unsaturated hydrocarbons is essentially of the van der Waals type.

3. The general conclusions to be drawn from this work are remarkably similar to those of a previous investigation using several elementary gases as adsorbates. Specifically the differences in surface activity as shown by the heat measurements with hydrocarbons, as with the elementary gas adsorbates, appear to parallel the rubber reinforcing properties of the blacks which have been investigated.

4. We have found no marked difference between the differential heats of adsorption for the saturated and corresponding unsaturated hydrocarbons. Hence it may be said that the results so far lend no support to the theory that the reinforcing effect of carbon black in rubber is in some way associated with the unsaturated character of the latter. It is hoped that further experimental investigations now being planned may yield further evidence to check this point.

AMHERST, MASS. RECEIVED MARCH 26, 1947

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Decomposition of Benzoyl Peroxide in Solvents. II. Ethers, Alcohols, Phenols and Amines

BY PAUL D. BARTLETT AND KENZIE NOZAKI[1]

In a previous paper[2] it was shown that in solvents which do not markedly accelerate the decomposition of benzoyl peroxide, this decomposition is of mixed order and can be resolved kinetically into a spontaneous unimolecular reaction and a radical-induced chain reaction which is of higher order. In this paper we report an investigation of the decomposition of benzoyl peroxide in solvents which have a strongly accelerating effect upon the decomposition.

Experimental Results

The Decomposition of Benzoyl Peroxide in Ethers.—Earlier it was found that the decomposition of benzoyl peroxide in dioxane and ethyl ether was much faster than in most other solvents.[2] To test the generality of the rapid reaction, a number of ethers were tried as solvents for the decomposition. The results summarized in Table I indicate that the ethers vary all the way from diethyl ether, in which the reaction is over 60% complete in five minutes, down to anisole and diphenyl ether, which behave as normal aromatic solvents in which the reaction is less than 15% complete in an hour. This is a range of more than 50-fold in rate of reaction under comparable conditions. Ethers containing phenyl and methyl groups appear to be less reactive than the others.

TABLE I

THE DECOMPOSITION OF BENZOYL PEROXIDE IN ETHERS AT 79.8°

Ether	% Decomposition of a 0.197 *M* solution 5 min.	10 min.	15 min.	30 min.	60 min.	240 min.
Dimethyl	2.7		11.2			
Diethyl	61.2	75.2				
Di-*i*-propyl	22.3		59.2			
Di-*n*-butyl	31.6		68.9			
t-Butyl methyl	10.1		26.8			
Divinyl			23.5	46.2		
Dioxane				67.6	82.4	
Anisole					14.5	47.3
Phenetole					59.6	93.3
Diphenyl					14.7	45.7

The effect of oxygen was determined since oxygen inhibition is a characteristic of many chain reactions involving free radicals. The results from the decomposition of benzoyl peroxide in *n*-butyl ether, listed in Table II, suggest that oxygen has a marked inhibitory effect. In fact, the iodometric peroxide titer of samples heated in air first decreased and then increased beyond the original value. This must have been due to the formation of new peroxides from the oxygen in the air. Free radicals from the decomposition of benzoyl peroxide were undoubtedly involved in the latter reaction since pure *n*-butyl ether was found to form no peroxide under the experimental conditions. The results listed in the table for the decompositions in air do not give a true indication of the amount of benzoyl peroxide decomposed because of the formation of new peroxides. However, it is evident that very little decomposed since over half of the benzoyl peroxide separated as fine white crystals when a mixture of *n*-butyl ether and benzoyl peroxide was cooled after having been heated in air for thirty minutes at 79.8°.

TABLE II

THE EFFECT OF OXYGEN ON THE DECOMPOSITION OF BENZOYL PEROXIDE IN *n*-BUTYL ETHER AT 79.8°

Conditions	% Decomposition of 0.2 *M* peroxide 5 min.	15 min.	30 min.
Vacuum	31.6	68.9	87.5
Air	2.7	0.7	−10.8

The decomposition of benzoyl peroxide accelerated by ether was carried out in the presence of vinyl acetate to determine whether free radicals capable of initiating polymerization were formed. Benzoyl peroxide was decomposed in 1:1 mixtures

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[1] Pittsburgh Plate Glass Fellow, 1943–1946.

[2] Part I: Nozaki and Bartlett, THIS JOURNAL, **68**, 1686 (1946). See also Cass, *ibid.*, **68**, 1976 (1946).

by volume of vinyl acetate and *n*-butyl ether. For comparison similar mixtures with cyclohexane in place of the ether were submitted to the same experimental conditions. The results are shown in Table III.

TABLE III

THE POLYMERIZATION OF VINYL ACETATE WITH 1.0% BENZOYL PEROXIDE

Solvent[a]	Temp., °C.	Time, hr.	% Polymerization	% Decomp. of Bz_2O_2
Cyclohexane	60	1.5	55.8	8.5
n-Butyl ether	60	1.5	48.7	9.2
Cyclohexane	25	24	24.2	0.7
n-Butyl ether	25	24	20.3	1.3

[a] Proportions by volume: 1 vinyl acetate, 1 solvent.

The principal result is a marked leveling effect of the vinyl acetate upon the rate of decomposition of peroxide, which is not very different in the 50% *n*-butyl ether solution from what it is in the 50% cyclohexane solution. What difference there is, however, is in the direction of *greater* decomposition of peroxide and *less* polymerization in the presence of the ether. It follows that (1) the free radicals normally involved in the decomposition of benzoyl peroxide in di-*n*-butyl ether must be readily captured by vinyl acetate in 1:1 mixtures by volume, and (2) the slight additional decomposition of peroxide in the presence of the ether does not give rise to additional polymerization. The latter conclusion is in harmony with our previous interpretation[2] of chain decomposition of peroxide as consuming one radical for each radical produced.

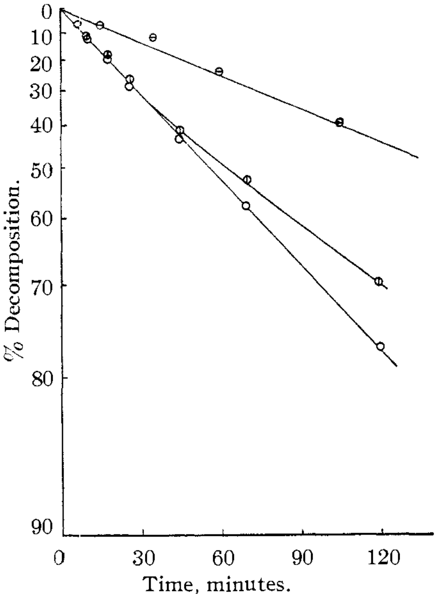

Fig. 1.—The decomposition of benzoyl peroxide in di-*n*-butyl ether at 60°: ○, $P_0 = 0.0212\ M$; ⦶, $P_0 = 0.195\ M$; ⊖, $P_0 = 0.0212\ M$, solvent 50% cyclohexane. The ordinate scale is proportional to log (100 − % decomposition), permitting this quantity to be plotted directly for a unimolecular reaction.

An investigation of the kinetics of benzoyl peroxide decomposition in *n*-butyl ether at 60° was made and the results are summarized in Table IV and plotted in Fig. 1. It appears that the decomposition may well be of first order with respect to benzoyl peroxide and retarded by the products of the reaction. The results from the decomposition in the 1:1 mixture of *n*-butyl ether and cyclohexane leave uncertain the order of the reaction with respect to ether.

TABLE IV

THE DECOMPOSITION OF BENZOYL PEROXIDE IN *n*-BUTYL ETHER AT 60°

Run 1 Ether alone		Run 2 Ether alone		Run 3 Cyclohexane–ether	
Time, min.	*P* m./l.	Time, min.	*P* m./l.	Time, min.	*P* m./l.
0.0	0.195	0.0	0.0212	0.0	0.0212
6.0	.180	6.0	.0198	15.0	.0195
10.0	.170	10.0	.0187	35.0	.0186
17.0	.159	17.0	.0171	60.0	.0160
26.0	.142	26.0	.0150	105.0	.0128
45.0	.114	45.0	.0119	165.0	.0107
70.0	.091	70.0	.0089	240.0	.0077
120.0	.059	120.0	.0048		

The products from the decomposition of benzoyl peroxide in *n*-butyl ether at 60° were investigated and the results are summarized in Table V.

TABLE V

THE DECOMPOSITION OF BENZOYL PEROXIDE IN *n*-BUTYL ETHER AT 60°

	Wt., g.	Moles
Original ether	7.8	0.060
Original Bz_2O_2	5.0	.0206
Carbon dioxide	0.29	.0066
Butene	..	< .0025
Butyraldehyde	Small amt.	
Butyl alcohol	None	
Solid acids (mostly benzoic acid)	2.4	
High boiling products	2.0	

Solid acids, mostly benzoic acid, accounted for about half of the original benzoyl peroxide. There was very little evidence as to the nature of the ether decomposition products. A similar analysis of products from the decomposition of benzoyl peroxide in ethyl ether indicated that less than one-tenth of a mole of acetaldehyde was produced per mole of benzoyl peroxide. Kharasch, Kane and Brown[3] isolated considerable quantities of ethyl *n*-butyrate and ethyl isobutyrate from solutions of *n*-butyryl and isobutyryl peroxides in ethyl ether, suggesting that esters in which the acid component is supplied by the acyl peroxide and the alcohol component by the ether are important products in the reaction under study. Very recently Cass[4] has shown clearly that benzoyl peroxide reacts with diethyl ether at

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(3) Kharasch, Kane and Brown, THIS JOURNAL, **63**, 526 (1941).

(4) Cass, *ibid.*, **69**, 500 (1947).

37° to give a good yield of benzoic acid and the acylal, α-ethoxyethyl benzoate, parallel results being obtained in the cases of dioxane and ethyleneglycol diethyl ether. It seems reasonable that these acylals might give rise to esters by decomposition at higher temperatures, and that our higher-boiling products may have consisted largely of such acylals and their decomposition products. If such is not the case, then the ether must have been attached at the higher temperature with cleavage at the carbon–oxygen bond.

The Decomposition of Benzoyl Peroxide in Alcohols.—The rate of oxygen decomposition of benzoyl peroxide in several alcohols has been measured and the results are summarized in Table VI. The rate in *t*-butyl alcohol appears to be unusually low. The rate of benzoyl peroxide decomposition in aliphatic alcohols is of the same order of magnitude as in ethers.

TABLE VI

THE PERCENTAGE DECOMPOSITION OF 0.197 *M* BENZOYL PEROXIDE IN ALCOHOLS AT 79.8°

Alcohol	5 Min.	10 Min.
Methyl	33.0	46.3
Ethyl	70.6	81.8
Isopropyl	86.7	95.1
t-Butyl	8.4	16.2
n-Butyl	19.8	34.8

The decomposition of benzoyl peroxide in ethyl alcohol was found to be inhibited by oxygen. A 0.2 *M* solution which had been heated at 60° for thirty minutes in air showed only a 2.3% decomposition by iodometric analysis while a solution heated under the same conditions in the absence of oxygen was 61.2% decomposed.

An investigation of the kinetics of benzoyl peroxide decomposition in ethyl alcohol at 60° was carried out, and the results are summarized in Table VII and plotted in Fig. 2. As in di-*n*-butyl ether, the decomposition may be interpreted as first order with respect to benzoyl peroxide but retarded by the products of the reaction. The results are similar to those observed with *n*-butyl ether except that the retardation is more marked in this case.

TABLE VII

THE DECOMPOSITION OF BENZOYL PEROXIDE IN ETHYL ALCOHOL AT 60.0°

Run 1		Run 2	
Time, min.	*P*, m./l.	Time, min.	*P* m./l.
0.0	0.197	0.0	0.0208
5.0	.162	5.0	.0172
10.0	.128	10.0	.0135
17.0	.103	17.0	.00985
30.0	.0772	30.0	.00590
45.0	.0614	45.0	.00409
		65.0	.00261

The products from the reaction of benzoyl peroxide with isobutyl alcohol have been investigated by Gelissen and Hermans.[5] From a mole (242 g.) of benzoyl peroxide they obtained 0.70 mole of carbon dioxide, 0.24 mole of benzene, 0.24 mole of aldehyde, 163 g. of solid acids containing mostly benzoic acid but some isobutoxybenzoic acid and phenylbenzoic acid, less than 40 g. (0.225 mole) of isobutyl benzoate and small amounts of salicylic acid and diphenyl.

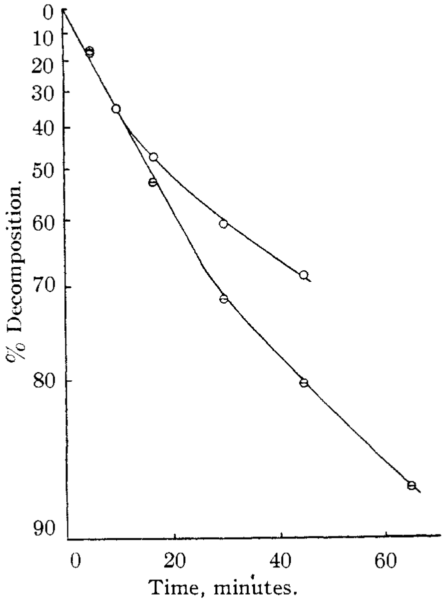

Fig. 2.—The decomposition of benzoyl peroxide in ethanol at 60°: ○, P_0 = 0.197 *M*; ⊖, P_0 = 0.0208 *M*.

The Decomposition of Benzoyl Peroxide in Phenols.—Phenol and methyl substituted phenols were investigated as solvents for benzoyl peroxide decomposition (Table VIII). It was found that benzoyl peroxide decomposed very rapidly in all of the phenols tried and the rates of reaction were of the same order of magnitude as the rates in ethers and alcohols. Methyl substitution increases the rate and is most effective in the para position. The rapid reaction in mesi-

TABLE VIII

THE DECOMPOSITION OF 0.197 *M* BENZOYL PEROXIDE IN PHENOLS

Phenol	Condition	Temp., °C.	% Decomposition of Bz_2O_2 5 Min.	10 Min.	15 Min.
Phenol	Vacuum	60.0			36.1
Phenol	Vacuum	79.8	30.5		
m-Cresol	Vacuum	60.0			72.2
m-Cresol	Air	60.0			70.1
m-Cresol	Vacuum	79.8	72.7	87.6	
o-Cresol	Vacuum	60.0			91.5
o-Cresol	Vacuum	79.8	82.5		
o-Cresol	Oxygen	79.8	75.6		
p-Cresol	Vacuum	60.0			98.5
p-Cresol	Vacuum	79.8	97.8		
p-Cresol	Air	79.8	97.8		
Mesitol	Air	60.0		98.8	99.5

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(5) Gelissen and Hermans, *Ber.*, **58B**, 765 (1925).

tol suggests that interaction with the peroxide involves the hydroxyl group rather than the benzene ring.

Oxygen is only a slight inhibitor for the reaction in phenols. This is in sharp contrast to the situation with ethers and alcohols.

A study of the kinetics of benzoyl peroxide decomposition in *m*-cresol at 60° was made (Table IX and Fig. 3). The slight difference in slope between the concentrated and dilute peroxide solutions suggests that the reaction is predominantly first order with a very small contribution from a higher order term.

TABLE IX

THE DECOMPOSITION OF BENZOYL PEROXIDE IN *m*-CRESOL AT 60°

Run 1		Run 2	
Time, min.	P, m./l.	Time, min.	P, m./l.
0.00	0.192	0.0	0.0200
5.0	.154	5.0	.0162
10.5	.123	10.5	.0132
17.0	.0928	17.0	.0101
30.0	.0520	30.0	.0065
45.0	.0286	45.0	.0035

An investigation of the products from the reaction of benzoyl peroxide with phenol at 60–80° was made. From 5.0 g. of phenol and 5.0 g. of benzoyl peroxide was obtained 3.0 g. of practically pure benzoic acid, a small amount of carbon dioxide and 2.0 g. of high boiling products containing some terphenyl. There was no evidence of salicylic or phenoxybenzoic acid.

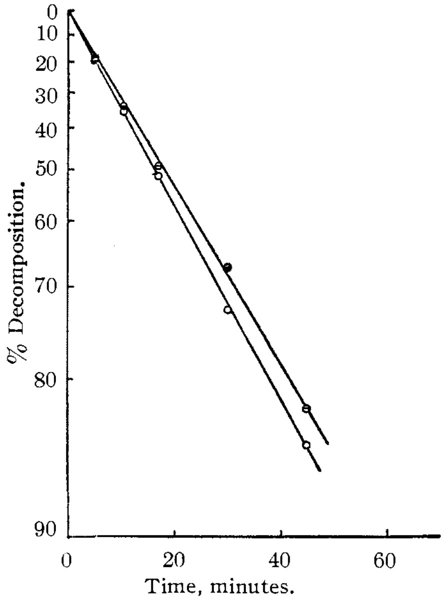


Fig. 3.—The decomposition of benzoyl peroxide in *m*-cresol at 60°: ○, P_0 = 0.192 *M*; ⊖, P_0 = 0.0200 *M*.

The Decomposition of Benzoyl Peroxide in Amines.—Preliminary observations indicated that benzoyl peroxide reacted explosively when mixed with amines such as aniline, dimethylaniline, *n*-butylamine and triethylamine. Ammonia is also effective in inducing the decomposition. A benzene solution 0.197 *M* in benzoyl peroxide and 0.115 *M* in ammonia was warmed to 30–35° and it was found that 12.6 and 46.8% of the peroxide had decomposed after one and four hours, respectively. A gelatinous precipitate of ammonium benzoate formed during the reaction. Under the same conditions without added ammonia, benzoyl peroxide did not decompose to a measurable extent.

A study of the triphenylamine–benzoyl peroxide reaction in benzene indicated that oxygen is only a slight inhibitor for the reaction (Table X). Similar results were obtained when benzoyl peroxide was decomposed in presence of triethylamine. The results agree with those obtained with phenols but are in sharp contrast with those obtained with ethers and alcohols.

TABLE X

THE EFFECT OF OXYGEN ON THE TRIPHENYLAMINE–BENZOYL PEROXIDE REACTION IN BENZENE AT 79.8°

$(Bz_2O_2)_0$ = 0.185 *M*, $((C_6H_5)_3N)_0$ = 0.185 *M*

Conditions	% Decomposition of Bz_2O_2 15 min.	60 min.
Vacuum	19.3	56.1
Air	17.4	51.8
Oxygen	15.5	51.2

The decomposition of benzoyl peroxide induced by triethylamine was carried out in the presence of vinyl acetate to determine if free radicals capable of initiating polymerization were formed. The results shown in Table XI indicate that very little if any polymerization occurred.

TABLE XI

THE POLYMERIZATION OF VINYL ACETATE WITH 1.0% BENZOYL PEROXIDE

Added substances	Amt., %	Temp., °C.	Time, hr.	% Polymerization	% Decomp. of Bz_2O_2
Triethylamine	1	56	1.0	< 5	100
None		56	1.0	25	Low
Triethylamine	1	25	18.0	< 5	75
None		25	18.0	< 5	Low

The above results are interesting in connection with our observation that tetraphenylhydrazine, a source of diphenylamino radicals, is no catalyst and probably a slight inhibitor for styrene polymerization while hexaphenylethane, pentaphenylethane and diphenyl disulfide have some initiating action (Table XII). This suggests that nitrogen free radicals show a strong preference for attacking benzoyl peroxide over initiating polymerization.

Attempts were made to study kinetically the decomposition of benzoyl peroxide in the presence of different amines. It was found that the rate of reaction fell off rapidly with time in several solvents and that a precipitate formed. The precipitate was found to be the benzoate salt of an amine and it was assumed that the falling off was due to the removal of the amine from solution. To avoid this difficulty triphenylamine, a very weak base, was chosen for study.

TABLE XII

THE POLYMERIZATION OF STYRENE AT 79.8°

Added substance	Concn., m./l.	% Polymerization 18 hours	% Polymerization 28 hours
Blank	...	8.2-11.7	13.5-15.5
$(C_6H_5)_2NN(C_6H_5)_2$	0.149	2.4	10.0
$(C_6H_5)_3CC(C_6H_5)_3$	.103	25.5	30.3
$(C_6H_5)_3CC(C_6H_5)_2H$	.122	19.3	29.6
$(C_6H_5)SS(C_6H_5)$	.229	14.1	16.3

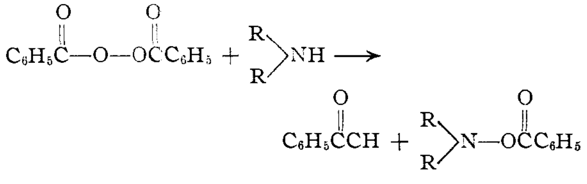
The results of a kinetic investigation of the reaction between triphenylamine and benzoyl peroxide in benzene at 79.8° are given in Table XIII and are plotted in Fig. 4. From the initial rates it appears that the reaction is of first order with respect to peroxide. However, within the runs with low initial peroxide concentrations, a falling off in rate with time is observed. From runs 2 and 3 it appears that the reaction is of first or lower order with respect to amine.

TABLE XIII

THE REACTION OF BENZOYL PEROXIDE WITH TRIPHENYLAMINE IN BENZENE AT 79.8°

Run 1 $((C_6H_5)_3)_0$ = 0.185 M Time, min.	P, m./l.	Run 2 $((C_6H_5)_3)_0$ = 0.194 M Time, min.	P, m./l.	Run 3 $((C_6H_5)_3)_0$ = 0.372 M Time, min.	P, m./l.
0.0	0.185	0.0	0.0208	0.0	0.0198
7.0	.166	7.0	.0187	7.0	.0166
15.0	.148	15.0	.0168	15.0	.0143
25.0	.131	25.0	.0151	25.0	.0116
40.0	.104	40.0	.0130	45.0	.00796
60.0	.0810	60.0	.0103	75.0	.00505
95.0	.0493	95.0	.00772		
150.0	.0220	150.0	.00470		
240.0	.0094				

The products from the decomposition of benzoyl peroxide in amines have been carefully investigated by Gambarjan and co-workers.[6] With secondary amines which have been investigated most thoroughly, the reaction may be formulated as follows



$$C_6H_5\overset{O}{\overset{\|}{C}}{-}O{-}O\overset{O}{\overset{\|}{C}}C_6H_5 + \begin{matrix}R\\R\end{matrix}\!\!>\!NH \longrightarrow C_6H_5\overset{O}{\overset{\|}{C}}CH + \begin{matrix}R\\R\end{matrix}\!\!>\!N{-}O\overset{O}{\overset{\|}{C}}C_6H_5$$

The products may be isolated with alkyl amines but the hydroxylamine benzoates have a tendency to decompose into benzoic acid and a Schiff base.[7] With diphenylamine the same reaction is assumed to occur but the hydroxylamine benzoate rearranges to N-benzoyl-*o*-hydroxydiphenylamine.[8]

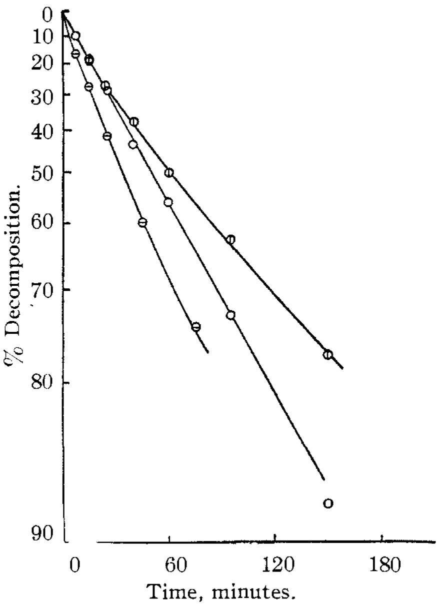


Fig. 4.—The decomposition of benzoyl peroxide in benzene in the presence of triphenylamine at 79.8°: ⦶, P_0 = 0.0208 (Amine)$_0$ = 0.194; O, P_0 = 0.185 (Amine)$_0$ = 0.185; ⊖, P_0 = 0.0198 (Amine)$_0$ = 0.372.

Some tetraphenylhydrazine probably is formed since it is isolated in 30% yield from a mixture of acetyl peroxide and diphenylamine. From benzylamine, a primary amine, the hydroxylamine benzoate was isolated and found to react readily with another amine molecule to give benzyl benzamide.[9] Gambarjan and Kazarian[10] isolated secondary amines from the reaction of benzoyl peroxide with several tertiary amines.

Discussion

The results of the experiments cited above lead to the following conclusions concerning the nature of the decomposition reactions. (1) The reactions are chain reactions involving free radicals. The evidence for this rests largely on the oxygen inhibition of the decomposition in ethers and alcohols but it is also supported by the apparent retardation of the decomposition by the products of the reaction. (2) The intermediate radicals are more reactive toward benzoyl peroxide, or less reactive toward one another, or both, than benzoate radicals. This is a necessary assumption to explain the rapid rates of decomposition of benzoyl peroxide in these solvents if it is assumed that the rate of the spontaneous, truly unimolecular decomposition of benzoyl peroxide is about the same in all solvents. (3) About half of the benzoyl peroxide is generally accounted for as benzoic acid. (4) The reactions are very close to first order with respect to peroxide.

A mechanism which at first appeared to explain

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[6] Gambarjan, *Ber.*, **58B**, 1775 (1925).

[7] Gambarjan and Cialtician, *ibid.*, **60B**, 390 (1927).

[8] Gambarjan, *ibid*, **42**, 4003 (1910).

[9] Gambarjan, Cialtician and Babajan, *Bull. inst. sci. R. S. S. d'Armenie*, 265 (1931).

[10] Gambarjan and Kazarian, *J. Gen. Chem., U. S. S. R.*, **3**, 222 (1933).

all of the facts listed above involved the transfer of a single electron from the oxygen or nitrogen atom of the solvent to benzoate radicals, giving chain-carrying radicals of the type $(R_3N)^+$ or $(R_2O)^+$. To test this mechanism tritolylaminium perchlorate, $(C_7H_7)_3N^+ClO_4^-$, was prepared and added to solutions of benzoyl peroxide. The results summarized in Table XIV indicate that although the free radical salt does induce some decomposition, it is not especially effective. The intense blue-violet color of the tritolylaminium free radicals did not disappear rapidly in the presence of benzoyl peroxide; no fading in color was observed except in chloroform at 79.8°. On the other hand, tritolylamine was found to be a very effective accelerator for the decomposition of benzoyl peroxide (Table XV). The reaction mixtures were colored yellow-orange and there was no evidence of a blue color. Thus, the above mechanism was shown to be incorrect.

TABLE XIV

THE DECOMPOSITION OF BENZOYL PEROXIDE IN THE PRESENCE OF TRITOLYLAMINIUM PERCHLORATE

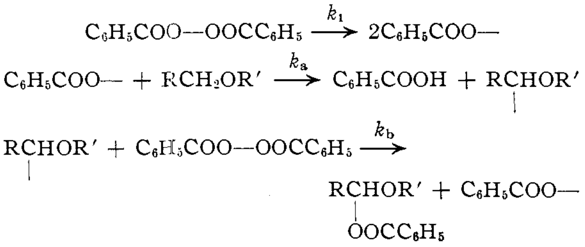
				% Decomp. of Bz_2O_2	
T, °C.	Solvent	$(Bz_2O_2)_0$	(T. A. P.)$_0$	1 Hour	16 Hours
25	$CHCl_3$	0.197	0.0232	2.0	9.2
79.8	$CHCl_3$	.197	.0350	41.0	
79.8	$CHCl_3$	.197	.00	12.8	
79.8	HOAc	.197	.0350	37.5	
79.8	HOAc	.197	.00	33.3	

TABLE XV

THE DECOMPOSITION OF BENZOYL PEROXIDE IN THE PRESENCE OF TRITOLYLAMINE

				% Decomposition of Bz_2O_2			
T, °C.	Solvent	$(Bz_2O_2)_0$	(T. A.)$_0$	0.25 Hour	1 Hour	4 Hours	6 Hours
79.8	Benzene	0.197	0.209	99.0			
25.0	Benzene	0.197	0.209		23.1	60.0	81.0

Clear evidence of the nature of the chain reaction in ethers is the recent isolation by Cass of acylals from the reaction of benzoyl peroxide with these solvents at lower temperatures than those of most of our work. From Cass' results, which are in harmony with the point of attack in the chain autoxidation of ethers,[11] we must formulate the ether reaction as follows



$$C_6H_5COO{-}OOCC_6H_5 \xrightarrow{k_1} 2C_6H_5COO{-}$$

$$C_6H_5COO{-} + RCH_2OR' \xrightarrow{k_a} C_6H_5COOH + R\underset{|}{C}HOR'$$

$$R\underset{|}{C}HOR' + C_6H_5COO{-}OOCC_6H_5 \xrightarrow{k_b} R\underset{OOCC_6H_5}{\underset{|}{C}}HOR' + C_6H_5COO{-}$$

Let us designate the benzoate radicals by the symbol ρ and the alkoxyalkyl radicals formed from the ether by R. Radical reunion, terminating reaction chains, may occur by any of three reactions

$$\rho + \rho \xrightarrow{k_3} \rho\rho$$

$$R + R \xrightarrow{k_4} RR$$

$$\rho + R \xrightarrow{k_5} \rho R$$

It can be shown that the order of the over-all peroxide decomposition depends upon which chain-terminating reaction is predominant. Induced peroxide decomposition should be of the one-half, three-halves, or first order, respectively, when the chains are terminated exclusively by the reactions having k_3, k_4 or k_5. It is perhaps an over-simplification to assume that one of these modes of chain termination should function to the exclusion of the others, yet it is highly reasonable that the union of unlike radicals (k_5) should be greatly favored over the union of like radicals, since the literature abounds in examples of such preference in reaction rate and equilibrium.[12] This is the mode of chain termination which would yield the observed first-order peroxide decomposition. The product of chain termination would also be indistinguishable in this case from the product of the chain-propagating step. Since the same alkoxyalkyl radical is doubtless also intermediate in the autoxidation of ether, it is not surprising that oxygen combines readily with it and so inhibits the chain decomposition of benzoyl peroxide in the ether as a solvent. The relatively low rates of decomposition in methyl ethers are then merely a consequence of the greater difficulty of breaking a primary as compared to a secondary carbon–hydrogen link. Diphenyl ether lacks the accelerating power of the aliphatic ethers because it lacks the α-hydrogen which is essentially involved in the chain reaction.

The close similarity between the course of the reaction in ethers and in alcohols, and their common susceptibility to inhibition by oxygen, suggests that the chain reaction in alcohols might also involve attack by the benzoate radical upon hydrogen in the alpha position in the alcohol. There are several arguments in favor of this view; it accounts for the formation of aldehyde and of oxygen-sensitive radicals, and for the much lower rate of peroxide decomposition in *t*-butyl alcohol than in alcohols having α-hydrogen. The finding of some alkoxy-benzoic acid, however, seems to argue the presence of at least some alkoxyl radicals. The formation of esters might be most directly explained by a third mode of decomposition in which the alcohol is cleaved at the carbon–oxygen bond. Energetically the most favored mode of

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(11) Rieche, "Alkylperoxyde und Ozonide," Dresden, 1931, p. 73.

(12) See, for example, the cases of triphenylmethyl and diphenylmethyl (Bachmann and Wiselogle, *J. Org. Chem.*, **1**, 354 (1936)), of diarylnitrogen and triphenylmethyl radicals (Wieland, *Ann.*, **381**, 206 (1911); *Ber.*, **48**, 1078 (1915)), of aryloxy and triphenylmethyl radicals (Pummerer and Frankfurter, *Ber.*, **47**, 1472 (1914); Goldschmidt and Schmidt, *Ber.*, **55**, 3197 (1922)), and even of differently substituted triarylmethyl radicals (Marvel and Himel, THIS JOURNAL, **64**, 2227 (1942); Himel and Mueller, *ibid.*, **65**, 1654 (1943).

cleavage, this might be more important in alcohols than in ethers because of greater spatial availability of the alcoholic oxygen atom to attack. It seems likely, therefore, that the chain reaction in alcohols is not confined to a single path.

When we turn to phenols, which have no α-hydrogen, but which are known to be capable of dehydrogenation to aryloxy radicals[13] with possibilities of resonance stabilization, attack of the benzoate radicals upon the oxygen–hydrogen bond seems by far the most probable. The resistance of the chain reaction in phenolic solvents to inhibition by oxygen would be predicted on the basis of the oxygen-indifferent aryloxy radicals being chain carriers.

The fact that the reactions involve symmetrical fission of covalent bonds permits us to discuss them in terms of single-bond energies as is not possible in the present state of our knowledge with regard to reactions of polar type. The energies of normal O–H, C–H, N–H, C–O, and C–N single bonds are 110, 87, 84, 70, and 49 kcal. per mole, respectively.[14] The results which we have just discussed show that in ethers a carbon–hydrogen bond is broken rather than a carbon–oxygen bond, perhaps because of greater accessibility to attack, but perhaps also because of a degree of stabilizing resonance in the resultant α-alkoxyalkyl radical due to the dipolar structure $\mathrm{R{-}\overset{\oplus}{\underset{\cdot\cdot}{\dot{O}}}{-}\overset{\ominus}{\ddot{C}}HR}$. In phenols the stability of the resulting radical leads to breaking of an oxygen–hydrogen bond in preference to carbon–hydrogen or carbon–oxygen. Coming to amines we find that some of the energy relationships are reversed in comparison to alcohols. Thus the nitrogen–hydrogen bond is of slightly lower, rather than considerably higher, energy than the carbon–hydrogen bond, and the carbon–nitrogen bond is the weakest in the system by a substantial margin. These facts are reflected in the nature of the products reported from the decomposition of benzoyl peroxide in amines. From these products it appears that the nitrogen–hydrogen bond is attacked if there is one present; otherwise a carbon–nitrogen bond breaks, the low energy requirement for such fission overcoming the probable steric handicap.

In Part I of this series we showed that the decomposition of benzoyl peroxide in a number of solvents can be formulated as a spontaneous first-order decomposition accompanied by a concurrent induced decomposition of the three-halves order. It was pointed out, however, that circumstances such as degradative chain transfer to the solvent or to a dissolved inhibitor would be expected to raise the order of the induced decomposition from three-halves toward second. In the present group of highly accelerating solvents we find still other changes of order due to the mode of disappearance of the free radicals derived from the solvent, which control the induced decomposition. In reviewing the evidence in all solvents we find no assurance that there would be any induced decomposition at all except for intervention of the solvent. One can imagine a type of "slow" solvent whose effect might be due not so much to inhibition as to the fact that the solvent would be only slightly attacked by the radicals from benzoyl peroxide, which therefore react destructively with each other, probably while still in the "cage" of solvent in which they are first formed.[15] The most active solvents react with the radical pairs, converting them to benzoic acid and new radicals which preferentially attack undissociated benzoyl peroxide. A full understanding of the nature of the process will require careful study of the kinetics and products in each individual solvent.

Experimental Details

Materials.—The benzoyl peroxide was purified as described earlier.[2] Most of the solvents consisted of freshly distilled samples of the best commercial grades available. The tri-*p*-tolylamine was prepared from *p*-toluidine and *p*-iodotoluene, using copper powder and potassium carbonate in boiling nitrobenzene; m. p. 115°. The tritolylammonium perchlorate was prepared using the directions of Weitz and Schwechten.[16] The mesitol was prepared according to the procedure of Porter and Thurber,[17] except that the product was recrystallized from ligroin; m. p. 69°.

Procedures.—The experimental procedures did not differ significantly from those described earlier.[2] All reactions, unless otherwise specified, were carried out in sealed glass tubes and the samples were carefully degassed before sealing under vacuum. The iodometric method of peroxide analysis with acetic anhydride and sodium iodide was used. With phenols a small correction (1%) was necessary because of the reaction of the solvent with iodine. Polymerizations were followed by bromine addition, using standard bromide-bromate and thiosulfate solutions.

Reaction Products.—The products from the benzoyl peroxide–*n*-butyl ether reaction were analyzed in the following manner. The reaction was carried out in a large test-tube equipped with a side-arm reflux condenser, the open end of which was connected to an absorption train. The train consisted of a tube containing a standardized solution of bromine in methylene chloride at −80°, a trap at −80°, a tube containing Dehydrite, a tube containing Ascarite, another tube with Dehydrite and finally a bubbler. The sample was placed in the tube, which was immersed in a thermostat at 60°, and a slow stream of carbon dioxide-free nitrogen was passed through. After four hours the butene content was determined from the consumption of bromine and the carbon dioxide from the gain in weight of the Ascarite tube. The liquid residue was distilled and the low boiling fractions were found to contain butyraldehyde (2,4-dinitrophenylhydrazone) but no alcohols (no α-naphthylurethan). Extraction of the high boiling fraction with aqueous sodium carbonate, followed by acidification of the aqueous solution, resulted in the separation of the solid acids. The acids were extracted with ether, and the ether was evaporated. After one recrystallization from a mixture of ethyl alcohol and water, the material melted at 120°. Saponification of

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(13) Pummerer, *Ber.*, **47**, 2957 (1914); **52**, 1416 (1919); also ref. 12, Goldschmidt and Schmidt.

(14) Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1940, p. 53.

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

(16) Weitz and Schwechten, *Ber.*, **59**, 2307 (1926).

(17) Porter and Thurber, THIS JOURNAL, **43**, 1194 (1921).

the remaining high boiling fraction resulted in a small amount of benzoic acid.

The products from the benzoyl peroxide–phenol reaction were investigated in a similar manner. The solid acid mixture obtained by bicarbonate extraction, acidification, ether extraction, ether evaporation and drying, melted at 121° and had a neutral equivalent of 121 without recrystallization. No ferric chloride test could be obtained from solutions of the acid.

Summary

The decomposition of benzoyl peroxide in the presence of ten ethers, five alcohols, five phenols, and four amines has been studied quantitatively. In most of the ethers (anisole and diphenyl ether excepted) the reaction is very rapid. Although of first order, it is strongly inhibited by oxygen and is hence a chain reaction. The same is true of the peroxide decomposition in primary and secondary alcohols, the accelerating effect of *t*-butyl alcohol being less marked.

In the presence of phenols and amines oxygen inhibition is slight or lacking, but the decomposition still is of nearly first order with respect to peroxide.

The increased rate of decomposition of the peroxide in ethers and amines is not accompanied by increased polymerization of vinyl acetate present in the same solutions.

The products of the reaction have been investigated in several cases. Reasons are given for believing that benzoate radicals attack ethers with removal of α-hydrogen, phenols with removal of hydroxylic hydrogen, secondary amines with removal of hydrogen from nitrogen, tertiary amines with rupture of the carbon–nitrogen bond, and alcohols with rupture of carbon–hydrogen, oxygen–hydrogen, and possibly also carbon–oxygen bonds.

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The Mechanism of Addition of Grignard Reagents to Nitriles

BY C. GARDNER SWAIN[1]

The addition reactions of Grignard reagents are difficult to study kinetically due to their high speed. It has been demonstrated by competition experiments[2] that the relative reactivity of different addends with phenylmagnesium bromide is

$$CH_3COCH_3 > CH_3CHO > C_6H_5CHO > C_6H_5COCH_3 > C_6H_5NCO > C_6H_5COF > C_6H_5COC_6H_5 > C_6H_5COCl > C_6H_5COBr > C_6H_5COOEt > C_6H_5CN$$

Direct rate measurement is easily possible only with nitriles and esters, since the others react practically completely in a few minutes or less.

None of the studies which are reported in the literature establish the kinetic order of the reaction of any of these addends with a Grignard reagent or other organometallic compound. However, Gilman developed a sensitive color test[3] for the presence of organometallic reagents, and by assuming constant sensitivity for the test and noting the time for disappearance of a positive test on aliquots taken periodically from the reaction mixture, the series of relative reactivity of different nitriles[4] (Table I) and of different reagents[5,6] (Tables II and III) were established.

If there were a sluggish equilibrium between dialkylmagnesium, present in considerable concentration, and alkylmagnesium bromide in an ordinary Grignard solution, we should expect to find a complicated dependence of rate upon concentration in any kinetic study. Dioxane precipitations do not give a clear picture of the composition of solutions of Grignard reagents, because the composition of the precipitate changes at a rapid rate after the dioxane is added.[7]

With the aid of the color test, Gilman and Brown found that diphenylmagnesium completely free from halide reacts twenty times more slowly than phenylmagnesium bromide with *n*-valeronitrile. However, in the presence of equivalent magnesium iodide or bromide, diphenylmagnesium reacts within a few minutes to give phenylmagnesium iodide or bromide so completely that there is no detectable magnesium iodide or bromide left in the solution.[8] Similar results were obtained by Gilman and Fothergill on aliphatic Grignard reagents.[8] The simplicity of the kinetics which we actually obtained below with the *n*-butyl Grignard reagent support this idea that the equilibrium is either rapid or else well on the side of alkylmagnesium bromide.

Determination of the Kinetic Order

The reaction between *n*-butylmagnesium bromide and benzonitrile in ether solution was followed by measuring evolution of gas from aliquot samples taken periodically from the reacting solution. It is homogeneous and second order with a rate constant of $3.7 \pm 0.6 \times 10^{-4}$ l. mole^{-1} sec.$^{-1}$ at 25°, and $5.8 \pm 0.9 \times 10^{-5}$ at 0°. This corre-

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[1] National Research Fellow, 1945–1946; American Chemical Society Fellow, 1946–1947.

[2] Entemann and Johnson, THIS JOURNAL, **55**, 2900 (1933); Kharasch and Cooper, *J. Org. Chem.*, **10**, 46 (1946).

[3] Gilman and Schultze, THIS JOURNAL, **47**, 2002 (1925).

[4] Gilman and Lichtenwalter, *Rec. trav. chim.*, **55**, 588 (1936).

[5] Gilman and Young, *J. Org. Chem.*, **1**, 315 (1936).

[6] Gilman, St. John, St. John and Lichtenwalter, *Rec. trav. chim.*, **55**, 577 (1936).

[7] Noller and White, THIS JOURNAL, **59**, 1354 (1937).

[8] Gilman and Brown, *ibid.*, **52**, 1181 (1930); Gilman and Fothergill, *ibid.*, **51**, 3149 (1929).