

10-Chloro-7-hexylaminobenz[*c*]acridine. A. From 10-chloro-7-(2-chloroethylamino)-benz[*c*]acridine. Hydrochloride.—A mixture of 6.0 g. (0.016 mole) of 10-chloro-7-(2-chloroethylamino)-benz[*c*]acridine hydrochloride and 100 ml. of hexylamine was boiled under reflux for 4 hr. Upon cooling, the reaction mixture was poured into a large volume of ice-water and the precipitate collected by filtration and washed with water. Crystallization from ethanol yielded 4.5 g. (77%) of yellow crystals. For analysis, a sample was crystallized from isopropyl alcohol, m.p. 90–92°.

Anal. Calcd. for $C_{23}H_{23}ClN_2$: C, 76.12; H, 6.39; N, 7.72; Cl, 9.77. Found: C, 76.94; H, 6.58; N, 7.90; Cl, 9.91.

B. From 7,10-Dichlorobenz[*c*]acridine.—A mixture of 0.5 g. (0.0017 mole) of 7,10-dichlorobenz[*c*]acridine² and 100 ml. of hexylamine was boiled under reflux for 4 hr. The excess hexylamine was removed *in vacuo*, the residue was treated with 10% hydrochloric acid, the aqueous solution was decanted and the residue dissolved in absolute ethanol. The ethanol solution was made alkaline with ammonium hydroxide, and the precipitated base was collected by filtration, dried and crystallized from ethanol; yield 0.4 g. (66%), m.p. 90–92°; the melting point of a mixture with the product from A above showed no depression.

C. From 10-Chloro-7-[5-(1-piperidinyl)-pentylamino]-benz[*c*]acridine, Dihydrochloride.—A mixture of 2.0 g. (0.037 mole) of 10-chloro-7-[5-(1-piperidinyl)-pentylamino]-benz[*c*]acridine dihydrochloride dihydrate² and 100 ml. of hexylamine was boiled under reflux for 16 hr., cooled, and 75 ml. of hexylamine was removed *in vacuo*. The residue was poured with vigorous stirring into 500 ml. of water, the

aqueous mixture was acidified with 10% hydrochloric acid, and the waxy precipitate which separated was collected by filtration, washed with water and air-dried. The crude product was dissolved in 95% ethanol, made alkaline with ammonium hydroxide and the base collected by filtration, dried and crystallized from ethanol. The base weighed 1.1 g. (82%), m.p. 90–92°; the melting point of a mixture with the product from A above showed no depression.

4-Chloro-N-1-naphthylanthraniloyl Chloride.—Phosphorus pentachloride (30.8 g., 0.148 mole) was added portionwise to a suspension of 40 g. (0.135 mole) of 4-chloro-N-(1-naphthyl)-anthranilic acid in 350 ml. of dry petroleum ether (b.p. 80–110°). As each portion was added, the mixture was warmed gently until the reaction subsided. The mixture was boiled under reflux for 40 minutes and the petroleum ether solution decanted from the heavy sediment which separated. The residue was boiled with petroleum ether (b.p. 80–110°) and the petroleum ether solutions were discarded. The residue was dissolved in boiling benzene and diluted with petroleum ether (b.p. 80–110°), whereupon a flocculent purple solid separated. This impurity was collected by filtration and discarded. The filtrate was chilled and the crude acid chloride collected by filtration. A second crop was obtained by concentration of the filtrate; crude yield 36 g. (84%). Crystallization from a benzene-petroleum ether (b.p. 80–110°) mixture (decolorizing charcoal) gave 35 g. (82%) of yellow needles, m.p. 145° dec.

Anal. Calcd. for $C_{17}H_{11}Cl_2NO$: C, 64.57; H, 3.51; N, 4.43. Found: C, 65.00; H, 3.75; N, 4.77.

DETROIT, MICHIGAN

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF COLUMBIA UNIVERSITY]

The Reaction of Acyl Peroxides with Phenols¹

BY CHEVES WALLING AND RUSSELL B. HODGDON, JR.²

RECEIVED JULY 15, 1957

The reaction between benzoyl (and similar) peroxides and phenols follows second-order kinetics, first order in peroxide and in phenol. The reaction is accelerated by electron-supplying groups on the phenol and retarded by bulky *ortho*-substituents. Measurements with O-deuterated phenols give $k_H/k_D = 1.32 \pm 0.03$ in several systems. The reaction shows neither acid nor base catalysis, but the rate varies significantly with solvent, being slow in strongly hydrogen bonding media. Radical traps, polymerizable monomers and iodine, have no effect on reaction rate. It is concluded that the reaction is not a radical chain process, but probably involves a simple bimolecular "four-center" process without radical formation, and a possible reaction path is proposed.

In 1944 it was reported³ that, while styrene undergoes an only slightly retarded thermal polymerization in phenolic solvents, the benzoyl peroxide initiated polymerization was essentially inhibited. At the same time, it was noted that benzoyl peroxide decomposed very rapidly in *m*-cresol solution, and both results were suggested as arising from either a fast non-radical reaction between peroxide and phenol, or a radical-forming process yielding radicals which were too rapidly consumed by reaction with each other or the phenol to initiate polymerization. In 1947, as part of their now-classic investigation of the induced decomposition of benzoyl peroxide, Bartlett and Nozaki⁴ obtained more quantitative data on the decomposition rate in various phenols, noted that the reaction rate was first order in peroxide, and interpreted their results as the consequence of

an induced radical chain process. Subsequently, the nature of the products formed on refluxing equimolecular quantities of phenols and benzoyl peroxide in chloroform solution have been studied by Cosgrove and Waters⁵ who found that phenols with free *o*-positions give chiefly catechol mono-benzoates (I), 2,6-dimethylphenol is converted to 3,3,3',3'-tetramethyldiphenoquinone (II) in high yield and 2,4,6-trimethylphenol gives chiefly 2,4,6-trimethyl-4-benzoyloxycyclohexa-2,5-dienone (III). In every case most of the benzoyl peroxide residues not attached to aromatic nuclei are recovered as benzoic acid. In their discussion, Cosgrove and Waters have interpreted their products as the results of radical coupling and disproportionation, without considering the possible consequences of induced decomposition. Subsequently Wesseley and Schinzel⁶ have investigated the decomposition of acetyl peroxide in acetic acid in the presence of each of the three isomeric cresols, obtaining catechol monoacetates (together with lac-

(1) Taken from the dissertation of Russell B. Hodgdon, Jr., submitted in partial fulfillment of the requirements of the Ph.D. degree, 1957. Support of this work by a research contract with the Office of Ordnance Research, U. S. Army, is gratefully acknowledged.

(2) Texas Co. Fellow, 1955–1956.

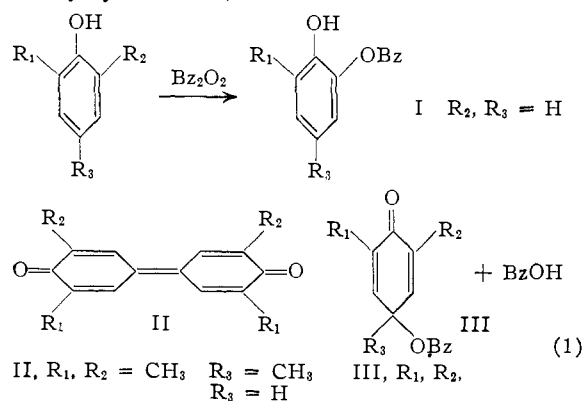
(3) C. Walling, THIS JOURNAL, **66**, 1602 (1944).

(4) P. D. Bartlett and K. Nozaki, *ibid.*, **69**, 2299 (1947).

(5) S. L. Cosgrove and W. A. Waters, *J. Chem. Soc.*, 3189 (1949); *ibid.*, 388 (1951).

(6) F. Wesseley and M. Schinzel, *Monatsh.*, **84**, 969 (1953).

tones of *o*-hydroxyphenylacetic acids), and Campbell and Coppinger⁷ have reported that 2,6-di-*t*-butyl-4-methylphenol reacts with *t*-butyl hydroperoxide to give 4-methyl-4-*t*-butylperoxy-2,6-di-*t*-butylcyclohexa-2,5-dienone.



We have been interested in the general reaction between peroxides and phenols, because of its apparent high rate, the variety of products formed and its possible relation to the behavior of phenolic antioxidants. This paper reports a largely kinetic study of the reaction of acyl peroxides, and leads us to the conclusion that the process is certainly not an induced radical chain, and, in most systems, probably does not involve free radicals at all.

Results

Over-all Kinetics.—Our major approach has been to investigate the rate of decomposition of 0.05 to 0.25 *M* peroxide solutions in different solvents in the presence of a considerable excess (2.5–5 *M* solutions) of a variety of phenols. With the exception of some high-temperature experiments discussed below, we find that the decompositions under these conditions are strictly pseudo-unimolecular, in agreement with Bartlett and Nozaki.⁴ Figure 1 shows a typical first-order plot for the decomposition of benzoyl peroxide in benzene at 30° in the presence of 2.0 *M* *p*-methoxyphenol, carried to 86% decomposition. Although first-order rate constants are independent of initial peroxide concentration, they vary linearly with phenol concentration, indicating that the over-all reaction is second order, following the rate-law

$$-d[\text{peroxide}]/dt = k_2[\text{peroxide}][\text{phenol}] \quad (2)$$

Typical data for benzoyl peroxide plus *m*-cresol appear in Table I, and comparable results are observed with other systems.

TABLE I
REACTION OF BENZOYL PEROXIDE WITH *m*-CRESOL IN BENZENE SOLUTION AT 30°

Peroxide, mole/l.	Cresol, moles/l.	$k_2 \times 10^7$, moles/liter sec.
0.06	3.75	27.5
.10	2.50	26.9
.10	3.75	27.4
.10	5.00	27.2
.20	3.75	27.8
.28	3.75	28.4

(7) T. W. Campbell and G. M. Coppinger, THIS JOURNAL, **74**, 1469 (1952).

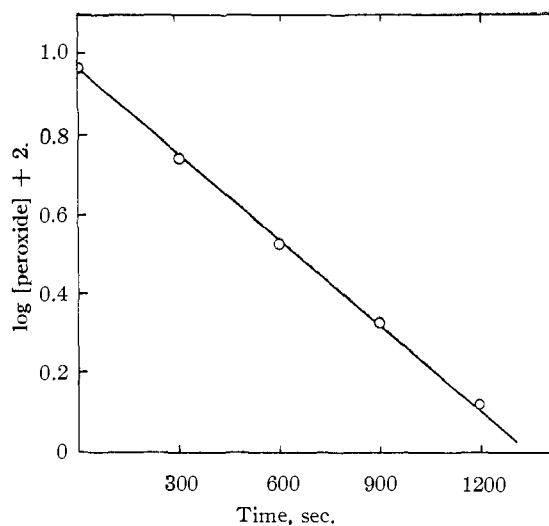


Fig. 1.—Reaction of 0.093 *M* benzoyl peroxide with 2 *M* *p*-methoxyphenol in benzene at 30°.

Effect of Phenol Structure.—The rate of decomposition of benzoyl peroxide in 3.75 *M* benzene solutions of a number of phenols have been measured and appear as second-order rate constants in Table II. Two conclusions appear evident. First,

TABLE II

RATES OF REACTION OF 0.1 *M* BENZOYL PEROXIDE AND 3.75 *M* PHENOLS IN BENZENE AT 30°

Substituent	$k_2 \times 10^7$	Substituent	$k_2 \times 10^7$
4-CH ₃ -2,6-di- <i>t</i> -C ₄ H ₉	<0.1	<i>m</i> -OC ₂ H ₅	45.2
2,4,6-tri- <i>t</i> -C ₄ H ₉	<0.1	2,4-di-CH ₃	48.5
None	5.7	<i>o</i> -OCH ₃	77.0
<i>m</i> -Cl	7.2	2,6-di-CH ₃	78.0
<i>m</i> -CH ₃	27.4	<i>p</i> -CH ₃	106.8
<i>p</i> -Cl	28.5	2,6-di-OCH ₃	267.4
2,6-di-isoC ₃ H ₇	29.9	<i>p</i> -OCH ₃	9021
<i>p</i> -Br	35.7		

strongly electron-supplying *p*-substituents, –CH₃ and –OCH₃, greatly accelerate the reaction, although there is plainly no simple Hammett $\rho\sigma$ relation, since the decomposition is notably faster in the presence of *p*-chloro- and *p*-bromophenol than in the presence of phenol itself. Second, the reaction is evidently subject to steric hindrance about the phenolic hydroxyl. 2,6-Dimethylphenol reacts more slowly than *p*-cresol, and 2,6-dimethoxyphenol more slowly than *p*-methoxyphenol. No reaction is detectable at 30° with phenols containing *t*-butyl groups in the 2- and 6-positions. In one pair of phenols, *m*-cresol and *p*-methoxyphenol, reaction rates have been measured over a temperature range, and the high rate with the latter arises from both a smaller value of ΔH^\ddagger and a larger value of ΔS^\ddagger ; see Table III.

Effect of Solvents.—We find that the rate of the reaction between benzoyl peroxide and phenols varies very significantly with solvent, Table IV. There is certainly no correlation with dielectric constant, since the reactions are fast in nitrobenzene and slow in alcohols compared with their rates in benzene. On the other hand, rates are definitely slow in solvents bearing carbonyl or hy-

TABLE III
EFFECT OF TEMPERATURE ON BENZOYL PEROXIDE-PHENOL REACTIONS, BENZENE SOLUTION

T, °C.	$k_2 \times 10^7$	
	<i>m</i> -Cresol ^a	<i>p</i> -Methoxyphenol ^b
0	1.1	460
20	11.1	3310
30	27.4	8040
35	44.7	14100
40	80.5	18900
ΔH^\ddagger , kcal./mole	17.4	15.3
ΔS^\ddagger , cal./deg.	-26.7	-22.3

^a 0.1 M peroxide, 3.75 M phenol. ^b 0.1 M peroxide, 2.5 M phenol.

droxyl groups which should form strong hydrogen bonds with phenols. There is also a good correlation between solvent effects on reaction rates for the two phenols studied, as shown by the linearity of a log-log plot, Fig. 2.

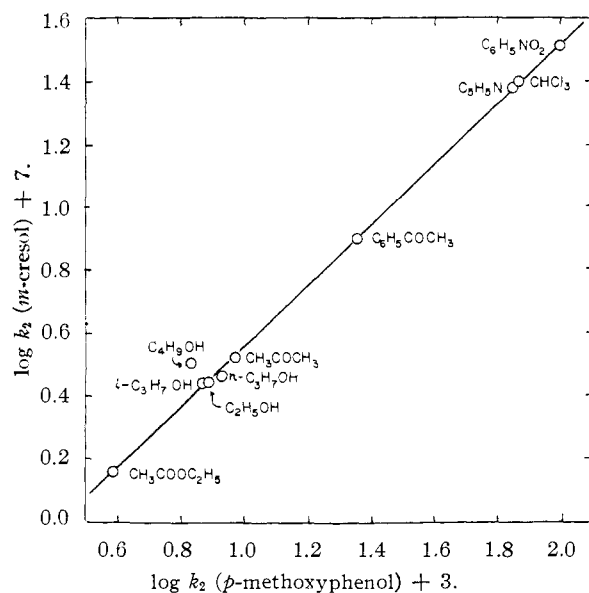


Fig. 2.—Comparison of solvent effects on reaction of benzoyl peroxide with *m*-cresol and *p*-methoxyphenol at 30°.

Our data show no indication of acid or base catalysis for the reaction. The rates in acetic acid are low, and in pyridine no faster than in other aromatic solvents. In the presence of stronger base (phenoxide ion) the reaction takes another course, for, when 2,6-dimethylphenol is heated in chloroform with benzoyl peroxide, phenyl benzoate and potassium benzoate are produced, presumably by a reaction paralleling the usual preparation of perbenzoic acid⁸ (the rapid decomposition of peracids in warm alkali is well known).

In the radical chain decomposition of benzoyl peroxide in the presence of ethers, the chain is suppressed by reactive monomers such as methyl methacrylate,⁹ but here rates are comparable to those in the presence of other carbonyl compounds. We also have investigated the reaction in the

(8) H. von Pechmann and L. Vanino, *Ber.*, **27**, 1510 (1894).

(9) C. G. Swain, W. Stockmeyer and T. Clarke, Jr., *THIS JOURNAL*, **72**, 5426 (1950).

TABLE IV
SOLVENT EFFECTS ON BENZOYL PEROXIDE-PHENOL REACTIONS AT 30°

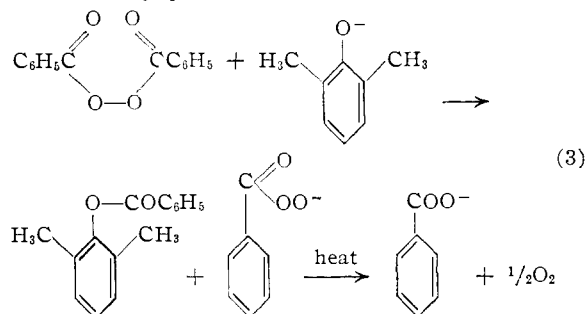
Solvent	$k_2 \times 10^7$	
	<i>m</i> -Cresol 3.75 M	<i>p</i> -Methoxyphenol 2.50 M
Nitrobenzene	33.7	9900
Benzene	27.4	7600
Chloroform	27.3	7600
Pyridine	26.0	7300
Acetophenone	8.3	2300
Acetone	3.4	910
<i>n</i> -Propyl alcohol	3.1	820
<i>i</i> -Propyl alcohol	2.9	750
Ethyl alcohol	2.8	770
<i>t</i> -Butyl alcohol	2.6	660
Acetic acid	0.7	111
Ethyl acetate	..	380
Diethyl maleate	..	1300
Methyl methacrylate	..	1500

presence of iodine as a potential effective radical trap,^{10,11} but detect no effect on either reaction rate or products.

Other Peroxides.—Although most of our study has been on benzoyl peroxide, we have compared rates, and a few products, obtained with other peroxides. Results with *p*-methoxyphenol appear in Table V, and it is evident that there is little correlation with decomposition rates in inert solvents which lie roughly in the order: acetyl peroxide, benzoyl peroxide > *t*-butyl perbenzoate > *t*-butyl hydroperoxide.¹²

TABLE V
COMPARISON OF PEROXIDE REACTIONS WITH *p*-METHOXYPHENOL (2.5 M IN BENZENE AT 30°)

	$k_2 \times 10^7$
Benzoyl peroxide	7870
Acetyl peroxide	380
<i>t</i> -Butyl hydroperoxide	240
<i>t</i> -Butyl perbenzoate	70



The products obtained from some of the other peroxides were investigated in the presence of 2,6-dimethylphenol, since with benzoyl peroxide it yields the easily isolated diphenoquinone in good (60–70%) yield. Comparable yields were obtained with both acetyl peroxide and *t*-butyl perbenzoate, and, with the latter, peroxide residues were identified almost quantitatively as benzoic

(10) G. S. Hammond, *ibid.*, **72**, 3737 (1950); G. S. Hammond and L. M. Soffer, *ibid.*, **72**, 4711 (1950).

(11) A. Rembaum and M. Szwarc, *ibid.*, **77**, 3486 (1955).

(12) A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954.

acid and *t*-butyl alcohol. The conversion of 2,6-disubstituted phenols to diphenoquinones, incidentally, appears to be a general reaction, and gives 60–70% yields from both 2,6-diisopropyl- and 2,6-dimethoxyphenol and benzoyl peroxide.

In contrast to the results of thermal peroxide decompositions, essentially no CO₂ is evolved in any of our 30° reactions, even with acetyl peroxide which decomposes thermally with CO₂ evolution even in the presence of such efficient radical traps as iodine.¹¹

Isotope Effects.—In order to see whether scission of the phenolic O–H bond is involved in the rate-determining step of peroxide–phenol reactions we have determined decomposition rates in the presence of O-deuterated phenols, with results given in Table VI in terms of k_H/k_D ratios (relative rates in the presence of phenol and deuterated phenol). All experiments show a small isotope effect, $k_H/k_D = 1.32 \pm 0.03$, which appears essentially constant in spite of changes in phenol, peroxide and solvent.

TABLE VI

Peroxide	Phenol	Solvent	k_H/k_D
Benzoyl	<i>p</i> -OCH ₃	Benzene	1.30
Benzoyl	<i>p</i> -OCH ₃	Ethyl acetate	1.31
Benzoyl	2,6-di-CH ₃ -	Benzene	1.29
Acetyl	<i>p</i> -OCH ₃	Benzene	1.35

Higher Temperature Experiments.—Two sets of experiments were conducted at higher temperatures where radical production by thermal dissociation of peroxides would be expected to compete with the peroxide–phenol reaction. In one, acetyl peroxide was decomposed at 60° in 1:1 benzene–styrene solvent in the presence of varying amounts of *m*-cresol; see Table VII.

TABLE VII

DECOMPOSITION OF 0.1 M ACETYL PEROXIDE IN 1:1 BENZENE-STYRENE IN THE PRESENCE OF <i>m</i> -CRESOL AT 60°			
<i>m</i> -Cresol	$k_d \times 10^{5c}$	CO ₂ , %	R_p (%/min.) ^b
0.0	14	56.4	0.177
.1	11
.25	9
.35	8
.5	8
.7	11
.8	14	6.0	.015
.8 ^a	14	5.9	...
1.0	18	..	.003
2.0	34	..	.000

^a In benzene solvent. ^b Rate of styrene polymerization. ^c Apparent first order decomposition rate of peroxide.

The data indicate that the rate of peroxide decomposition goes through a slight minimum (57% of the rate in the absence of *m*-cresol) in the presence of 0.4–0.5 M *m*-cresol. At the same time, CO₂ evolution is greatly repressed and styrene polymerization strongly retarded. In contrast, we find that the presence of 0.8 M *m*-cresol has only a slight retarding effect on styrene polymerization initiated by 0.1 M azobisisobutyronitrile, which proceeds at 58% of the rate in the absence of *m*-cresol.

Our polymerization results thus parallel previous observations.³

As noted in Table II, 2,4,6-tri-*t*-butylphenol does not react with benzoyl peroxide at a measurable rate at 30°. This phenol is particularly interesting since Cook¹³ and Muller and Ley¹⁴ find that oxidizing agents convert it to the relatively stable blue 2,4,6-tri-*t*-butylphenoxy radical. When a benzene solution 0.1 M in this phenol and in benzoyl peroxide is heated at reflux, the blue color of the radical begins to appear immediately, finally fading after about 24 hours. Under these conditions the peroxide fragments appear as benzoic acid and biphenyl, the usual products of radical decomposition. Similarly, in chloroform we obtain benzoic acid (85%) and hexachloroethane (54%). The rate of peroxide decomposition appears to be somewhat higher than first order, but initially gives $k_d = 6.5 \times 10^{-5} \text{ sec.}^{-1}$, approximately the same as in benzene alone¹² where at 80° $k_d = 4.3 \times 10^{-5}$. More accurate comparison is not feasible because of our approximate temperature and the probability of some induced decomposition in our system.

Discussion

Our results lead to the following general conclusions about the reaction between acyl peroxides and phenols, present in large excess at 30°: 1. Reactions are quite cleanly bimolecular, first order in both phenol and peroxide. 2. The reaction is strongly accelerated by electron-supplying groups on the phenol, although the effect follows no simple Hammett $\rho\sigma$ relationship. 3. The reaction is notably subject to steric hindrance about the phenolic OH. 4. The reaction shows a small, constant isotope effect with O-deuterated phenols. 5. Rates vary greatly with different peroxides, and do not parallel their rates of thermal decomposition. 6. Rates vary markedly with solvent, and, qualitatively, are depressed in solvents which showed hydrogen-bond with phenols. 7. The reaction shows no evidence of acid or base catalysis. 8. Radical traps—polymerizable monomers, iodine and oxygen⁴—have no effect upon rate or (even for iodine) upon products. With polymerizable monomers no polymer is formed. 9. With neither benzoyl peroxide nor acetyl peroxide is CO₂ evolved in the reaction.

Items 1 and 8 seem to us compelling evidence against any radical chain mechanism for the peroxide–phenol reaction since we have not been able to devise any plausible kinetic scheme consistent with a bimolecular reaction and since radical traps are effective in repressing other peroxide chain decompositions.^{4,9,10}

Item 8 is as well a negative test for any presence of free radicals since there is no evidence for the initiation of polymerization, and iodine is extremely effective in trapping radicals formed on the thermal dissociation of peroxides. Item 9 is also negative evidence, for Szwarc's results¹¹ show plainly that acetoxy radicals from acetyl peroxide lose CO₂ almost immediately and before they can undergo re-

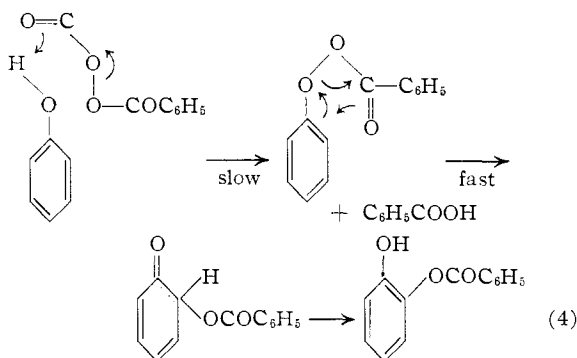
(13) C. D. Cook, *J. Org. Chem.*, **18**, 261 (1953); C. D. Cook and R. C. Woodworth, *THIS JOURNAL*, **75**, 6242 (1953).

(14) E. Muller and K. Ley, *Z. Naturforsch.*, **86**, 694 (1953); *Chem. Ber.*, **87**, 922 (1954).

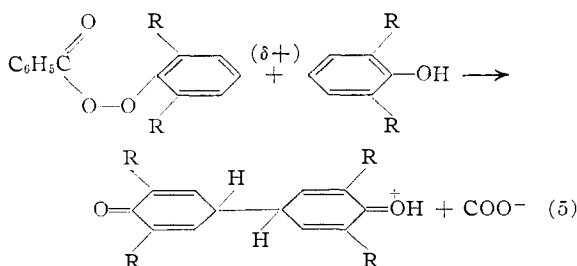
action with even highly reactive molecules. We find similarly that acetyl peroxide, heated in moist carbon tetrachloride in the presence of iodine, gives CO_2 , CH_4 and CH_3I in contrast to benzoyl peroxide which is converted almost quantitatively to benzoic acid under similar conditions.¹⁰

At this point we must infer that the peroxide-phenol reaction is either a non-radical process, or that any radical intermediates formed are complexed or involved with the phenol so as not to exhibit their expected reactions. Although there is some precedent for the latter in Hammond's conclusions about the complexing of peroxy radicals and phenolic antioxidants,¹⁵ until definite evidence for the presence of radical intermediates is uncovered we prefer the former interpretation.

Items 2, 3 and 6 indicate that any such process directly involves attack on the phenolic OH group either in the rate-determining step, or in some prior rapid equilibrium, while 2 suggests that the phenol behaves as a nucleophilic reagent. The peroxide must react either by carbonyl addition or displacement on oxygen, and the latter might be formulated (for phenols with a free *o*-position) by a scheme such as



While such a path is certainly speculative, it indicates that the process is essentially a succession of "four-center" reactions,¹⁶ the second of which may be electronically analogous to the Claisen rearrangement. The large negative entropy of activation (Table III) is also certainly consistent with such a picture. The formation of diphenoquinones from 2,6-disubstituted phenols can be formulated from the same intermediate followed by



proton loss and tautomerization to the hydroquinone, and then further oxidation. In support of

(15) C. E. Boozer, G. S. Hammond, C. E. Hamilton and J. N. Sen, *THIS JOURNAL*, **77**, 3233 (1955). Similar evidence for the complexing of chlorine atoms also has appeared recently; G. A. Russell, *ibid.*, **79**, 2977 (1957); C. Walling and B. Miller, *ibid.*, **79**, 4181 (1957).

(16) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc, New York, N. Y., 1956, Chapter 24.

the last step, we find that this type of hydroquinone is oxidized almost instantly by benzoyl peroxide. The formation of benzyloxydienones from 2,4,6-trisubstituted phenols can be formulated similarly, analogously to the *p*-Claisen rearrangement.

Our higher temperature experiments, although they are in part puzzling, suggest that, even if the fast bimolecular reaction between peroxides and phenols is not a radical process, radicals from peroxides, when formed, do react rapidly with phenols. Thus the thermal decomposition of benzoyl peroxide evidently oxidizes 2,4,6-tri-*t*-butylphenol to its phenoxy radical, while relatively small amounts of *m*-cresol greatly suppress the initiation of styrene polymerization by acetyl peroxide. The initial drop in rate of peroxide decomposition in the presence of small amounts of *m*-cresol may represent the inhibition of some induced decomposition, but we are unable to give any more quantitative interpretation to the results in Table VII. Similar minima in the rate of decomposition of benzoyl peroxide in the presence of various phenols have recently been reported by Batten and Mulcahy¹⁷ who note that phenols also inhibit the fast induced chain decomposition of this peroxide in dioxane. They too conclude that benzoyl peroxide phenol reactions are bimolecular reactions rather than induced chains, but prefer a mechanism involving free radical intermediates.

Experimental

Materials.—Benzoyl peroxide employed was recrystallized from chloroform-methanol. Other peroxides were commercial materials, the acetyl peroxide being used as a 20% solution in diethyl phthalate. Liquid phenols were purified by distillation, while solid phenols were dissolved in benzene and precipitated with petroleum ether. Deuterated phenols were prepared by equilibrating 0.08-mole samples for 24 hours with 1.2 moles of 99.5% D_2O , followed by removal of the D_2O - H_2O under high vacuum. Solvents were redistilled commercial materials.

Kinetic runs were carried out in a stirred thermostat at $30.0 \pm 0.1^\circ$ (or other temperature) and followed by titration of aliquots using KI in acetic acid and 0.1 *N* thiosulfate. With *t*-butyl perbenzoate the procedure was modified in that iodine liberation was carried out in 25 cc. of isopropyl alcohol containing 1 cc. of 20% H_2SO_4 , since the reaction in acetic acid is slow and incomplete.

Determination of CO_2 Evolution.—Carbon dioxide formed in representative decompositions was determined by carrying out the reactions in a closed system connected to an ascarite tube. Evolved gases were aspirated through the tube, and the gain in weight determined.

Products from 2,6-Disubstituted Phenols.—Benzoyl peroxide, 12.1 g., and 2,6-dimethylphenol, 6.1 g. (equimolar quantities), were refluxed together for six hours in 200 cc. of benzene. The red diphenoquinone separated during reaction, and was filtered off on cooling; yield 3.8 g. (62.3%). Benzoic acid, 10.7 g. (88.4%), was recovered from the filtrate by extracting with sodium bicarbonate solution and acidifying. Similar results, 52.4% diphenoquinone, 92.6% benzoic acid, were obtained on three weeks reaction at room temperature. The diphenoquinone also was obtained using acetyl peroxide or *t*-butyl perbenzoate. Refluxing equimolar quantities of 2,6-dimethoxyphenol and *t*-butyl perbenzoate in benzene gave 79.2% of the purple 3,3',5,5'-tetramethoxydiphenoquinone, m.p. 272-274°. On reduction with zinc and acetic acid at 100° for 15 min. it was converted to the white hydroquinone, m.p. 310-312°. *Anal.* Calcd.: C, 62.8; H, 5.9. Found: C, 63.4; H, 5.4.

Under the same conditions 2,6-diisopropylphenol gives red 3,3',5,5'-tetraisopropyldiphenoquinone (65.1%), m.p. 211-212°. Reduction as above converts it to the hydro-

(17) J. J. Batten and M. F. R. Mulcahy, *J. Chem. Soc.*, 2948 (1956); J. J. Batten, *ibid.*, 2959 (1956).

quinone, m.p. 108–110°. *Anal.* Calcd.: C, 81.4; H, 9.6. Found: C, 81.1; H, 9.3.

The reaction of benzoyl peroxide with 2,6-dimethylphenoxide ion was carried out by adding a solution of 0.05 mole of the potassium salt in 200 cc. of methanol to 0.05 mole of benzoyl peroxide suspended in 100 cc. of methanol over an hour. The peroxide dissolved during the addition, and the mixture was refluxed for five hours. Working up the mixture gave 5.5 g. of benzoic acid, 1.4 g. of 2,6-dimethylphenol and 7.9 g. of crude 2,6-dimethylphenyl benzoate. The ester was hydrolyzed to give 3.2 g. of additional phenol and 3.9 g. of acid; total recovery phenol, 75%, benzoic acid, 78%.

Products from *t*-Butyl Perbenzoate Reactions.—A chloroform solution, 4 *M* in *p*-methoxyphenol, and *t*-butyl perbenzoate was allowed to react for 24 hours at room temperature. Extraction with sodium bicarbonate gave a 93% recovery of benzoic acid, and fractional distillation 81% *t*-butyl alcohol. In a similar experiment in the presence of *m*-cresol the yields were 92 and 84% of acid and alcohol, respectively. In neither experiment could any identifiable product be obtained from the phenol.

Benzoyl Peroxide and Tri-*t*-butylphenol.—A solution 2.62 g. of 2,4,6-tri-*t*-butylphenol and 2.42 g. of benzoyl peroxide in 50 cc. benzene was refluxed for 8 hours. The blue

color of the phenoxy radical appeared within 10 minutes, and faded after 5 hours. By working up the reaction mixture, 42.2% benzoic acid and 22% biphenyl were recovered, typical products of the radical decomposition of the peroxide.

Polymerization Experiments.—The experiments listed in Table VII were carried out under nitrogen. Peroxide disappearance and CO₂ evolution were determined as described above, and polymer was determined on an aliquot by precipitation with methanol, drying and weighing.

Experiments in the Presence of I₂.—A mixture of 9.5 g. (0.069 mole) of acetyl peroxide (as a 17.6% solution in diethyl phthalate), 20.3 g. of I₂, 4 cc. of water and 245 cc. of CCl₄ was heated for 48 hours at 80°. The evolved gases were passed through an ascarite tube and collected over water. The reaction mixture was fractionated, and the products identified as CO₂ (0.134 mole), CH₄ (0.05 mole) and CH₃I (0.046 mole).

The non-involvement of iodine in the reaction of phenols with benzoyl peroxide was shown by refluxing a mixture of 6.1 g. of 2,6-dimethylphenol, 12.1 g. of benzoyl peroxide, 10 g. of iodine and 225 cc. of benzene for 8 hours. The same diphenoquinone was formed as described above and titration of an aliquot of reaction mixture with thiosulfate showed no consumption of iodine.

NEW YORK 27, N. Y.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Polymerization through Coördination. I^{1a}

BY KENNETH V. MARTIN^{1b}

RECEIVED AUGUST 15, 1957

A number of bis- α -thiopicolinamido compounds have been synthesized. These have been successfully polymerized by chelation with suitable metal ions. Investigation of the thermal properties of these polymers has shown a number of them to be stable above 300°. In particular, the 4,4'-bis- α -thiopicolinamido-diphenyl sulfone-zinc (II) polymer can be heated at 360° without appreciable loss in weight or change in infrared spectra.

Recent advances in jet-aircraft manufacture have shown that there is a need for new rubbers, oils and plastics that will not decompose at 400°. Thus, over the last several years a number of people have directed research toward the synthesis of polymers which would be stable at elevated temperatures. It appeared probable that this property might be realized in a polymer containing recurring chelated metal atoms. Many coördination compounds exhibit marked heat stability. For example, copper(II)-phthalocyanine can be heated at 500° without decomposition.²

It is apparent that three approaches are available for the preparation of such "coördination polymers," *viz.* (a) preformed metal complexes may be polymerized through the functional groups which they contain; (b) an organic polymer containing a recurring chelate group can be treated with suitable metal salts to form the metal derivative; (c) a polymer may be formed by the reaction of metal atom-donor atom coördination. In this paper approach (c) has been followed. It should be mentioned, however, that "coördination polymers" have been obtained by methods a³ and b.⁴

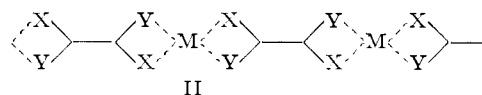
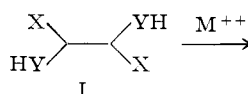
(1) (a) This research was supported in whole by the United States Air Force Contract No. AF 33(616)-3209, monitored by the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio. (b) Polychemicals Dept., E. I. du Pont de Nemours and Co., Experimental Station, Wilmington, Delaware.

(2) C. E. Dent and R. P. Linstead, *J. Chem. Soc.*, 1027 (1934).

(3) J. C. Bailar, Jr., and K. V. Martin, unpublished results.

(4) F. Lions and K. V. Martin, *THIS JOURNAL*, **79**, 2733 (1957).

In order to form a linear polymer using method (c) a molecule of molecular structure I is required. X and Y represent suitable donor atoms, two of



these donor atoms being associated with acidic hydrogen atoms. Then, on reaction with a bivalent metal atom of coördination number four (copper(II), nickel(II), etc.) two protons are lost from each molecule of I and a non-charged linear polymer II is formed. It is obvious that many variations of I are possible; however, use of different donor atoms and other metal ions may result in the formation of a charged or a cross-linked polymer. This is not desirable. Several examples of reactions of this type have been described. Wilkins and Wittbecker⁵ treated a number of tetraketones with beryllium(II) salts and polymers were obtained having structures similar to II. Also, coördination polymers have been formed from 4-hydroxy-5-formyl-salicylaldehyde,⁶ rubeanic acid⁷

(5) J. P. Wilkins and E. L. Wittbecker, U. S. Patent 2,659,711, Nov. 17, 1953.

(6) R. H. Bailes and M. Calvin, *THIS JOURNAL*, **69**, 1892 (1947).

(7) J. C. Bailar, Jr., "Advances in Chelate Chemistry," Polytechnic Institute of Brooklyn, Brooklyn, N. Y., 1955, p. 52.