqrt{k_1k_t/k_4(k_x + k_t)}$

The same equation would apply if k_t had the significance of the rate constant for a benzoate radical's diffusing out of contact with its partner.

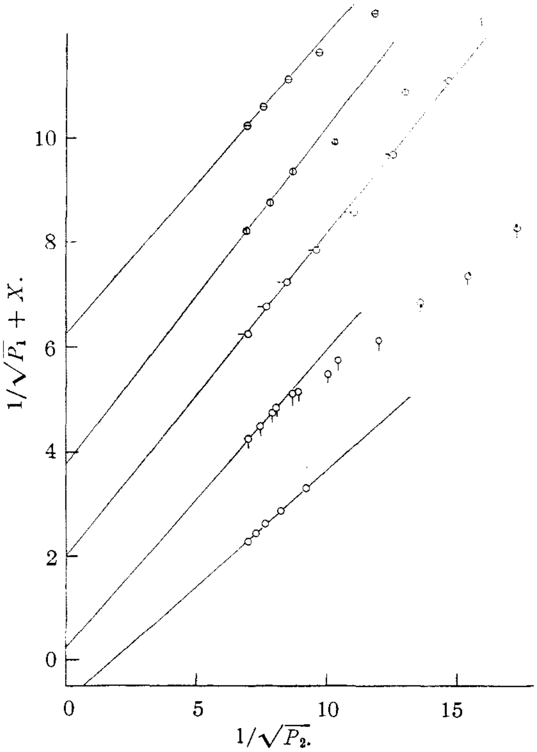

Fig. 2.—Benzoyl peroxide decomposition in solvents at 79.8°: ⊖, ethyl acetate ($X = 8$); ⦶, acetic acid ($X = 6$): -⊙, cyclohexane ($X = 4$); ♀, acetic anhydride ($X = 2$): and ⊙ acetic anhydride + reaction products ($X = 0$).

The value of the ratio a in any solvent may be determined experimentally by using data from two runs with different initial concentrations of peroxide and with samples taken at the same time intervals in the two runs. After the same time, the value of the right-hand member of equation 4 is the same for both runs, and the logarithmic terms may be equated. If P_1 and P_2 are the peroxide concentrations at equal times in the two runs, one obtains

$$\ln\frac{a + \sqrt{P_1}}{\sqrt{P_1}} = \ln\frac{a + \sqrt{P_2}}{\sqrt{P_2}} + \ln C \qquad (5)$$

which may be converted to the form

$$\frac{1}{\sqrt{P_1}} = \frac{C}{\sqrt{P_2}} + \frac{C - 1}{a} \qquad (6)$$

From a plot of $1/\sqrt{P_1}$ against $1/\sqrt{P_2}$ a straight line should be obtained from whose slope and *Y*-intercept a may be calculated.

Rate Measurements at 79.8°.—Kinetic measurements of benzoyl peroxide decomposition in eleven of the solvents listed in Table III have been carried out under oxygen-free conditions and the equations derived above have been applied to them. The experimental results in

TABLE IV

THE DECOMPOSITION OF BENZOYL PEROXIDE IN BENZENE AT 79.8°

Run 1				Run 2			
t, hr.	P M/L	$\frac{1}{\sqrt{P}}$	$\ln \frac{a + \sqrt{P}}{\sqrt{P}}$	t, hr.	P M/L	$\frac{1}{\sqrt{P}}$	$\ln \frac{a + \sqrt{P}}{\sqrt{P}}$
0.00	0.197	2.25	1.004	0.00	0.0206	6.98	1.848
1.00	.166	2.45	1.058	1.00	.0179	7.46	1.905
2.25	.131	2.75	1.135	2.25	.0149	8.20	1.987
4.00	.0975	3.20	1.241	4.00	.0120	9.12	2.079
6.00	.0703	3.77	1.361	6.00	.00900	10.50	2.203
8.25	.0485	4.53	1.500	8.25	.00700	11.90	2.310
12.00	.0277	6.00	1.723	12.00	.00429	15.2	2.537
16.25	.0159	7.90	1.953	16.25	.00256	19.8	2.783

TABLE V

THE DECOMPOSITION OF BENZOYL PEROXIDE IN SOLVENTS AT 79.8°: TABLE OF CONSTANTS

Solvent	a	k_1, hr.$^{-1}$	k_i, $(M/L)^{-1/2}$ hr.$^{-1}$
Carbon tetrachloride	0.563	0.075	0.133
Benzene	.767	.118	.154
Toluene	.767	.118	.154
Nitrobenzene	.767	.118	.154
t-Butylbenzene	.214	.118	.552
Cyclohexene	.417	.0695	.167
Ethyl iodide	.593	.145	.244
Cyclohexane	.195	.229	1.17
Ethyl acetate	.245	.323	1.32
Acetic acid	.159	.293	1.84
Acetic anhydride	.245	.270	1.10
Acetic anhydride + reaction products	.753	.242	0.321

benzene, which are typical, are shown in Table IV. For the seven solvents in which the reaction is slowest, carbon tetrachloride, cyclohexene, nitrobenzene, benzene, toluene, ethyl iodide and t-butylbenzene, plots of $1/\sqrt{P_1}$ against $1/\sqrt{P_2}$ gave straight lines from which a was calculated. Plots of $\ln (a + \sqrt{P})/\sqrt{P}$ against time resulted in straight lines (Fig. 4), as predicted by equation 4, and k_1 was determined from the slopes of these lines. The values of a and k_1 together with values of k_i, calculated using the relationship $k_i = k_1/a$, are summarized in Table V. The results obtained with the four solvents in which benzoyl peroxide decomposition was most rapid (excluding amines, ethers, alcohols and phenols) were somewhat different. Although a plot of $1/\sqrt{P_1}$ against $1/\sqrt{P_2}$ resulted in a straight line with cyclohexane, this was not the case with acetic

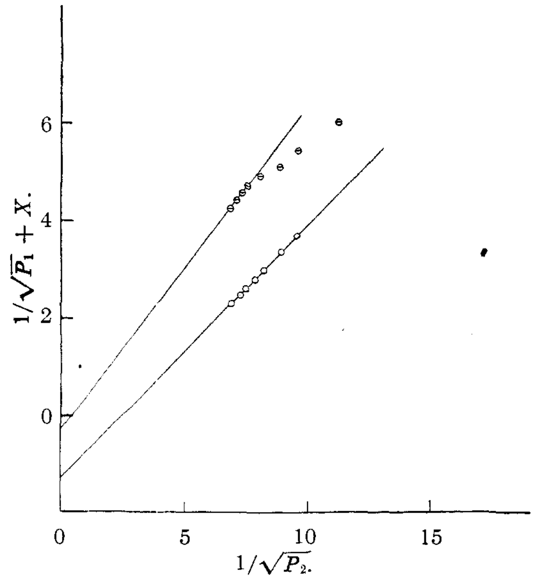

Fig. 3.—Benzoyl peroxide decomposition in solvents at 60.0°: ⊖, acetic anhydride ($X = 2$); and ⊙, benzene ($X = 0$).

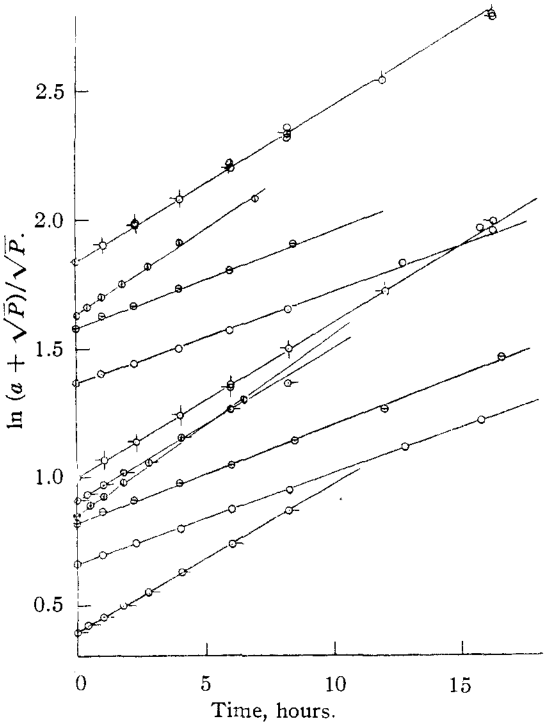

Fig. 4.—Benzoyl peroxide decomposition in solvents at 79.8°: ϕ, benzene (a = 0.767): -⊙, toluene (a = 0.767); ọ, nitrobenzene (a = 0.767); ⦶, ethyl iodide (a = 0.593); ⊖, carbon tetrachloride (a = 0.563); ⊙, cyclohexene (a = 0.417): and ⊙-, t-butylbenzene (a = 0.214).

anhydride, ethyl acetate and acetic acid (Fig. 2). For the last three solvents a definite decrease in slope occurred as the reaction proceeded and the initial slope was used in the calculation of a. Plots of $\ln (a + \sqrt{P})/\sqrt{P}$ against time did not result in straight lines for the four solvents (Fig. 5). Instead, a definite falling off with time, generally greater in the more concentrated solutions, was observed. The rate constants summarized in Table V were calculated from the initial slopes of the curves.

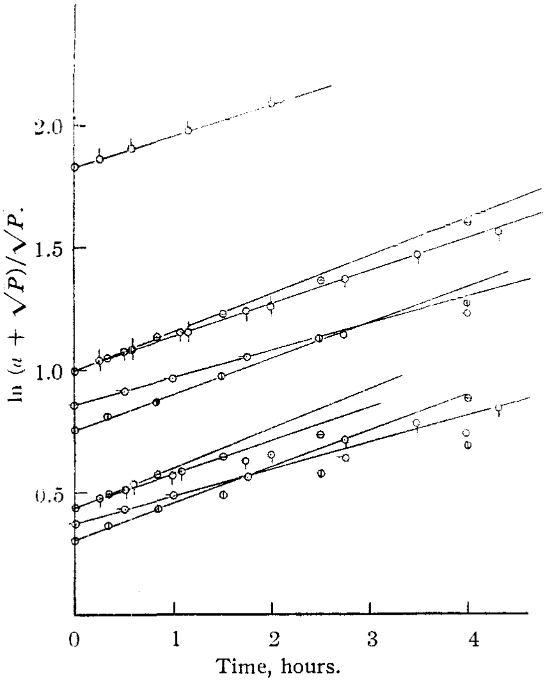

Fig. 5.—Benzoyl peroxide decomposition in solvents at 79.8°: ȯ, acetic anhydride + reaction products (a = 0.753); ⊖, ethyl acetate (a = 0.245); ♀, acetic anhydride (a = 0.245); ·⊙, cyclohexane (a = 0.195); and ⦶, acetic acid (a = 0.159).

Since the rate constants for benzoyl peroxide decomposition in cyclohexane, acetic anhydride, acetic acid and ethyl acetate are much greater than in aromatic solvents, it seemed possible that aromatic substances could act as inhibitors for benzoyl peroxide decomposition in these solvents. Since the decomposition of benzoyl peroxide results in aromatic products, these substances might be responsible for the falling off of the rate of reaction with time. The amount of this inhibition should increase as larger fractions of the peroxide are decomposed and it should be most noticeable in solutions containing a high initial concentration of peroxide. The slower solvents should show little or none of this inhibition since the solvents themselves are comparable as inhibitors to the products from the decomposition of benzoyl peroxide. Our experimental results are in agreement with these expectations. The constants for the aliphatic solvents, determined by extrapolation of straight lines through a few early points, are of course less reliable than those for the aromatic solvents.

To test this explanation a 0.197 M solution of benzoyl peroxide in acetic anhydride was heated at 80° until all of the peroxide had decomposed. The reaction mixture was used as the solvent for the decomposition of some additional benzoyl peroxide. Kinetic studies indicated that the rate of decomposition was slower than in pure acetic anhydride and that the rate no longer fell off within a run (Figs. 2, 5). The calculated rate constants (Table V) show that k_1 was decreased very slightly and k_i was decreased three and a half times.

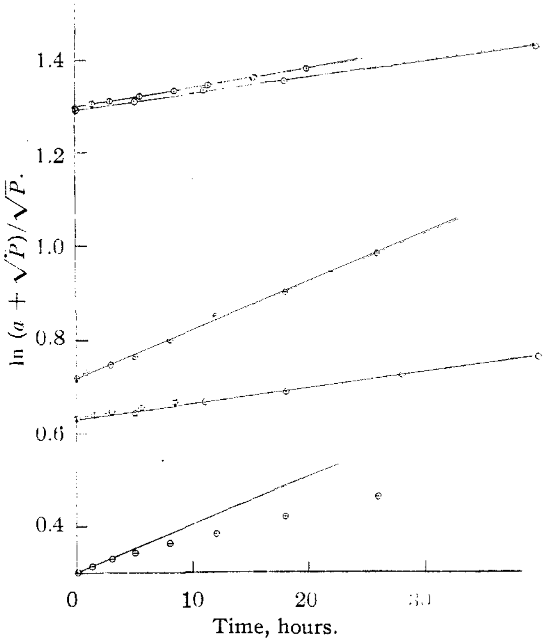

Fig. 6.—Benzoyl peroxide decomposition in solvents at 60.0°: ⊙, benzene (a = 0.386); ⊖, acetic anhydride (a = 0.152); and ⦶, styrene (a = 0.386).

Rate Measurements at 60°.—A study of the rate of benzoyl peroxide decomposition in benzene and acetic anhydride at 60° was made to determine the activation energies of the unimolecular and induced reactions in these solvents. The data plotted in Figs. 3 and 6 enabled us to calculate the constants summarized in Table VI.

TABLE VI

THE DECOMPOSITION OF BENZOYL PEROXIDE IN SOLVENTS

Solvent	Temp., °C.	a	k_1, hr.$^{-1}$	k_i, $(M/L)^{-1/2}$ hr.$^{-1}$	E_1	E_i
Acetic anhydride	60.0	0.152	0.0200	0.132	30,700	25,000
Acetic anhydride	79.8	.245	.270	1.10		
Benzene	60.0	.386	.00700	0.0181	33,300	25,230
Benzene	79.8	.767	.118	0.154		

Application of the Arrhenius equation gave the tabulated activation energies. It is observed that the unimolecular reaction has a higher activation energy than the induced one, resulting in more chain decomposition at lower temperatures. The value of E_1 in benzene is greater than the values reported by Kamenskaya and Medvedev[3] (29.6 kcal.) and by McClure, Robertson and Cuthbertson[2] (31.0 kcal.) in this solvent. If this difference is significant it is due to the fact that the values of these workers referred to the over-all rate, including unresolved chain decomposition with a lower activation energy. Since k_i is a composite rate constant, the activation energy E_i does not refer to a single reaction but is made up of contributions from all the elementary reactions in the system.

A study of the kinetics of benzoyl peroxide decomposition in styrene was made at 60°. On account of difficulties introduced by the polymerization of the styrene, the accuracy was poorer than in other solvents. Since the data did not permit an accurate determination of a from a plot of $1/\sqrt{P_1}$ against $1/\sqrt{P_2}$, the value of a in benzene was used. With this value of 0.386 it was found that a plot of ln $(a + \sqrt{P}/\sqrt{P}$ against time gave straight lines (Fig. 6). From the slopes of the two plots made in this way k_1 was found to be equal to 7.58 and 8.10×10^{-3} hr.$^{-1}$ for the concentrated and dilute runs, respectively. The corresponding values of k_i are 1.96 and 2.09×10^{-2} (m./l.)$^{-1/2}$ hr.$^{-1}$. These values of k_1 and k_i are reasonably close to those in benzene, although the free radicals responsible for the induced decomposition are presumably different in the two solvents.

Induced Peroxide Decomposition and Polymerization.—The assumption of a unimolecular decomposition of benzoyl peroxide and the usual free radical mechanism[8a] for vinyl polymerization leads to a predicted linear relation between log M (M = monomer concentration) and $\sqrt{P}$. Such a plot applied to the data in Table VII gives curves for the two runs which differ in slope by 60%. On the other hand, the assumption of both unimolecular and chain decomposition of the peroxide leads to the relation

$$\log M = \log (\sqrt{P} + a) + \text{constant} \qquad (7)$$

With a value of $a = 0.386$, a plot of log M against log $(\sqrt{P} + a)$ results in lines with slopes of 17.8 and 18.1 for the runs with high and low peroxide concentrations, respectively.

The occurrence of chain decomposition of benzoyl peroxide is significant also in connection with the variation, previously noted,[9] in the efficiency of polymerization of allyl acetate by different concentrations of benzoyl peroxide. If every peroxide molecule decomposing were to give rise to the same number of polymerization chains, no variation in dM/dP would be expected with changing peroxide concentration. However, every peroxide molecule which decomposes by reaction with a free radical is wasted as far as initiating polymerization chains is concerned, since it consumes a free radical for each one produced. Chain decomposition of peroxide can account for part of the variation in dM/dP with peroxide concentration, while a further part must be due to reaction of radicals with one another prior to initiation of polymerization chains. Although values of k_1 and k_i can be computed for allyl acetate as solvent, these are not significant since the free radical concentration in allyl acetate is not proportional[4] to the square root of P. It should be noted also that some departure from this proportionality must occur in any solvent which shows a tendency to inhibit the chain decomposition. Such an inhibitory effect means that active free radicals have been converted into less active or into inactive ones by reaction with the solvent, and thus the disappearance of chain carriers is no longer by a bimolecular reaction of them alone. In the limiting case in which radicals from the peroxide react with the solvent or with new peroxide molecules but not with one another, and the radicals arising from the solvent produce no chain reaction, the kinetics of peroxide decomposition would be described by the equation of D. J. Brown.[5] Qualitatively, then, we can say that the less important the chain decomposition is, the more likely it is to be of second rather than three-halves order with respect to peroxide. In such a case, there should be a linear relation between $1/P_1$ and $1/P_2$ rather than between $1/\sqrt{P_1}$ and $1/\sqrt{P_2}$. In the case of acetic anhydride (Fig. 2) this way of plotting the data is fully as satisfactory as the use of Equation (6), as would be expected if inhibitors are present.

TABLE VII

THE DECOMPOSITION OF BENZOYL PEROXIDE IN STYRENE AT 60°

t, hr.	(Styrene) m./l.	log (Styrene)	P, m./l.	$1/\sqrt{P}$	ln $(a + \sqrt{P})/\sqrt{P}$
			Run 1		
0.00	8.35	0.922	0.1906	2.290	0.6348
1.50	7.43	.871	.1858	2.320	.6396
3.00	6.70	.826	.1810	2.350	.6470
5.50	5.42	.734	.1735	2.400	.6555
8.50	4.06	.609	.1662	2.452	.6670
			Run 2		
0.00	8.70	0.9395	0.02090	6.910	1.299
1.50	8.34	.9212	.02055	6.975	1.306
3.00	8.04	.9053	.02025	7.030	1.312
5.50	7.50	.8751	.01962	7.135	1.323
8.50	6.99	.8445	.01900	7.250	1.335
11.50	6.46	.8102	.01840	7.370	1.346
15.50	5.81	.7642	.01766	7.525	1.363
20.00	5.15	.7118	.01677	7.720	1.381

The Order of Decomposition Rates in Different Solvents.—The extreme variation in k_1 revealed in Table V is from 0.0695 for cyclohexene

---

(9) Ref. 4, p. 820.

to 0.323 for ethyl acetate, or about 4.5-fold. The extreme variation in k_i is from 0.133 for carbon tetrachloride to 1.84 for acetic acid, or about 14-fold. The order of over-all rates in which the solvents fall in Table III is very nearly that of k_i and not of k_1, so that the induced decomposition is seen to be the chief, though not the only, factor in the variation of rate from one solvent to another.

There are probably two different mechanisms involved in the action of solvents to diminish chain decomposition of benzoyl peroxide. Aromatic and unsaturated solvent molecules react with free radicals by addition to yield new radicals. With saturated solvent molecules a free radical can react by removal of an atom, leaving a new radical which is a fragment of the solvent molecule. Whether these radicals from the solvent react preferentially with other free radicals or with benzoyl peroxide must determine the extent to which the solvent limits chain decomposition. In general the stabler free radicals show the greater reactivity toward other radicals in preference to attacking molecules. The radical CCl_3 must be relatively inactive toward benzoyl peroxide, although this would not necessarily have been predicted in view of its ability to participate in the polymerization of styrene.[10]

Experimental

Reagents.—*Benzoyl peroxide* from the Eastman Kodak Company was twice precipitated from a chloroform solution with methanol and was dried by evacuation on an oil pump for two days. The *carbon tetrachloride*, *acetic acid*, *acetic anhydride*, *ethyl alcohol*, *benzene* and *toluene* were taken from freshly opened bottles of analytical reagents. The *t-butylbenzene*, *cyclohexene* and *ethyl iodide*, Eastman Kodak Company products, were distilled through an eight-inch Widmer column. The *nitrobenzene* was dried over phosphorus pentoxide, purified by two crystallizations, and then distilled through a 50 theoretical-plate column; b.p. 81° (12–13 mm.). The *cyclohexane* was heated with a nitrating mixture at its boiling point for one hour. After washing and drying, it was twice crystallized and was then distilled through a 50 theoretical-plate column; m. p. 6.5°. The allyl acetate data reported are those of Bartlett and Altschul.[4]

Experimental Procedure.—Benzoyl peroxide was weighed out and then dissolved and made up to volume in a solvent. Samples (generally 1 cc.) of solution were pipetted into drawn-out test-tubes, the solutions were exhaustively evacuated, and the tubes were sealed under vacuum. The evacuation procedure consisted of cooling in a Dry Ice–alcohol mixture, evacuation on an oil pump for fifteen minutes and warming to room temperature with dissolution of the peroxide. This was repeated twice before sealing. The tubes were completely immersed in an oil thermostat regulated to ±0.01°.

The analytical procedure involved the use of acetic anhydride as the solvent and powdered sodium iodide as the source of iodine. After allowing ten minutes for the liberation of iodine, water was added and the iodine was titrated to a starch end-point with 0.1 *N* thiosulfate for the concentrated solution and 0.01 *N* thiosulfate for the dilute solution. A positive correction of 0.13 cc. of 0.01 *N* thiosulfate was applied to the end-point.

Summary

The thermal decomposition of benzoyl peroxide in a number of solvents is shown to consist of a spontaneous unimolecular decomposition accompanied by a chain decomposition induced by free radicals. The kinetics is that of simultaneous first- and three-halves-order reactions in some cases, and first- and second-order in others. The equations are derived and the velocity constants determined in eleven solvents. The chain decomposition can be retarded by inhibitors (including oxygen), accelerated by foreign free radicals, is greater in most aliphatic than in aromatic solvents, is relatively more prominent at lower than at higher temperatures, and is the chief though not the only cause of variations in the rate of decomposition of benzoyl peroxide from one solvent to another.

CAMBRIDGE 38, MASS. RECEIVED JANUARY 17, 1946

---

[10] Breitenbach and Maschin, *Z. physik. Chem.*, **A187**, 175 (1940).

[CONTRIBUTION FROM THE DEPARTMENT OF SANITARY ENGINEERING, HARVARD GRADUATE SCHOOL OF ENGINEERING

The Mechanism of the Hydrolysis of Chlorine

BY J. CARRELL MORRIS

A few years ago Shilov and Solodushenkov,[1] employing the experimental technique originally developed by Hartridge and Roughton,[2] succeeded in measuring the extremely rapid rate of hydrolysis of chlorine. They found the reaction to be substantially complete in less than a second even at 1°. Their results were interpreted on the basis of the reaction

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^- \qquad (1)$$

which led to the kinetic equation

$$-d[Cl_2]/dt = m[Cl_2] - n[HOCl][H^+][Cl^-] \quad (1)$$

The published results of Shilov and Solodushenkov are shown in Table I. The first five columns contain their data and calculations; the other columns list figures obtained in later paragraphs of this paper. In the table the symbol *A* stands for the analytical concentration of the chlorine solution in moles per liter before dilution; *a* is the analytical concentration after dilution. The equilibrium constant for chlorine hydrolysis according to Jakowkin[3] is represented by *K*, the

---

[1] Shilov and Solodushenkov, *Compt. rend. acad. sci. l'URSS*, **3**, No. 1, 17 (1936).

[2] Hartridge and Roughton, *Proc. Roy. Soc. London*, **A104**, 376 (1923).

[3] Jakowkin, *Z. physik. Chem.*, **29**, 655 (1899).